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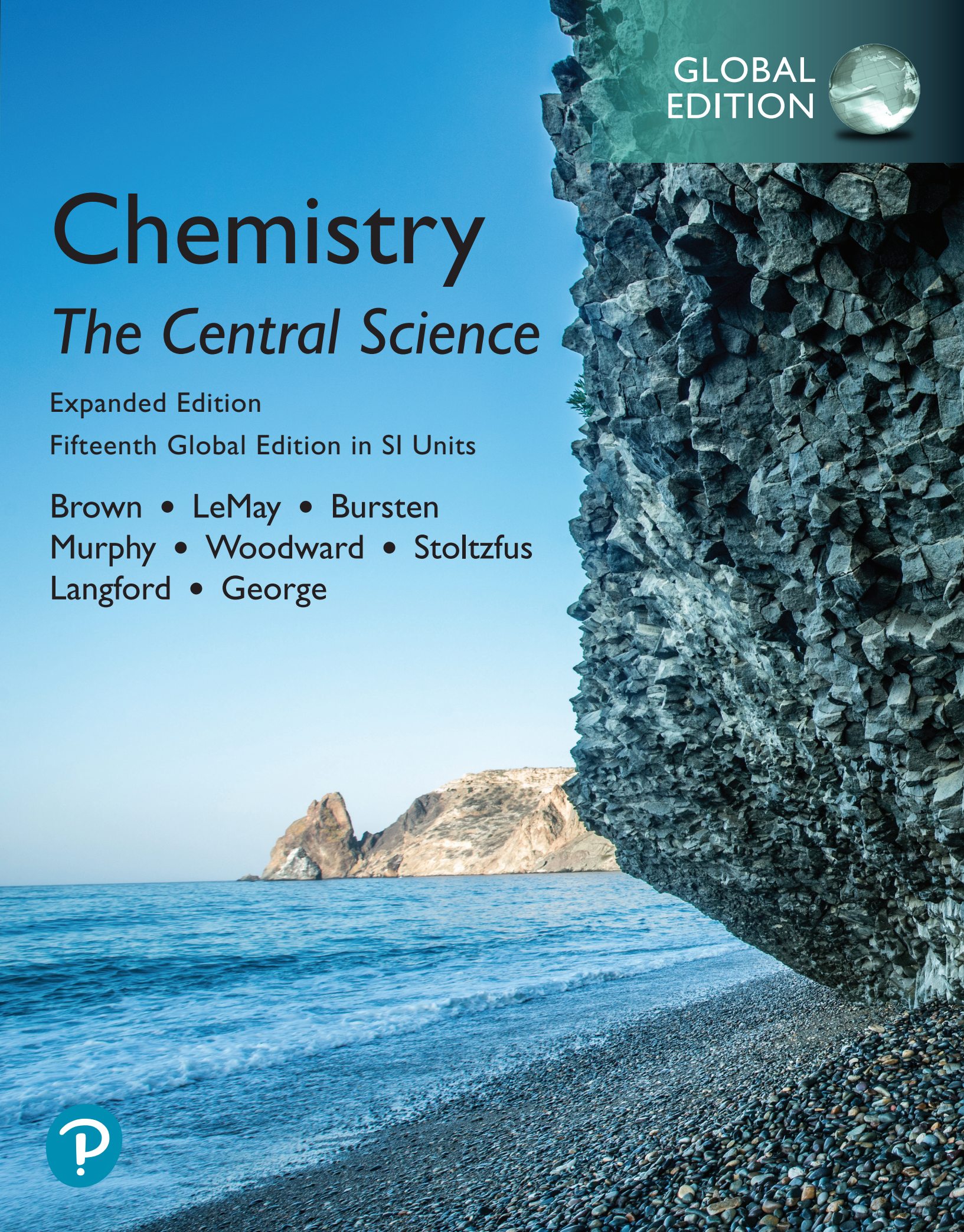
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The Central Science

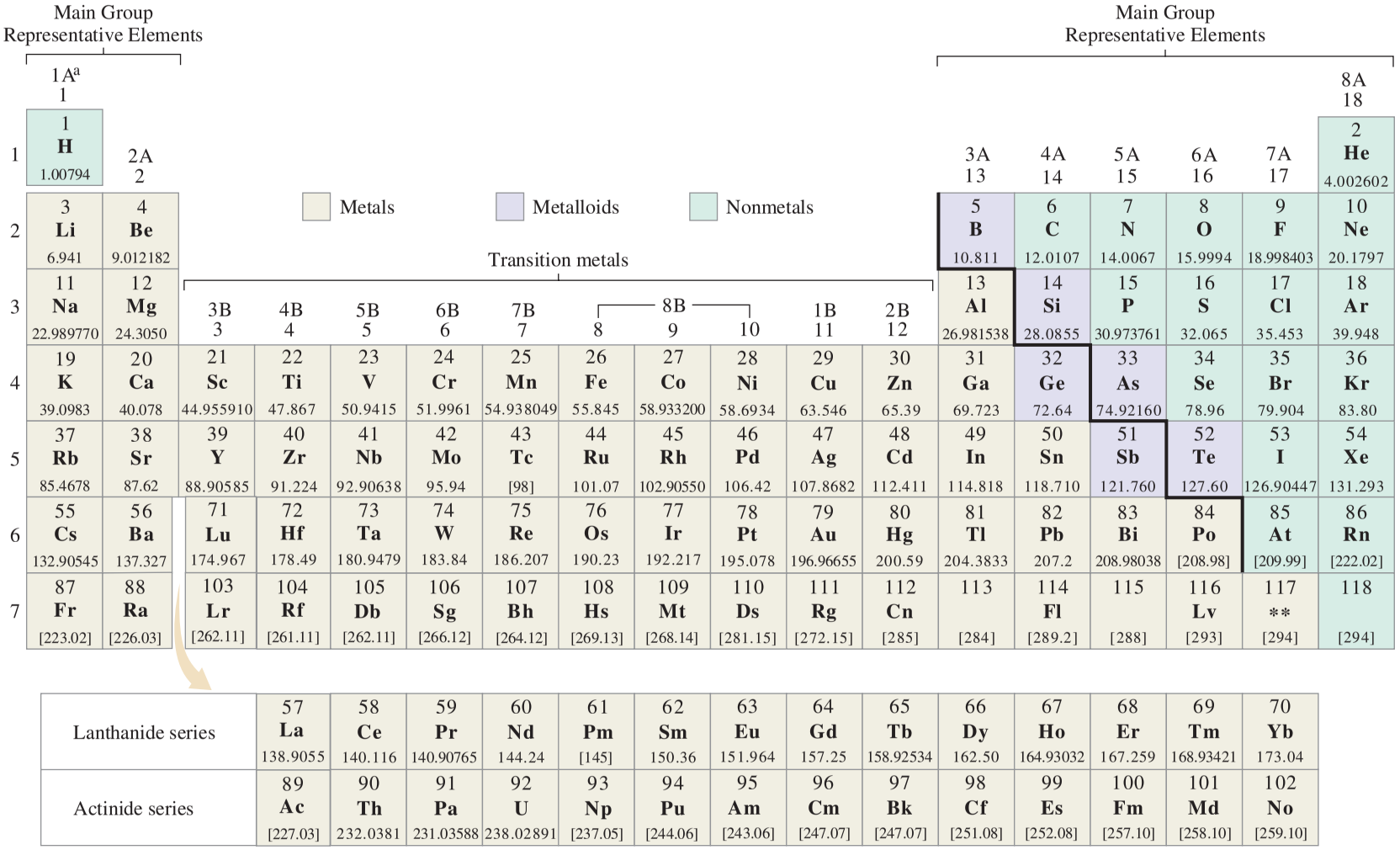
Expanded Edition

Fifteenth Global Edition in SI Units

Brown • LeMay • Bursten
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Periodic Table of the Elements



[a] The labels on top (1A, 2A, etc.) are common American usage. The labels below these (1, 2, etc.) are those recommended by the International Union of Pure and Applied Chemistry (IUPAC).

Except for elements 114 and 116, the names and symbols for elements above 113 have not yet been decided.

Atomic weights in brackets are the names of the longest-lived or most important isotope of radioactive elements.

Further information is available at http://www.webelements.com

** Discovered in 2010, element 117 is currently under review by IUPAC.

List of Elements with Their Symbols and Atomic Weights

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227.03a
Aluminum	Al	13	26.981538
Americium	Am	95	243.06a
Antimony	Sb	51	121.760
Argon	Ar	18	39.948
Arsenic	As	33	74.92160
Astatine	At	85	209.99a
Barium	Ba	56	137.327
Berkelium	Bk	97	247.07a
Beryllium	Be	4	9.012183
Bismuth	Bi	83	208.98038
Bohrium	Bh	107	270.1a
Boron	B	5	10.81
Bromine	Br	35	79.904
Cadmium	Cd	48	112.414
Calcium	Ca	20	40.078
Californium	Cf	98	251.08a
Carbon	C	6	12.0107
Cerium	Ce	58	140.116
Cesium	Cs	55	132.905452
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.9961
Cobalt	Co	27	58.933194
Copernicium	Cn	112	285.2[a]
Copper	Cu	29	63.546
Curium	Cm	96	247.07a
Darmstadtium	Ds	110	281.2a
Dubnium	Db	105	268.1a
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	252.08a
Erbium	Er	68	167.259
Europium	Eu	63	151.964
Fermium	Fm	100	257.10a
Flerovium	Fl	114	289.2a
Fluorine	F	9	18.9984016
Francium	Fr	87	223.02a
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.723
Germanium	Ge	32	72.64
Gold	Au	79	196.966569
Hafnium	Hf	72	178.49
Hassium	Hs	108	269.1a
Helium	He	2	4.002602a
Holmium	Ho	67	164.93033
Hydrogen	H	1	1.00794
Indium	In	49	114.818
Iodine	I	53	126.90447
Iridium	Ir	77	192.217
Iron	Fe	26	55.845
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	262.11a
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Livermorium	Lv	116	293[a]
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.3050
Manganese	Mn	25	54.938044
Meitnerium	Mt	109	278.2a
Mendelevium	Md	101	258.10a
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.95
Moscovium	Mc	115	289.2a
Neodymium	Nd	60	144.24
Neon	Ne	10	20.1797
Neptunium	Np	93	237.05a
Nickel	Ni	28	58.6934
Nihonium	Nh	113	286.2[a]
Niobium	Nb	41	92.90637
Nitrogen	N	7	14.0067
Nobelium	No	102	259.10a
Oganesson	Og	118	294.2a
Osmium	Os	76	190.23
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.973762
Platinum	Pt	78	195.078
Plutonium	Pu	94	244.06a
Polonium	Po	84	208.98a
Potassium	K	19	39.0983
Praseodymium	Pr	59	140.90766
Promethium	Pm	61	145a
Protactinium	Pa	91	231.03588
Radium	Ra	88	226.03a
Radon	Rn	86	222.02a
Rhenium	Re	75	186.207a
Rhodium	Rh	45	102.90550
Roentgenium	Rg	111	282.2a
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	267.1a
Samarium	Sm	62	150.36
Scandium	Sc	21	44.955908
Seaborgium	Sg	106	269.1a
Selenium	Se	34	78.97
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium	Na	11	22.989770
Strontium	Sr	38	87.62
Sulfur	S	16	32.065
Tantalum	Ta	73	180.9479
Technetium	Tc	43	98a
Tellurium	Te	52	127.60
Tennessine	Ts	117	293.2a
Terbium	Tb	65	158.92534
Thallium	Tl	81	204.3833
Thorium	Th	90	232.0377
Thulium	Tm	69	168.93422
Tin	Sn	50	118.710
Titanium	Ti	22	47.867
Tungsten	W	74	183.84
Uranium	U	92	238.02891
Vanadium	V	23	50.9415
Xenon	Xe	54	131.293
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.90584
Zinc	Zn	30	65.39
Zirconium	Zr	40	91.224

[a]Mass of longest-lived or most important isotope.

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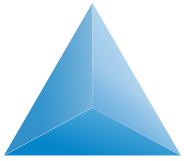
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To our students,
whose enthusiasm and curiosity
have often inspired us,
and whose questions and suggestions
have sometimes taught us.

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PREFACE

To the Instructor

Philosophy

We the authors of *Chemistry: The Central Science* are delighted and honored that you have chosen us as your instructional partners for your chemistry class. Collectively we have taught chemistry to multiple generations of students. So we understand the challenges and opportunities of teaching a class that so many students take. We have also been active researchers who appreciate both the learning and the discovery aspects of the chemical sciences. Our varied, wide-ranging experiences have formed the basis of the close collaborations we have enjoyed as coauthors. In writing our book, our focus is on the students: we try to ensure that the text is not only accurate and up-to-date but also clear and readable. We strive to convey the breadth of chemistry and the excitement that scientists experience in making new discoveries that contribute to our understanding of the physical world. We want the student to appreciate that chemistry is not a body of specialized knowledge that is separate from most aspects of modern life, but central to any attempt to address a host of societal concerns, including renewable energy, environmental sustainability, and improved human health.

Publishing the fifteenth edition of this text bespeaks an exceptionally long record of successful textbook writing. We are appreciative of the loyalty and support the book has received over the years, and mindful of our obligation to justify each new edition. We begin our approach to each new edition with an intensive author retreat, in which we ask ourselves the deep questions that we must answer before we can move forward. What justifies yet another edition? What is changing in the world not only of chemistry, but with respect to science education and the qualities of the students we serve? How can we help your students not only learn the principles of chemistry, but also become critical thinkers who can think more like chemists? The answers lie only partly in the changing face of chemistry itself. The introduction of many new technologies has changed the landscape in the teaching of sciences at all levels. The use of the Internet in accessing information and presenting learning materials has markedly changed the role of the textbook as one element among many tools for student learning. Our challenge as authors is to maintain the text as the primary source of chemical knowledge and practice while at the same time integrating it with the new avenues for learning made possible by technology. This edition continues to incorporate a number of those new methodologies, including use of computer-based classroom tools, such as Learning Catalytics™, a cloud-based active learning analytics and assessment system, and web-based tools, particularly Pearson Mastering Chemistry, which is continually evolving to provide more effective means of testing and evaluating student performance, while giving the student immediate and helpful feedback. Pearson Mastering Chemistry not only provides feedback on a question by question basis but, using Knewton-enhanced adaptive follow-up assignments, it now continually adapts to each student, offering a personalized learning experience.

As authors, we want this text to be a central, indispensable learning tool for students. Whether as a physical book or in electronic form, it can be carried everywhere and used at any time. It is the best resource for students to obtain the information outside of the classroom needed for learning, skill development, reference, and test preparation. The text, more effectively than any other instrument, provides the depth of coverage and coherent background in modern chemistry that students need to serve their professional interests and, as appropriate, to prepare for more advanced chemistry courses.

If the text is to be effective in supporting your role as instructor, it must be addressed to the students. We have done our best to keep our writing clear and interesting and the book attractive and well illustrated. The book has numerous in-text study aids for students including carefully placed descriptions of problem-solving strategies. We hope that our cumulative experiences as teachers is evident in our pacing, choice of examples, and the kinds of study aids and motivational tools we have employed. We believe students are more enthusiastic about learning chemistry when they see its importance relative to their own goals and interests; therefore, we have highlighted many important applications of chemistry in everyday life. We hope you make use of this material.

It is our philosophy, as authors, that the text and all the supplementary materials provided to support its use must work in concert with you, the instructor. A textbook is only as useful to students as the instructor permits it to be. This book is replete with features that help students learn and that can guide them as they acquire both conceptual understanding and problem-solving skills. There is a great deal here for the students to use, too much for all of it to be absorbed by any student in a one-year course. You will be the guide to the best use of the book. Only with your active help will the students be able to utilize most effectively all that the text and its supplements offer. Students care about grades, of course, and with encouragement they will also become interested in the subject matter and care about learning. Please consider emphasizing features of the book that can enhance student appreciation of chemistry, such as the *Chemistry Put To Work* and *Chemistry and Life* boxes that show how chemistry impacts modern life and its relationship to health and life processes. Also consider emphasizing conceptual understanding (placing less emphasis on simple manipulative, algorithmic problem solving) and urging students to use the rich online resources available.

Organization and Contents

The first five chapters give a largely macroscopic, phenomenological view of chemistry. The basic concepts introduced—such as nomenclature, stoichiometry, and thermochemistry—provide necessary background for many of the laboratory experiments usually performed in chemistry. We believe that an early introduction to thermochemistry is desirable because so much of our understanding of chemical processes is based on considerations of energy changes. As before, we discuss bond enthalpies in the Thermochemistry chapter to emphasize the connection between the macroscopic properties of substances and the submicroscopic world of atoms and bonds. We believe this enables an effective, balanced approach to teaching thermodynamics in general chemistry, as well as provides students with an introduction to some of the global issues involving energy production and consumption. It is no easy matter to walk the narrow pathway between—on the one hand—trying to teach too much at too high a level and—on the other hand—resorting to oversimplifications. As with the book as a whole, the emphasis has been on imparting *conceptual* understanding, as opposed to presenting equations into which students are supposed to plug numbers.

The next four chapters (Chapters 6–9) deal with electronic structure and bonding. For more advanced students, *A Closer Look* boxes in Chapters 6 and 9 highlight radial probability functions and the phases of orbitals. Our approach of placing this latter discussion in *A Closer Look* box in Chapter 9 enables those who wish to cover this topic to do so, while others may wish to bypass it.

In Chapters 10–13, the focus of the text changes to the next level of the organization of matter: examining the states of matter. Chapters 10 and 11 deal with gases, liquids, and intermolecular forces, while Chapter 12 is devoted to solids, presenting a contemporary view of the solid state as well as of modern materials accessible to general chemistry students. The chapter provides an opportunity to show how abstract chemical bonding concepts impact real-world applications. The modular organization of the chapter allows instructors to tailor coverage to focus on the materials (semiconductors, polymers, nanomaterials, and so forth) that are most relevant to students and instructors alike. This section of the book concludes with Chapter 13, which covers the formation and properties of solutions.

The next several chapters examine the factors that determine the speed and extent of chemical reactions: kinetics (Chapter 14), equilibria (Chapters 15–17), thermodynamics (Chapter 19), and electrochemistry (Chapter 20). Also in this section is a chapter on environmental chemistry (Chapter 18), in which the concepts developed in preceding chapters are applied to a discussion of the atmosphere and hydrosphere. This chapter has increasingly come to be focused on green chemistry and the impacts of human activities on Earth's water and atmosphere.

After a discussion of nuclear chemistry (Chapter 21), the book has two survey chapters. Chapter 22 deals with nonmetals, and Chapter 23 with the chemistry of transition metals, including coordination compounds. These last three chapters are developed in an independent, modular fashion and can be covered in any order.

Organic chemistry is central to all living things and Chapters 24–32 lead us on a journey from elementary hydrocarbons to elaborate bio-organic molecules. Much of what we discuss is treated from a fundamental level so students' transition to tertiary studies in organic chemistry is smooth and rapid. We place emphasis on the core reactions observed in organic chemistry and treat many cases mechanistically. This fosters a deep understanding of why organic molecules react in the way they do, thereby giving students an opportunity to understand much more chemistry than is discussed.

Chapter 24 provides a foundation to our examination of organic chemistry by using hydrocarbons to illustrate how we represent and name organic molecules. It goes on to provide an overview of the functional groups—the reactive parts of the molecule—on which we build our understanding of organic chemistry. The shape of a molecule may be pivotal in determining its reactivity, particularly in a biological context, and Chapter 25 leads to an in-depth discussion of stereochemistry. The next six chapters cover the fundamental reactions encountered in organic chemistry, at each step building to the application of these reactions in a modern world (for example, polymerisation in Chapters 26 and 29) and their essential role in the chemistry of life (for example, carbohydrates in Chapter 28, fats in Chapter 29, proteins and nucleic acids in Chapter 31). Chapter 30 investigates aromatic compounds as a separate class. Here, it is important for the student to note the differences in reactivity to the alkenes studied in Chapter 26.

Finally, Chapter 32 stands alone as a reference guide to mass spectrometry, NMR spectroscopy, and IR spectroscopy. Whether these topics are taught with much emphasis on the technology is up to the instructor. What we believe is most important is students' development at complex problem-solving, bringing two or more concepts together to draw a logical conclusion. The approach to solving molecular structure also confirms their knowledge of the basic principles of organic chemistry, bonding, functional groups and drawing structural formulas. Our coverage of organic chemistry gives students a unique perspective and challenges the very 'standard format' often seen in a first-year text.

Our chapter sequence provides a fairly standard organization, but we recognize that not everyone teaches all the topics in the order we have chosen. We have, therefore, made sure that instructors can make common changes in teaching sequence with no loss in student comprehension. In particular, many instructors prefer to introduce gases (Chapter 10) after stoichiometry (Chapter 3) rather than with states of matter. The chapter on gases has been written to permit this change with *no* disruption in the flow of material. It is also possible to treat balancing redox equations (Sections 20.1 and 20.2) earlier, after the introduction of redox reactions in Section 4.4.

We have brought students into greater contact with descriptive organic and inorganic chemistry by integrating examples throughout the text. Students will find pertinent and relevant examples of "real" chemistry woven into all the chapters to illustrate principles and applications. Some chapters, of course, more directly address the "descriptive" properties of elements and their compounds, especially Chapters 4, 7, 11, 18, 22, and 23. We also incorporate descriptive organic and inorganic chemistry in the exercises found throughout each chapter.

New to This Edition

It is perhaps a natural tendency for chemistry textbooks to grow in length with succeeding editions, but it is one that we have resisted. There are, nonetheless, many updates to features to serve students and instructors better in the classroom. *Chemistry: The Central Science* has traditionally been valued for its clarity of writing, its scientific accuracy and currency, its strong end-of-chapter exercises, and its consistency in level of coverage. The book was updated in a way that did not compromise these characteristics, and we have also continued to employ an open, clean design in the layout of the book.

The art program for the fifteenth edition continues the trajectory set in the previous two editions: to make greater and more effective use of the figures as learning tools, by drawing the reader more directly into the figure. The style of the art enhances clarity with a clean and modern look. This includes white-background annotation boxes with crisp, thin leaders; rich and saturated colors in the art, and use of 3D renderings. Using statistics from Pearson Mastering Chemistry, we have shifted some Exercises to the ends of sections, where students are more likely to attempt them before moving on to more complex questions. Also in the ends of sections are new Self-Assessment Exercises that provide immediate assessment and feedback content in the form of multiple-choice questions meant to test the concepts learnt in the section. In the Pearson eText, these exercises provide specific wrong-answer feedback.

Updates to subject matter in chapter text, Sample Exercises, and assessment content reflect current trends in teaching chemistry.

Each section now opens with new section-opening text and images that enhance students' understanding of the concepts introduced in that section as well as explicate the historical contexts around key inventions and discoveries in chemistry.

This edition features eight detailed chapters on organic chemistry for instructors and students who have more in-depth course discussions on organic chemistry than those covered in the shorter, 24-chapter variant of this book. An additional chapter on spectrometry is also available. All these additional chapters come with the wealth of Sample Exercises, essay features, assessment content, and updated art that has made the title a favorite with students and instructors the world over.

- The essays titled *Strategies in Chemistry,* which provide advice to students on problem solving and "thinking like a chemist," have been renamed *Strategies for Success* to better convey their usefulness to the student.

Key Features in This Edition

Chemistry: The Central Science, continues to provide relevant, up-to-date content—be it art or assessment material—that enhances the clarity and effectiveness of the text. Key features for this edition include the following:

- The treatment of energy and thermochemistry draws on significant revisions to previous editions. The introduction of the concept of energy in Chapter 1 allows instructors greater freedom in the order in which they cover the material. For example, this arrangement facilitates coverage of Chapters 6 and 7 immediately following Chapter 2, a sequence that is in line with an atoms-first approach to teaching general chemistry. The discussion of bond enthalpies in Chapter 5 emphasizes the connection between macroscopic quantities, like reaction enthalpies, and the submicroscopic world of atoms and bonds. We feel this leads to a better integration of thermochemical concepts with the surrounding chapters. Bond enthalpies are revisited in Chapter 8 after students have developed a more sophisticated view of chemical bonding.
- The text continues to provide students with a clear discussion, superior problem sets, and better real-time feedback on students' understanding of the material. This is based on the authors' insight into student usage of the interactive e-book platform, such as the most frequently highlighted passages and the accompanying notes and questions.
- Extensive effort has gone into creating enhanced content for the Pearson eText for the book. These features make the eText so much more than just an electronic copy of the physical textbook. Self-Assessment Exercises at the end of each section are enhanced with specific wrong-answer feedback in the Pearson eText. New Smart Figures take key figures from the text and bring them to life through animation and narration. Smart Sample Exercises animate key sample exercises from the text, offering students a more in-depth and detailed discussion than can be provided in the printed text. These interactive features also include follow-up questions, which can be assigned in Pearson Mastering Chemistry.
- Finally, Subtle but important changes have been made to allow students to quickly reference important concepts and assess their knowledge of the material. Key points are set in italic with line spaces above and below for greater emphasis. The skills-based *How To . . .* features offer step-by-step guidance for solving specific types of problems such as Drawing Lewis Structures, Balancing Redox Equations, and Naming Acids. These features, with numbered steps encased by a thin rule, are integrated into the main discussion and are easy to find. Finally, each Learning Objective is now correlated to specific end-of-chapter exercises. This allows students to test their mastery of each learning objective when preparing for quizzes and exams.

We have continued to emphasize conceptual exercises in the end-of-chapter, problems. In each chapter, we begin the exercises with the well-received *Visualizing Concepts* category. These exercises are designed to facilitate conceptual understanding through use of models, graphs, photographs, and other visual materials. They precede the regular end-of-chapter exercises and are identified in each case with the relevant chapter section number. A generous selection of *Integrative Exercises,* which give students the opportunity to solve problems that integrate concepts from the present chapter with those of previous chapters, is included at the end of each chapter. The importance of integrative problem solving is highlighted by the *Sample Integrative Exercise,* which ends each chapter beginning with Chapter 4. In general, we have included more conceptual end-of-chapter exercises and have made sure that there is a good representation of somewhat more difficult exercises to provide a better mix in terms of topic and level of difficulty. Many of the exercises are structured in a way that makes it easy to use them in Pearson Mastering Chemistry. We have made extensive use of the metadata from student use of Pearson Mastering Chemistry to analyze end-of-chapter exercises and make appropriate changes, as well as to develop *Learning Outcomes* for each chapter.

The essays in our well-received *Chemistry Put To Work* and *Chemistry and Life* series emphasize world events, scientific discoveries, and medical breakthroughs relevant to topics developed in each chapter. We maintain our focus on the positive aspects of chemistry without neglecting the problems that can arise in an increasingly technological world. Our goal is to help students appreciate the real-world perspective of chemistry and the ways in which chemistry affects their lives.

To the Student

Chemistry: The Central Science, Fifteenth Edition, has been written to introduce you to modern chemistry. As authors, we have, in effect, been engaged by your instructor to help you learn chemistry. Based on the comments of students and instructors who have used this book in its previous editions, we believe that we have done that job well. Of course, we expect the text to continue to evolve through future editions. We invite you to write to tell us what you like about the book so that we will know where we have helped you most. Also, we would like to learn of any shortcomings so we may further improve the book in subsequent editions. Our addresses are given at the end of the Preface.

Advice for Learning and Studying Chemistry

Learning chemistry requires both the assimilation of many concepts and the development of analytical skills. In this text, we have provided you with numerous tools to help you succeed in both tasks. If you are going to succeed in your chemistry course, you will have to develop good study habits. Science courses, and chemistry in particular, make different demands on your learning skills than do other types of courses. We offer the following tips for success in your study of chemistry:

Don't fall behind! As the course moves along, new topics will build on material already presented. If you don't keep up in your reading and problem solving, you will find it much harder to follow the lectures and discussions on current topics. Experienced teachers know that students who read the relevant sections of the text *before* coming to a class learn more from the class and retain greater recall. "Cramming" just before an exam has been shown to be an ineffective way to study any subject, chemistry included. So now you know. How important to you, in this competitive world, is a good grade in chemistry?

Focus your study. The amount of information you will be expected to learn may seem overwhelming. It is essential to recognize those concepts and skills that are particularly important. Pay attention to what your instructor is emphasizing. As you work through the *Sample Exercises* and homework assignments, try to see what general principles and skills they employ. A single reading of a chapter will generally not be enough for successful learning of chapter concepts and problem-solving skills. You will often need to go over assigned materials more than once. Don't skip the *Go Figure* features, *Sample Exercises,* and *Practice Exercises.* These are your guides to whether you are learning the material. They are also good preparation for test-taking. The *Learning Outcomes* and *Key Equations* at the end of the chapter will also help you focus your study.

Keep good lecture notes. Your lecture notes will provide you with a clear and concise record of what your instructor regards as the most important material to learn. Using your lecture notes in conjunction with this text is the best way to determine which material to study.

Skim topics in the text before they are covered in lecture. Reviewing a topic before lecture will make it easier for you to take good notes. First read the end-of-chapter *Summary;* then quickly read through the chapter, skipping Sample Exercises and supplemental sections. Paying attention to the titles of sections and subsections gives you a feeling for the scope of topics. Try to avoid thinking that you must learn and understand everything right away.

You need to do a certain amount of preparation before lecture. More than ever, instructors are using the lecture period not simply as a one-way channel of communication from teacher to student. Rather, they expect students to come to class ready to work on problem solving and critical thinking. Coming to class unprepared is not a good idea for any lecture environment, but it certainly is not an option for an active learning classroom if you aim to do well in the course.

After lecture, carefully read the topics covered in class. As you read, pay attention to the concepts presented and to the application of these concepts in the *Sample Exercises.* Once you think you understand a *Sample Exercise,* test your understanding by working the accompanying *Practice Exercise.*

Learn the language of chemistry. As you study chemistry, you will encounter many new words. It is important to pay attention to these words and to know their meanings or the entities to which they refer. Knowing how to identify chemical substances from their names is an important skill; it can help you avoid painful mistakes on examinations. For example, "chlorine" and "chloride" refer to very different things.

Attempt the assigned end-of-chapter exercises. Working the exercises selected by your instructor provides necessary practice in recalling and using the essential ideas of the chapter. You cannot learn merely by observing; you must be a participant. If you get stuck on an exercise, however, get help from your instructor, your teaching assistant, or another student. Spending more than 20 minutes on a single exercise is rarely effective unless you know that it is particularly challenging.

Learn to think like a scientist. This book is written by scientists who love chemistry. We encourage you to develop your critical thinking skills by taking advantage of features in this new edition, such as exercises that focus on conceptual learning, and the *Design an Experiment* exercises.

Use online resources. Some things are more easily learned by discovery, and others are best shown in three dimensions. If your instructor has included Pearson Mastering Chemistry with your book, take advantage of the unique tools it provides to get the most out of your time in chemistry.

The bottom line is to work hard, study effectively, and use the tools available to you, including this textbook. We want to help you learn more about the world of chemistry and why chemistry is the central science. If you really learn chemistry, you can be the life of the party, impress your friends and parents, and . . . well, also pass the course with a good grade.

Acknowledgments

The production of a textbook is a team effort requiring the involvement of many people besides the authors who contributed hard work and talent to bring this edition to life. Although their names don't appear on the cover of the book, their creativity, time, and support have been instrumental in all stages of its development and production.

Each of us has benefited greatly from discussions with colleagues and from correspondence with instructors and students both here and abroad. Colleagues have also helped immensely by reviewing our materials, sharing their insights, and providing suggestions for improvements. For this edition, we were particularly blessed with an exceptional group of accuracy checkers who read through our materials looking for both technical inaccuracies and typographical errors.

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Our authors value collaboration as an integral component to overall success. While each author brings unique talent, research interests, and teaching experiences, the team works together to review and develop the entire text. It is this collaboration that keeps the content ahead of educational trends and contributes to continuous innovations in teaching and learning throughout the text and technology.



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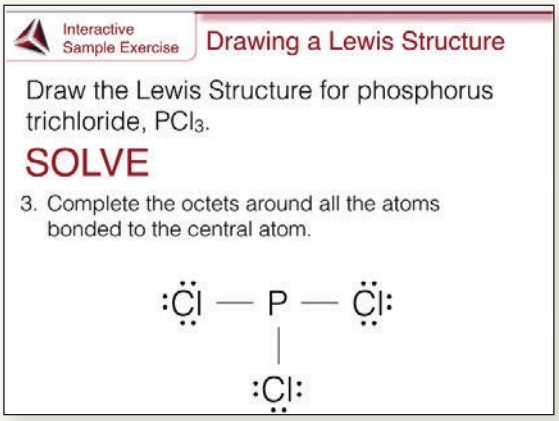
Adrian V. George received his BSc(Hons) and PhD degrees from The University of Reading in England and joined the staff there as a lecturer in 1984. After a short spell as a guest scientist at The University of California, Berkeley he moved to The University of Sydney in 1988. His research has ranged from organic synthesis at extremely high pressures and the development of new organometallic materials to the use of isotope ratio mass spectrometry in the detection of doping in competitive sports and chemistry education. He has conducted research in Japan and taught University level chemistry in Sweden. He has always had a passion for teaching and obtained a graduate certificate of education in 2000. He has been awarded a University of Sydney Excellence in Teaching award (1999), Vice Chancellor's award for Support of the Student Experience twice (2007, 2011), the inaugural Royal Australian Chemical Institute Centenary of Federation Teaching Award (2001), Australian College of Education Teaching Award (2001) and was part of a team that received the Carrick Institute Award for Programs that Enhance Learning (2007). He has been Director of First Year Studies in the School of Chemistry and the Associate Dean (Teaching and Learning) in the Faculty of Science at The University of Sydney. He currently divides his time between academic pursuits at The University of Sydney and rain forest regeneration in northern New South Wales.



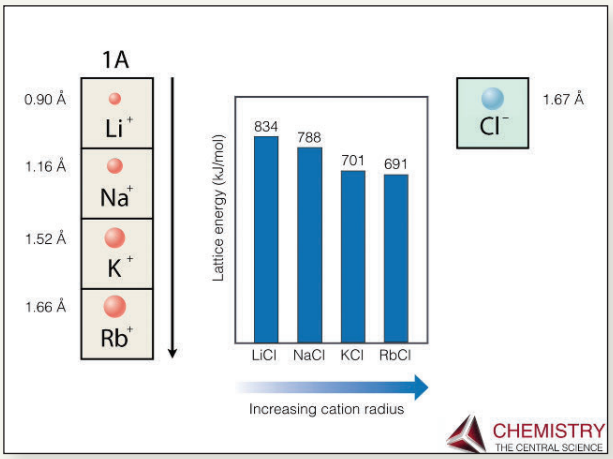
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New Levels of Student Interaction for Improved Conceptual Understanding

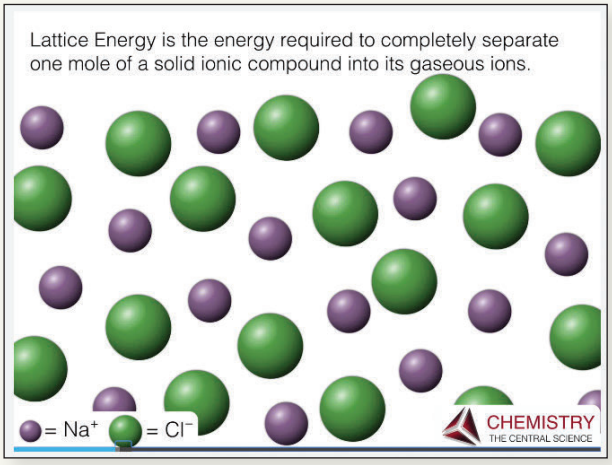
Assignable in Pearson Mastering Chemistry, unique features engage students through interactivity to enhance the reading experience and help them learn challenging chemistry concepts.



Interactive Sample Exercises bring key *Sample Exercises* in the text to life through animation and narration. Author Matt Stoltzfus uses the text's *Analyze–Plan–Solve–Check* technique to guide students through the problem-solving process. Play icons within the text identify each Interactive Sample Exercise. Clicking the icon in the eText launches a visual and conceptual presentation which goes beyond the static page. The *Practice Exercises* within each *Sample Exercise* can also be assigned in Pearson Mastering Chemistry where students will receive answer-specific feedback.

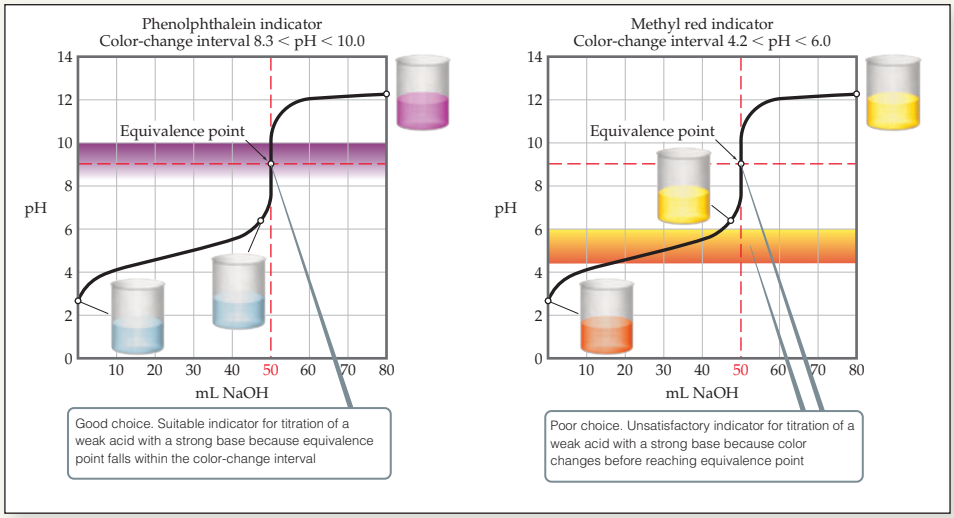


Smart Figures walk students through complex visual representations, dispelling common misconceptions before they take root. Each *Smart Figure* converts a static in-text figure into a dynamic process narrated by author Matt Stoltzfus. Play icons within the text identify each *Smart Figure*. Clicking the icon in the eText launches the animation. Smart Figures are assignable in Pearson Mastering Chemistry where they are accompanied by a multiple-choice question with answer-specific video feedback. Selecting the correct answer launches a brief wrap-up video that highlights the key concepts behind the answer.



Visually Revised to Better Help Students Build Chemistry

The visual program enhances clarity with a clean, modern look. Style changes include: expanded use of 3D renderings, new white annotation boxes with crisp leader lines, and a more saturated art palette.



Annotations offer expanded explanations; additional new leaders emphasize key relationships and key points in figures.

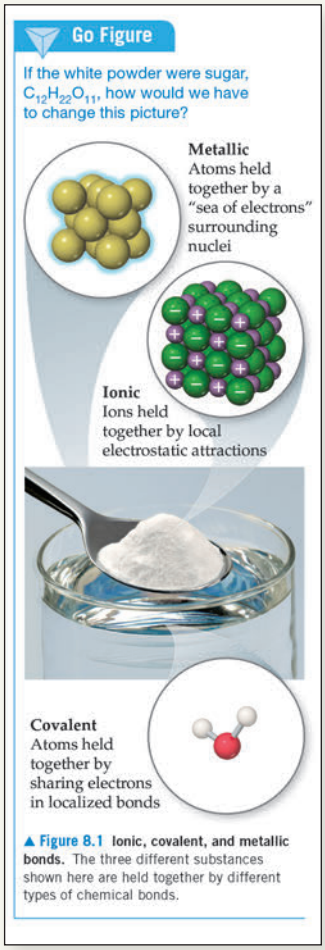
Before and after photos clearly show characteristics of endothermic and exothermic reactions. Added reaction equations connect the chemistry to what's happening in the photos.



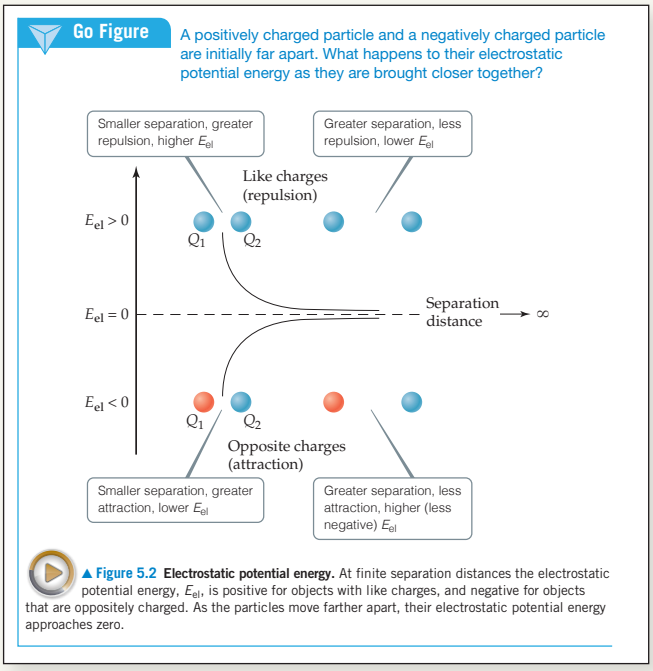
◀ **Figure 5.8 Endothermic and exothermic reactions.** In both instances, the system is defined as the reactants and products, while surroundings are the containers and everything else in the universe.

Knowledge and Understanding

The authors used the wealth of student data in Pearson Mastering Chemistry to identify the areas where students struggle most, revising discussions, figures, and exercises throughout the text to address misconceptions and encourage thinking about the real-world use of chemistry.



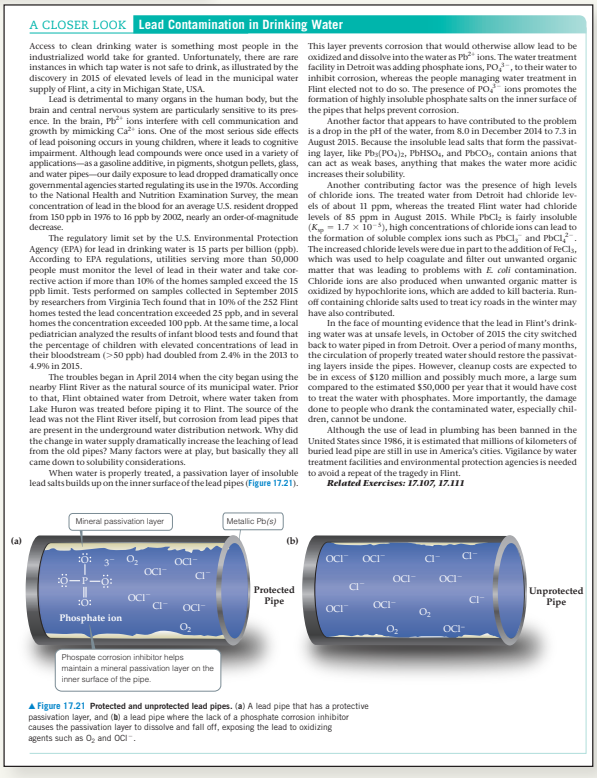
▲ **Figure 8.1 Ionic, covalent, and metallic bonds.** The three different substances shown here are held together by different types of chemical bonds.



▲ **Figure 5.2 Electrostatic potential energy.** At finite separation distances the electrostatic potential energy, E_{el}, is positive for objects with like charges, and negative for objects that are oppositely charged. As the particles move farther apart, their electrostatic potential energy approaches zero.

The author team utilized Mastering metadata to edit and clarify in-chapter *Go Figure* questions, as well as end-of-chapter problems. User data helped them to identify problematic questions and then modify, replace, or delete—resulting in a more diverse and polished set of problems.

A Closer Look features reflect news and discoveries in the field of chemistry, providing relevance and applications for students. End-of-chapter questions give students the chance to test whether they understood the concept or not.



A CLOSER LOOK **Lead Contamination in Drinking Water**

Access to clean drinking water is something most people in the industrialized world take for granted. Unfortunately, there are rare instances in which tap water is not safe to drink, as illustrated by the discovery in 2015 of elevated levels of lead in the municipal water supply of Flint, a city in Michigan State, USA.

Lead is detrimental to many organs in the human body, but the brain and central nervous system are particularly sensitive to its presence. In the brain, Pb^{2+} ions interfere with cell communication and growth by mimicking Ca^{2+} ions. One of the most serious side effects of lead poisoning occurs in young children, where it leads to cognitive impairment. Although lead compounds were once used in a variety of applications—as a gasoline additive, in pigments, shotgun pellets, glass, and water pipes—our daily exposure to lead dropped dramatically once governmental agencies started regulating its use in the 1970s. According to the National Health and Nutrition Examination Survey, the mean concentration of lead in the blood for an average U.S. resident dropped from 150 ppb in 1976 to 16 ppb by 2002, nearly an order-of-magnitude decrease.

The regulatory limit set by the U.S. Environmental Protection Agency (EPA) for lead in drinking water is 15 parts per billion (ppb). According to EPA regulations, utilities serving more than 50,000 people must monitor the level of lead in their water and take corrective action if more than 10% of the homes sampled exceed the 15 ppb limit. Tests performed on samples collected in September 2015 by researchers from Virginia Tech found that in 10% of the 252 Flint homes tested the lead concentration exceeded 25 ppb, and in several homes the concentration exceeded 100 ppb. At the same time, a local pediatrician analyzed the results of infant blood tests and found that the percentage of children with elevated concentrations of lead in their bloodstream (>50 ppb) had doubled from 2.4% in the 2013 to 4.9% in 2015.

The troubles began in April 2014 when the city began using the nearby Flint River as the natural source of its municipal water. Prior to that, Flint obtained water from Detroit, where water taken from Lake Huron was treated before piping it to Flint. The source of the lead was not the Flint River itself, but corrosion from lead pipes that are present in the underground water distribution network. Why did the change in water supply dramatically increase the leaching of lead from the old pipes? Many factors were at play, but basically they all came down to solubility considerations.

When water is properly treated, a passivation layer of insoluble lead salts builds up on the inner surface of the lead pipes (Figure 17.21). This layer prevents corrosion that would otherwise allow lead to be oxidized and dissolve into the water as Pb^{2+} ions. The water treatment facility in Detroit was adding phosphate ions, PO_4^{3-}, to their water to inhibit corrosion, whereas the people managing water treatment in Flint elected not to do so. The presence of PO_4^{3-} ions promotes the formation of highly insoluble phosphate salts on the inner surface of the pipes that helps prevent corrosion.

Another factor that appears to have contributed to the problem is a drop in the pH of the water, from 8.0 in December 2014 to 7.3 in August 2015. Because the insoluble lead salts that form the passivating layer, like $Pb_3(PO_4)_2$, $PbHSO_4$, and $PbCO_3$, contain anions that can act as weak bases, anything that makes the water more acidic increases their solubility.

Another contributing factor was the presence of high levels of chloride ions. The treated water from Detroit had chloride levels of about 11 ppm, whereas the treated Flint water had chloride levels of 85 ppm in August 2015. While $PbCl_2$ is fairly insoluble ($K_{sp} = 1.7 \times 10^{-5}$), high concentrations of chloride ions can lead to the formation of soluble complex ions such as $PbCl_3^-$ and $PbCl_4^{2-}$. The increased chloride levels were due in part to the addition of $FeCl_3$, which was used to help coagulate and filter out unwanted organic matter that was leading to problems with *E. coli* contamination. Chloride ions are also produced when unwanted organic matter is oxidized by hypochlorite ions, which are added to kill bacteria. Run-off containing chloride salts used to treat icy roads in the winter may have also contributed.

In the face of mounting evidence that the lead in Flint's drinking water was at unsafe levels, in October of 2015 the city switched back to water piped in from Detroit. Over a period of many months, the circulation of properly treated water should restore the passivating layers inside the pipes. However, cleanup costs are expected to be in excess of $120 million and possibly much more, a large sum compared to the estimated $50,000 per year that it would have cost to treat the water with phosphates. More importantly, the damage done to people who drank the contaminated water, especially children, cannot be undone.

Although the use of lead in plumbing has been banned in the United States since 1986, it is estimated that millions of kilometers of buried lead pipe are still in use in America's cities. Vigilance by water treatment facilities and environmental protection agencies is needed to avoid a repeat of the tragedy in Flint.

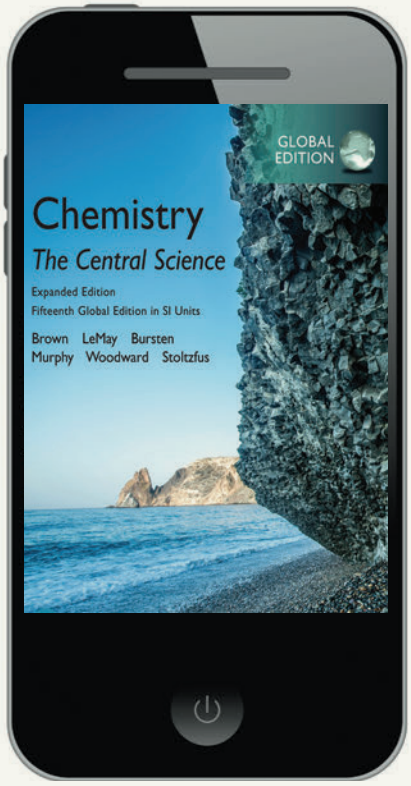
Related Exercises: 17.107, 17.111

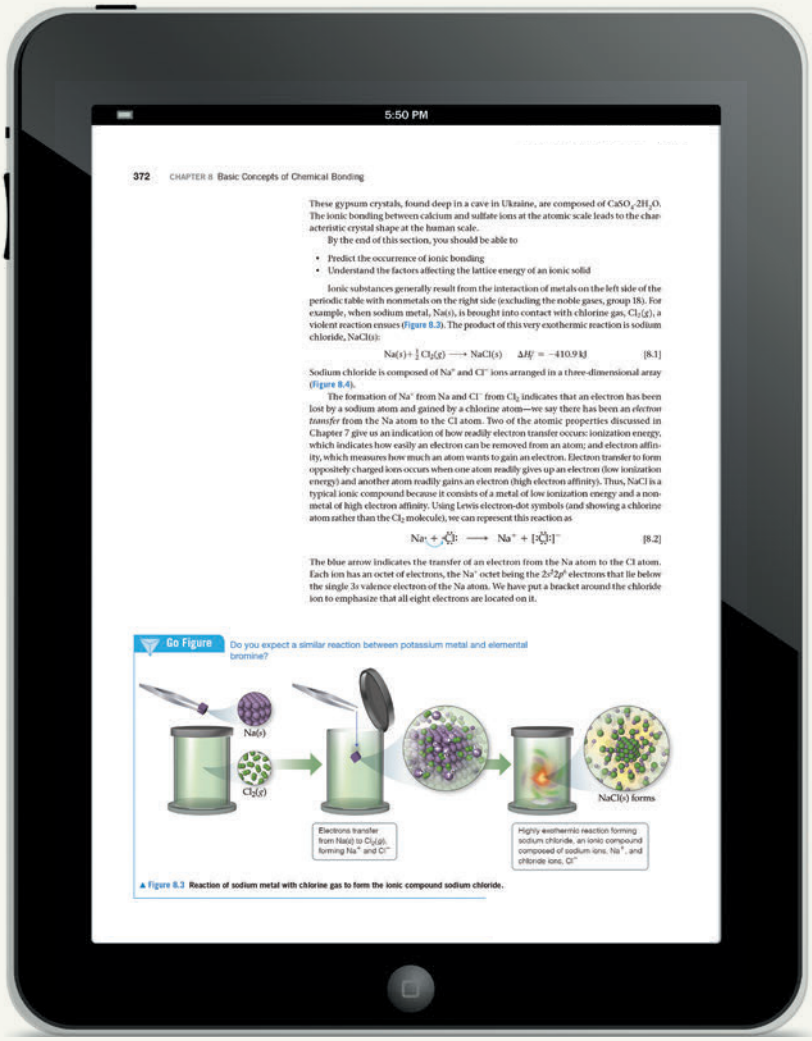
▲ **Figure 17.21 Protected and unprotected lead pipes.** (**a**) A lead pipe that has a protective passivation layer, and (**b**) a lead pipe where the lack of a phosphate corrosion inhibitor causes the passivation layer to dissolve and fall off, exposing the lead to oxidizing agents such as O_2 and OCl^-.

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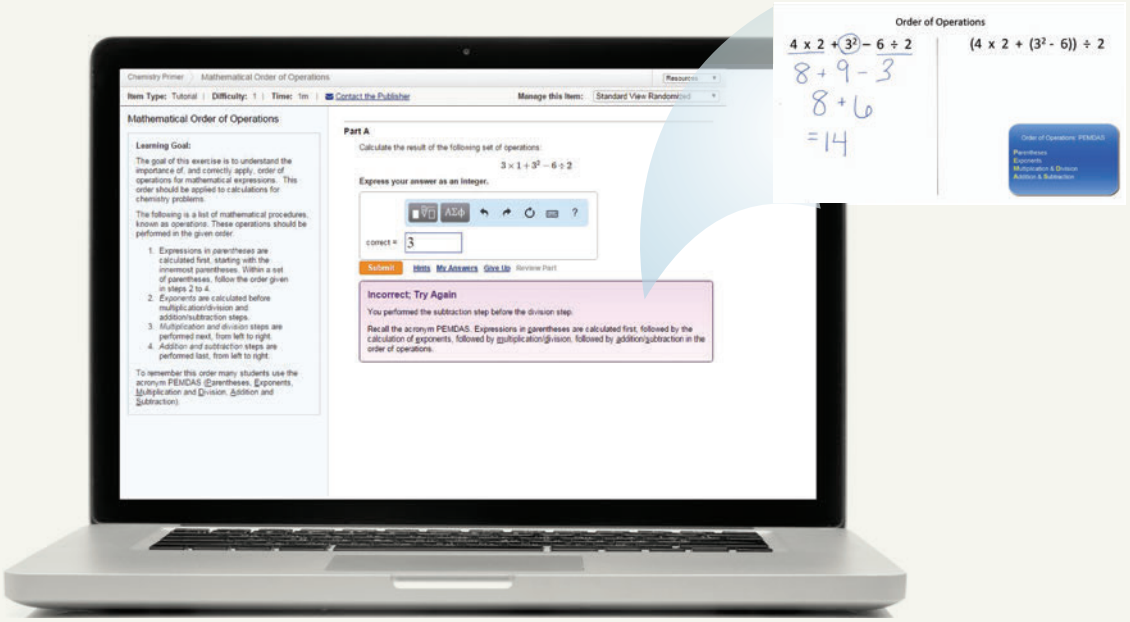


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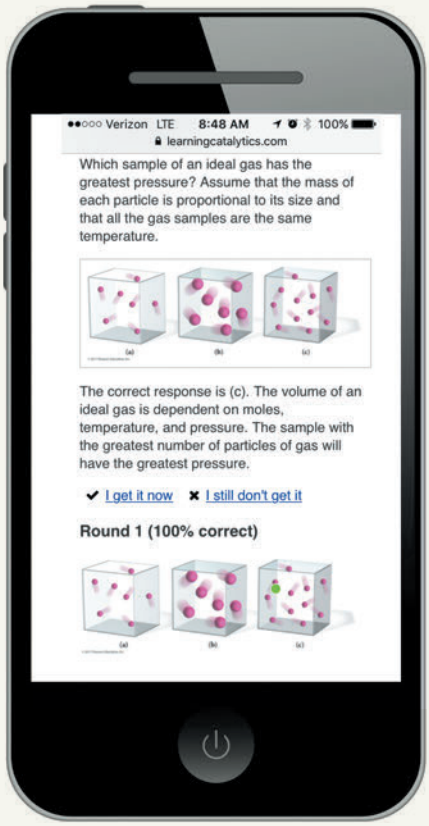
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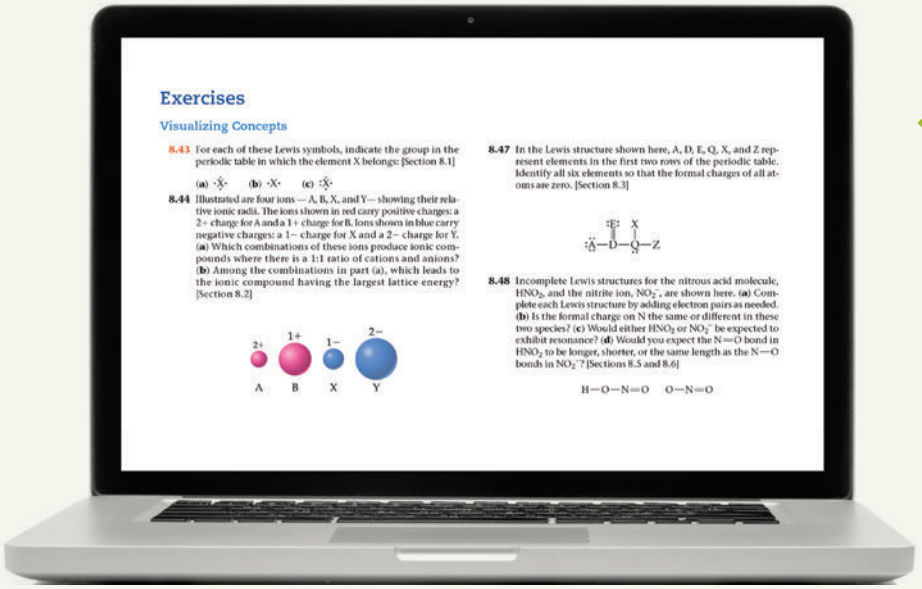
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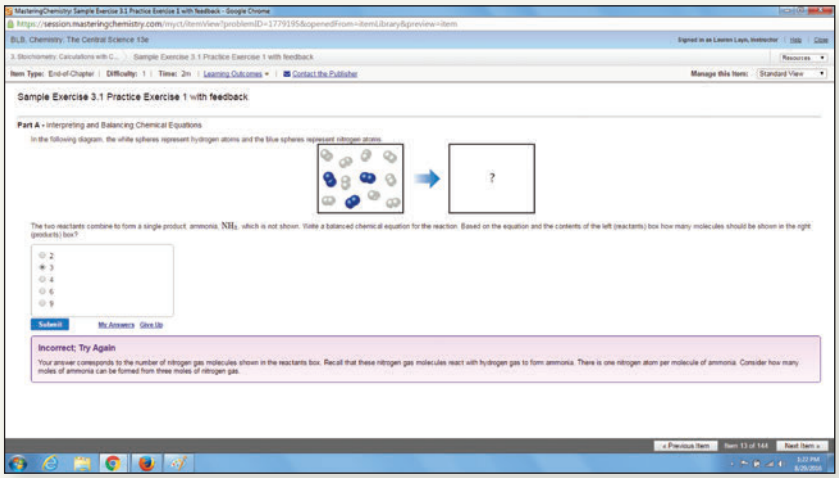


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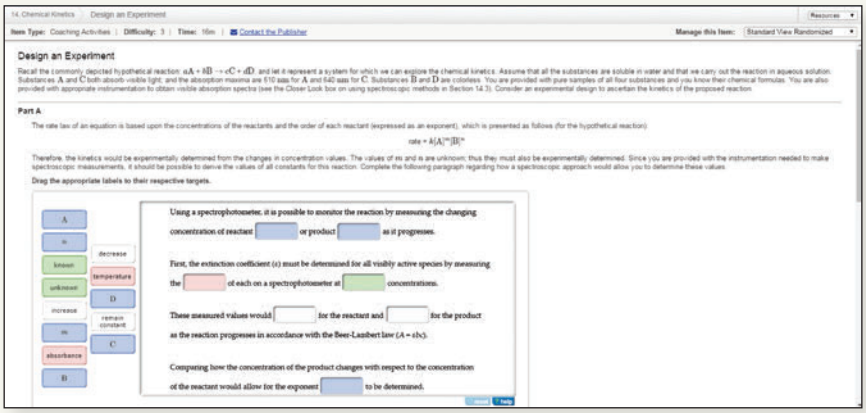
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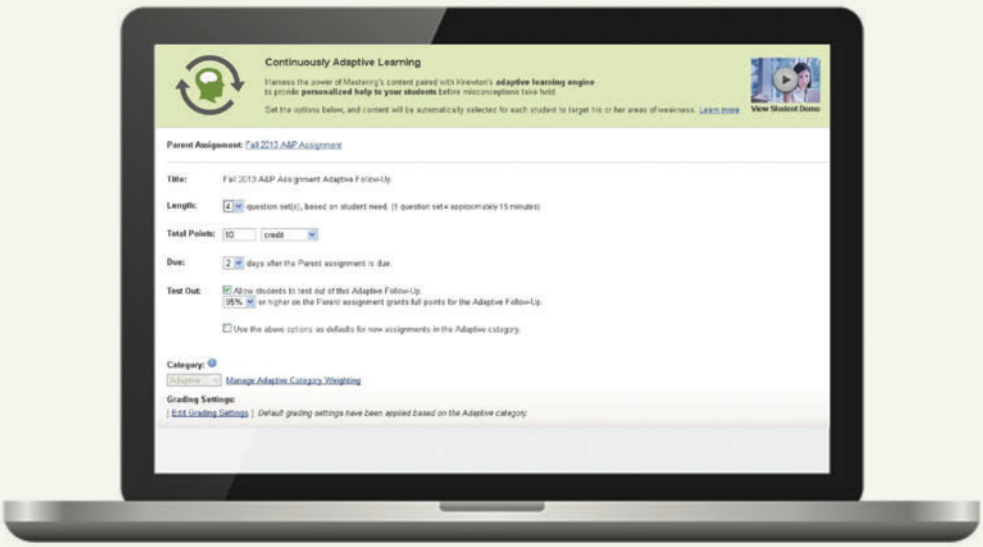
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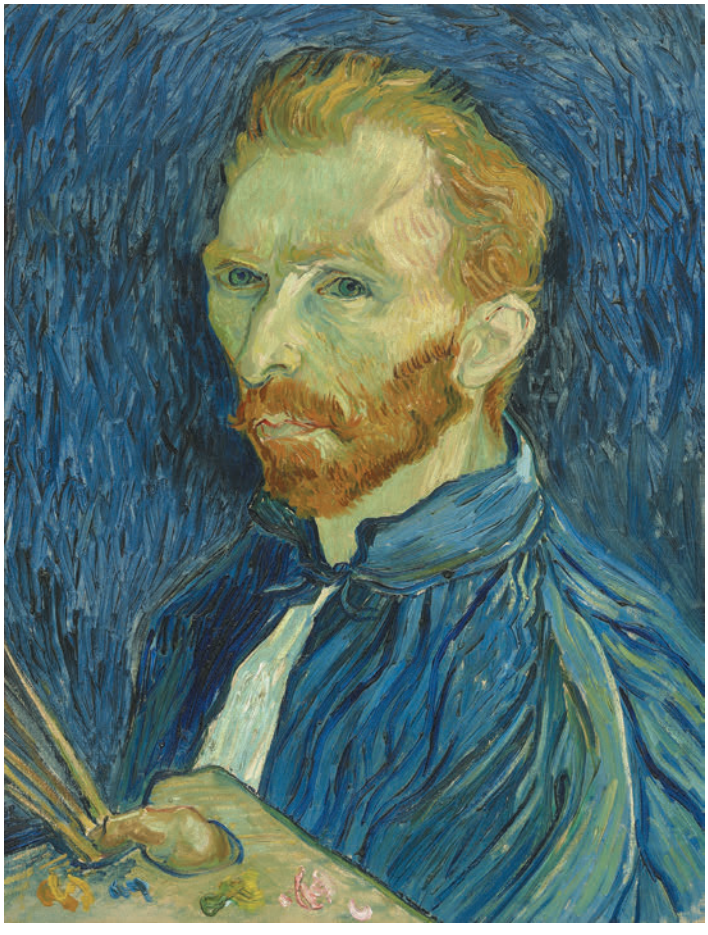
WHAT'S AHEAD

1.1 ▶ The Study of Chemistry
1.2 ▶ Classifications of Matter
1.3 ▶ Properties of Matter
1.4 ▶ The Nature of Energy
1.5 ▶ Units of Measurement
1.6 ▶ Uncertainty in Measurement
1.7 ▶ Dimensional Analysis

1

INTRODUCTION: MATTER, ENERGY, AND MEASUREMENT

1.1 The Study of Chemistry



The title of this book—*Chemistry: The Central Science*—reflects the fact that much of what goes on in the world around us involves chemistry. Everyday chemical processes include the changes that produce the brilliant colors of flowers, the ways our bodies process the food we eat, and the electrical energy that powers our cell phones.

This first chapter provides an overview of what chemistry is about and what chemists do. The "What's Ahead" list gives an overview of the chapter organization and of some of the ideas we will consider.

Chemistry is the study of matter, its properties, and the changes that matter undergoes. As you progress in your study, you will come to see how chemical principles operate in all aspects of our lives, from everyday activities like food preparation to more complex processes such as those that operate in the environment. We will also learn how the properties of substances can be tailored for specific applications by controlling their composition and structure. For example, the synthetic pigments chemists developed in the nineteenth century were used extensively by impressionist artists such as van Gogh.

Chemistry is at the heart of many changes we see in the world around us, and it accounts for the myriad different properties we see in matter. To understand how these changes and properties arise, we need to look far beneath the surfaces of our everyday observations.

By the end of this section, you should be able to

- Appreciate the scope of chemistry

The Atomic and Molecular Perspective of Chemistry

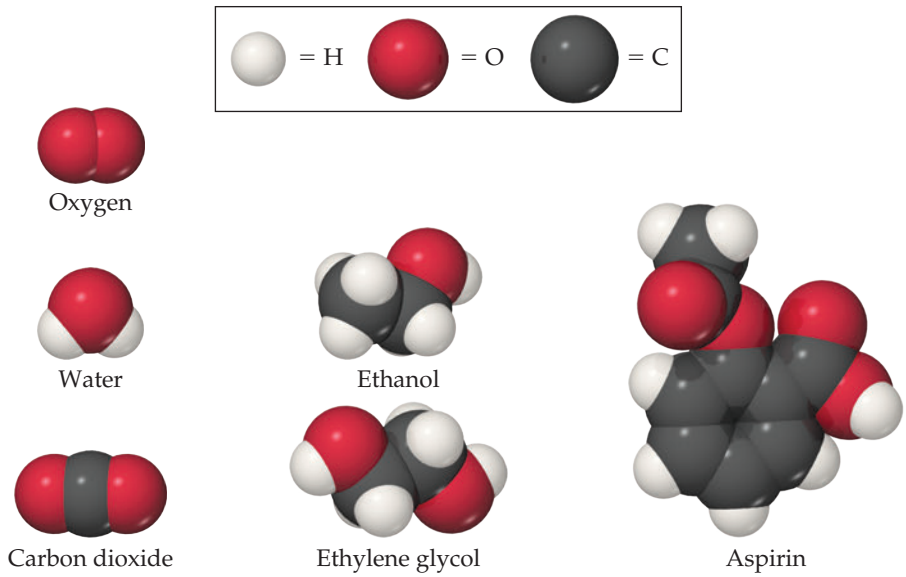
Chemistry is the study of the properties and behavior of matter. **Matter** is the physical material of the universe; it is anything that has mass and occupies space. A **property** is any characteristic that allows us to recognize a particular type of matter and to distinguish it from other types. This book, your body, the air you are breathing, and the clothes you are wearing are all samples of matter. We observe a tremendous variety of matter in our world, but countless experiments have shown that all matter is comprised of combinations of only about 100 substances called ***elements***. One of our major goals will be to relate the properties of matter to its composition, that is, to the particular elements it contains.

Chemistry also provides a background for understanding the properties of matter in terms of **atoms**, the almost infinitesimally small building blocks of matter. Each element is composed of a unique kind of atom. We will see that the properties of matter relate to both the kinds of atoms the matter contains (*composition*) and the arrangements of these atoms (*structure*).

In **molecules**, two or more atoms are joined in specific shapes. Throughout this text you will see molecules represented using colored spheres to show how the atoms are connected (**Figure 1.1**). The color provides a convenient way to distinguish between atoms of different elements. For example, notice that the molecules of ethanol and ethylene glycol in Figure 1.1 have different compositions and structures. Ethanol contains one oxygen atom, depicted by one red sphere. In contrast, ethylene glycol contains two oxygen atoms.

Even apparently minor differences in the composition or structure of molecules can cause profound differences in properties. For example, let's compare ethanol and ethylene glycol, which appear in Figure 1.1 to be quite similar. Ethanol is the alcohol in beverages such as beer and wine, whereas ethylene glycol is a viscous liquid used as automobile antifreeze. The properties of these two substances differ in many ways, as do their biological activities. Ethanol is consumed throughout the world, but you should *never* consume ethylene glycol because it is highly toxic. One of the challenges chemists undertake is to alter the composition or structure of molecules in a controlled way, creating new substances with different properties. For example, the common drug aspirin, shown in Figure 1.1, was first synthesized in 1897 in a successful attempt to

Go Figure Which molecule has the most carbon atoms? How many carbon atoms does it contain?



▲ **Figure 1.1 Molecular models.** The white, black, and red spheres represent atoms of hydrogen, carbon, and oxygen, respectively.

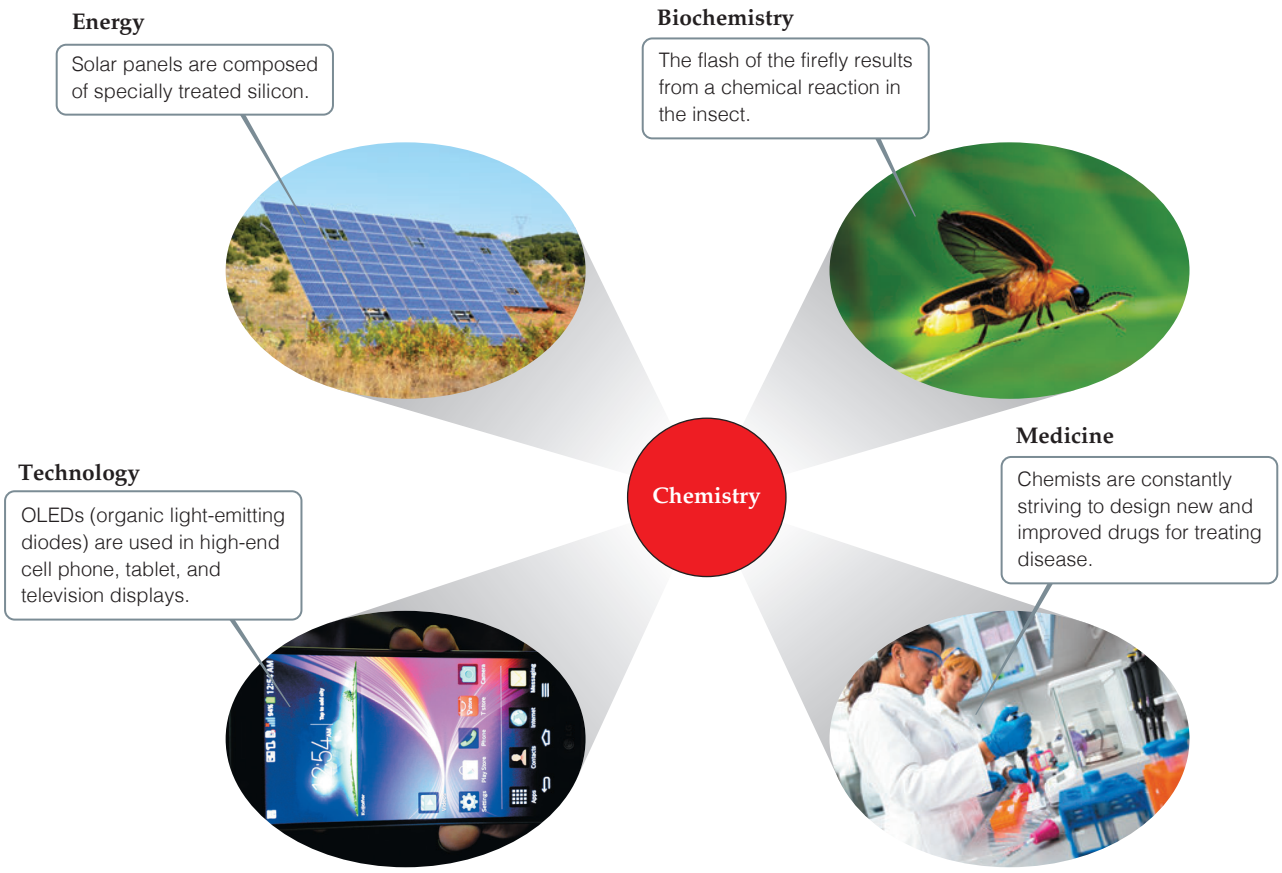
improve on a natural product extracted from willow bark that had long been used to alleviate pain.

Every change in the observable world—from boiling water to the changes that occur as our bodies combat invading viruses—has its basis in the world of atoms and molecules. Thus, as we proceed with our study of chemistry, we will find ourselves thinking in three realms: the *macroscopic* realm of ordinary-sized objects (*macro* = large), the *microscopic* realm of atoms and molecules, and the symbolic realm of how we represent these particles. We make our observations in the macroscopic world, but to understand that world, we must visualize how atoms and molecules behave at the microscopic level. Chemistry is the science that seeks to understand the properties and behavior of matter by studying the properties and behavior of atoms and molecules.

Why Study Chemistry?

Chemistry lies near the heart of many matters of public concern, such as improvement of health care, conservation of natural resources, protection of the environment, and the supply of energy needed to keep society running. Using chemistry, we have discovered and continually improved upon pharmaceuticals, fertilizers and pesticides, plastics, solar panels, light-emitting diodes (LEDs), and building materials. We have also discovered that some chemicals are harmful to our health or the environment. This means that we must be sure that the materials with which we come into contact are safe. As a citizen and consumer, it is in your best interest to understand the effects, both positive and negative, that chemicals can have, in order to arrive at a balanced outlook regarding their uses.

You may be studying chemistry because it is an essential part of your curriculum. Your major might be chemistry, or it could be biology, engineering, pharmacy, agriculture, geology, or some other field. Chemistry is central to a fundamental understanding of governing principles in many science-related fields. For example, our interactions with the material world raise basic questions about the materials around us. **Figure 1.2** illustrates how chemistry is central to several different realms of modern life.



▲ **Figure 1.2** **Chemistry is central to our understanding of the world around us.**

CHEMISTRY PUT TO WORK Chemistry and the Chemical Industry

Chemistry is all around us. For example, sugar is a chemical extracted from natural sources, refined by industry and sold across the world in a highly purified form. However, few realize the size and importance of the chemical industry. The chemical industry in the United States is estimated to be an $800 billion enterprise that employs over 800,000 people and accounts for 14% of all U.S. exports.

Who are chemists, and what do they do? People who have degrees in chemistry hold a variety of positions in industry, government, and academia. Those in industry work as laboratory chemists, developing new products (research and development); analyzing materials (quality control); or assisting customers in using products (sales and service). Those with more experience or training may work as managers or company directors. Chemists are important members of the scientific workforce in government (the National Institutes of Health, Department of Energy, and Environmental Protection Agency all employ chemists) and at universities. A chemistry degree is also good preparation for careers in teaching, medicine, biomedical research, information science, environmental work, technical sales, government regulatory agencies, and patent law.

Fundamentally, chemists do three things: They (1) make new types of matter: materials, substances, or combinations of substances with desired properties; (2) measure the properties of matter; and (3) develop models that explain and/or predict the properties of matter. One chemist, for example, may work in the laboratory to discover new drugs. Another may concentrate on the development of new instrumentation to measure properties of matter at the atomic level. Other chemists may use existing materials and methods to understand how pollutants are transported in the environment or how drugs are processed in the body. Yet another chemist will develop theory, write computer code, and run computer simulations to understand how molecules move and react. The collective chemical enterprise is a rich mix of all of these activities.



▲ **Figure 1.3** **Common chemicals used for household cleaning.**

Self-Assessment Exercise

1.1 Which of the following groups of substances involve the use of chemicals? Indicate all that apply.

(a) Paints, printer toner, food coloring

(b) Computer displays, LED lights, barcode readers

(c) Antiseptic cream, pain killers, energy drinks

(d) A light-weight bicycle frame, food packaging, a car exhaust catalytic converter

(e) Soap, shampoo, washing powder

Answers to Self-Assessment Exercises

1.1 All of them

1.2 Classifications of Matter



The study of any science starts with classification. This brings order to what we study much as the sorting of books in a library enables you to find the book you want.

Let's begin our study of chemistry by examining two fundamental ways in which matter is classified. Matter is typically characterized by (1) its physical state (gas, liquid, or solid) and (2) its composition (whether it is an element, a *compound*, or a *mixture*).

By the end of this section, you should be able to

- Understand the basic classification of matter

States of Matter

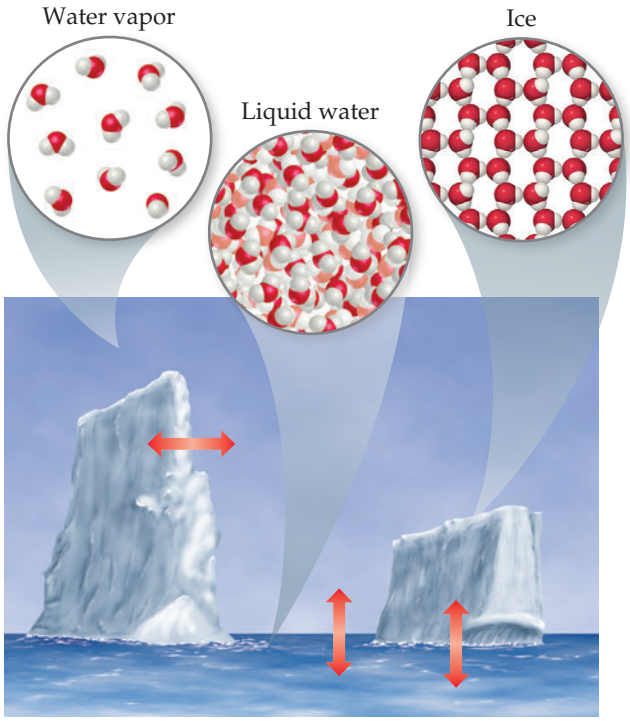
A sample of matter can be a gas, a liquid, or a solid. These three forms, called the **states of matter**, differ in some of their observable properties.

- A **gas** (also known as vapor) has no fixed volume or shape; rather, it uniformly fills its container. A gas can be compressed to occupy a smaller volume, or it can expand to occupy a larger one.
- A **liquid** has a distinct volume independent of its container, assumes the shape of the portion of the container it occupies, and is not compressible to any appreciable extent.
- A **solid** has both a definite shape and a definite volume and is not compressible to any appreciable extent.

The properties of the states of matter can be understood on the molecular level (**Figure 1.4**). In a gas the molecules are far apart and moving at high speeds, colliding repeatedly with one another and with the walls of the container. Compressing a gas decreases the amount of space between molecules and increases the frequency of collisions between molecules

but does not alter the size or shape of the molecules. In a liquid, the molecules are packed closely together but still move rapidly. The rapid movement allows the molecules to slide over one another; thus, a liquid pours easily. In a solid the molecules are held tightly together, usually in definite arrangements in which the molecules can wiggle only slightly in their otherwise fixed positions. Thus, the distances between molecules are similar in the liquid and solid states, but while the molecules are for the most part locked in place in a solid, they retain considerable freedom of motion in a liquid. Changes in temperature and/or pressure can lead to conversion from one state of matter to another, illustrated by such familiar processes as ice melting or water vapor condensing.

Go Figure In which form of water are the water molecules farthest apart?



▲ **Figure 1.4 The three physical states of water—water vapor, liquid water, and ice.** We see the liquid and solid states but cannot see the gas (vapor) state. The red arrows show that the three states of matter interconvert.

Pure Substances

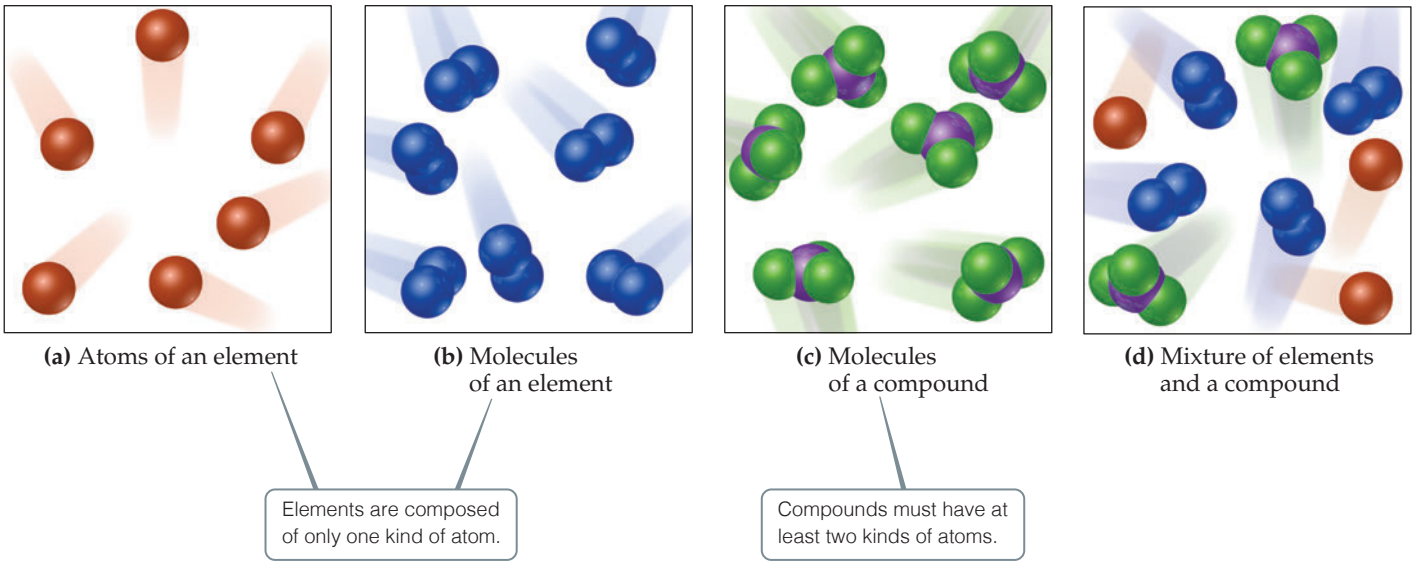
Most forms of matter we encounter—the air we breathe (a gas), the fuel we burn in our cars (a liquid), and the road they run on (a solid)—are not chemically pure. We can, however, separate these forms of matter into pure substances. A **pure substance** (usually referred to simply as a *substance*) is matter that has distinct properties and a composition that does not vary from sample to sample. Water and table salt (sodium chloride) are examples of pure substances.

All substances are either elements or compounds.

- **Elements** are substances that cannot be decomposed into simpler substances. On the molecular level, each element is composed of only one kind of atom [Figure 1.5(**a** and **b**)].
- **Compounds** are substances composed of two or more elements; they contain two or more kinds of atoms [Figure 1.5(**c**)]. Water, for example, is a compound composed of two elements: hydrogen and oxygen.

Figure 1.5(**d**) shows a mixture of substances. **Mixtures** are combinations of two or more substances in which each substance retains its chemical identity.

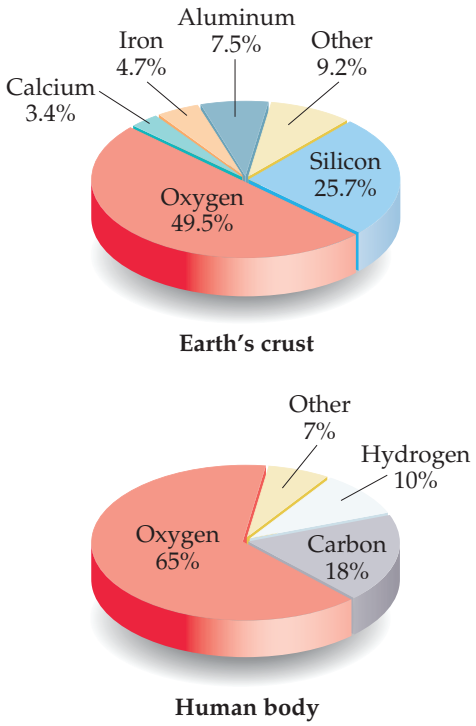
Go Figure How do the molecules of a compound differ from the molecules of an element?



▲ **Figure 1.5 Representation of elements, compounds, and mixtures.**

Go Figure

If the lower pie chart was drawn as the percentage in terms of number of atoms rather than the percentage in terms of mass, would the hydrogen slice of the pie get larger or smaller?



▲ **Figure 1.6 Relative abundances of elements.*** Elements in percent by mass in Earth's crust (including oceans and atmosphere) and the human body.

Elements

Currently, 118 elements are known, though they vary widely in abundance. Hydrogen constitutes about 74% of the mass in the Milky Way galaxy, and helium constitutes 24%. Closer to home, only five elements—oxygen, silicon, aluminum, iron, and calcium—account for over 90% of Earth's crust (including oceans and atmosphere), and only three—oxygen, carbon, and hydrogen—account for over 90% of the mass of the human body (**Figure 1.6**).

Table 1.1 lists some common elements, along with the chemical *symbols* used to denote them. The symbol for each element consists of one or two letters, with the first letter capitalized. These symbols are derived mostly from the English names of the elements, but sometimes they are derived from a foreign name instead (last column in Table 1.1). You will need to know these symbols and learn others as we encounter them in the text.

All of the known elements and their symbols are listed on the front inside cover of this text in a table known as the *periodic table*. In the periodic table, the elements are arranged in columns so that closely related elements are grouped together. We describe the periodic table in more detail in Section 2.5 and consider the periodically repeating properties of the elements in Chapter 7.

Compounds

Most elements can interact with other elements to form compounds. For example, when hydrogen gas burns in oxygen gas, the elements hydrogen and oxygen combine to form the compound water. Conversely, water can be decomposed into its elements by passing an electrical current through it (**Figure 1.7**).

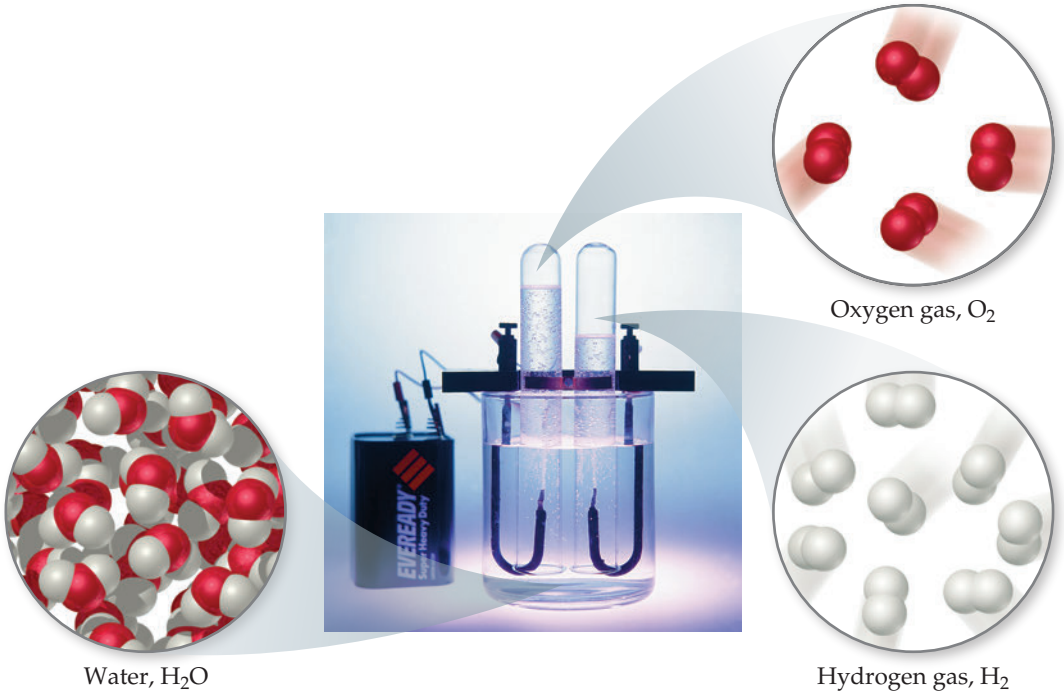
Decomposing pure water into its constituent elements shows that it contains 11% hydrogen and 89% oxygen by mass, regardless of its source. This ratio is constant because every water molecule has the same number of hydrogen and oxygen atoms. While the mass percentages make it seem that water is mostly oxygen, there are actually two hydrogen atoms and only one oxygen atom per molecule. The explanation for this apparent discrepancy comes from the fact that hydrogen atoms are much lighter than oxygen atoms. The mass composition, a macroscopic determination, corresponds to

TABLE 1.1 Some Common Elements and Their Symbols

Carbon	C	Aluminum	Al	Copper	Cu (from *cuprum*)
Fluorine	F	Bromine	Br	Iron	Fe (from *ferrum*)
Hydrogen	H	Calcium	Ca	Lead	Pb (from *plumbum*)
Iodine	I	Chlorine	Cl	Mercury	Hg (from *hydrargyrum*)
Nitrogen	N	Helium	He	Potassium	K (from *kalium*)
Oxygen	O	Lithium	Li	Silver	Ag (from *argentum*)
Phosphorus	P	Magnesium	Mg	Sodium	Na (from *natrium*)
Sulfur	S	Silicon	Si	Tin	Sn (from *stannum*)

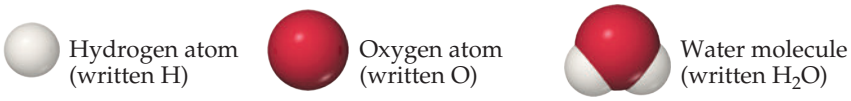
*U.S. Geological Survey Circular 285, U.S Department of the Interior.

Go Figure Is the volume of H_2 produced larger than the volume of O_2 produced because (a) hydrogen atoms are lighter than oxygen atoms, (**b**) hydrogen atoms are larger than oxygen atoms, or (**c**) each water molecule contains one oxygen atom and two hydrogen atoms?

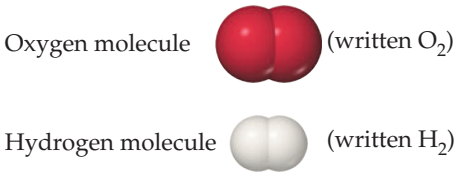


▲ **Figure 1.7 Electrolysis of water.** Water decomposes into its component elements, hydrogen and oxygen, when an electrical current is passed through it. The volume of hydrogen, collected in the right test tube, is twice the volume of oxygen.

the molecular composition, which consists of two hydrogen atoms combined with one oxygen atom:



The elements hydrogen and oxygen themselves exist naturally as diatomic (two-atom) molecules:



As seen in **Table 1.2**, the properties of water bear no resemblance to the properties of its component elements. Hydrogen, oxygen, and water are each a unique substance, a consequence of the uniqueness of their respective molecules.

TABLE 1.2 Comparison of Water, Hydrogen, and Oxygen

	Water	Hydrogen	Oxygen
State[a]	Liquid	Gas	Gas
Normal boiling point	100 °C	−253 °C	−183 °C
Density[a]	1000 kg/m^3	0.084 kg/m^3	1.33 kg/m^3
Flammable	No	Yes	No

[a] At room temperature and atmospheric pressure.

The observation that the elemental composition of a compound is always the same is known as the **law of constant composition** (or the **law of definite proportions**). French chemist Joseph Louis Proust (1754–1826) first stated the law in about 1800. Although this law has been known for 200 years, the belief persists among some people that a fundamental difference exists between compounds prepared in the laboratory and the corresponding compounds found in nature. This simply is not true. Regardless of its source—nature or a laboratory—a pure compound has the same composition and properties under the same conditions. Both chemists and nature must use the same elements and operate under the same natural laws. When two materials differ in composition or properties, either they are composed of different compounds or they differ in purity.

Mixtures

Most of the matter we encounter consists of mixtures of different substances. Each substance in a mixture retains its chemical identity and properties. In contrast to a pure substance, which by definition has a fixed composition, the composition of a mixture can vary. A cup of sweetened coffee, for example, can contain either a little sugar or a lot. The substances making up a mixture are called *components* of the mixture.

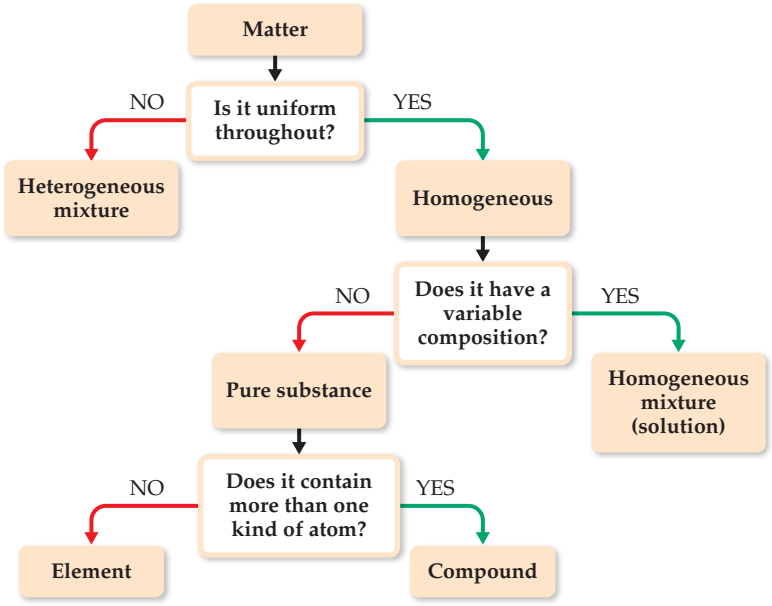
Some mixtures do not have the same composition, properties, and appearance throughout. Rocks and wood, for example, vary in texture and appearance in any typical sample. Such mixtures are *heterogeneous* [Figure 1.8(**a**)]. Mixtures that are uniform throughout are *homogeneous*. Air is a homogeneous mixture of nitrogen, oxygen, and smaller amounts of other gases. The nitrogen in air has all the properties of pure nitrogen because both the pure substance and the mixture contain the same nitrogen molecules. Salt, sugar, and many other substances dissolve in water to form **solutions**, which are homogeneous mixtures [Figure 1.8(**b**)]. Although the term *solution* conjures an image of a liquid, the term can also apply to solids, liquids, or gases.

Figure 1.9 summarizes the classification of matter into elements, compounds, and mixtures.



(a) (b)

▶ **Figure 1.8 Mixtures.** (**a**) Many common materials, including rocks, are heterogeneous mixtures. This photograph of granite shows a heterogeneous mixture of silicon dioxide and other metal oxides. (**b**) Homogeneous mixtures are called solutions. Many substances, including the blue solid shown here [copper(II) sulfate pentahydrate], dissolve in water to form solutions.



◀ **Figure 1.9 Classification of matter.** All pure matter is classified ultimately as either an element or a compound.

Sample Exercise 1.1

Distinguishing among Elements, Compounds, and Mixtures

"White gold" contains gold and a "white" metal, such as palladium. Two samples of white gold differ in the relative amounts of gold and palladium they contain. Both samples are uniform in composition throughout. Use Figure 1.9 to classify white gold.

SOLUTION

Because the material is uniform throughout, it is homogeneous. Because its composition differs for the two samples, it cannot be a compound. Instead, it must be a homogeneous mixture.

Practice Exercise

Aspirin is composed of 60.0% carbon, 4.5% hydrogen, and 35.5% oxygen by mass, regardless of its source. Use Figure 1.9 to classify aspirin.

Self-Assessment Exercise

1.2 Carbonated water, 'Soda Water', is water in which carbon dioxide has been dissolved under pressure. Classify soda water.

(a) A homogeneous solution of elements
(b) A homogeneous solution of compounds
(c) A heterogeneous mixture of elements
(d) A heterogeneous mixture of compounds

Exercises

1.3 Classify each of the following as a pure substance or a mixture. If a mixture, indicate whether it is homogeneous or heterogeneous: (**a**) air, (**b**) chocolate with almond, (**c**) aluminium, (**d**) iodine tincture.

1.4 Give the chemical symbol or name for the following elements, as appropriate: **(a)** helium, **(b)** platinum, **(c)** cobalt, **(d)** tin, **(e)** silver, **(f)** Sb, **(g)** Pb, **(h)** Br, **(i)** V, **(j)** Hg.

1.5 A solid white substance A is heated strongly in the absence of air. It decomposes to form a new white substance B and a gas C. The gas has exactly the same properties as the product obtained when carbon is burned in an excess of oxygen. Based on these observations, can we determine whether solids A and B and gas C are elements or compounds?

Answers to Self-Assessment Exercises

1.2 (b)

1.3 | Properties of Matter



We are familiar with many of the properties of materials around us—the hardness of steel, the flexibility of rubber, or the glow of a wood fire. If we delve a little deeper, we can classify these properties as one of two types. By the end of this section, you should be able to

- Distinguish between physical and chemical changes

Every substance has unique properties. For example, the properties listed in Table 1.2 allow us to distinguish hydrogen, oxygen, and water from one another. The properties of matter can be categorized as physical or chemical. **Physical properties** can be observed without changing the identity and composition of the substance. These properties include color, odor, density, melting point, boiling point, and hardness. **Chemical properties** describe the way a substance may change, or *react*, to form other substances. A common chemical property is flammability, the ability of a substance to burn in the presence of oxygen.

Some properties, such as temperature and melting point, are *intensive properties*. **Intensive properties** do not depend on the amount of sample being examined and are particularly useful in chemistry because many intensive properties can be used to *identify* substances. **Extensive properties** depend on the amount of sample, with two examples being mass and volume. Extensive properties relate to the *amount* of substance present.

Physical and Chemical Changes

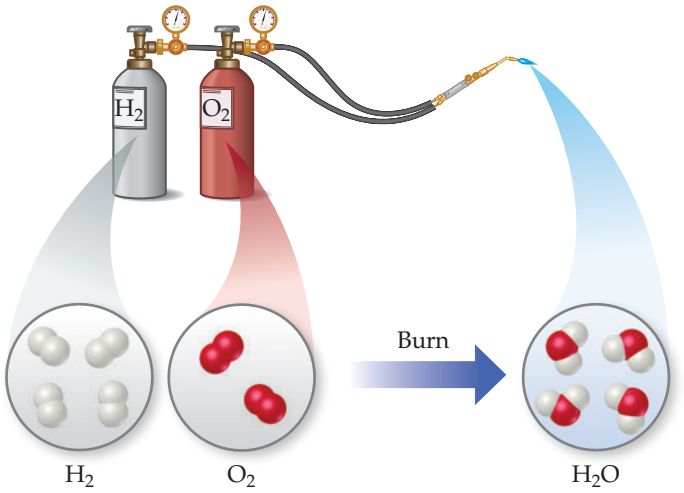
The changes substances undergo are either physical or chemical. During a **physical change**, a substance changes its physical appearance but not its composition. (That is, it is the same substance before and after the change.) The evaporation of water is a physical change. When water evaporates, it changes from the liquid state to the gas state, but it is still composed of water molecules, as depicted in Figure 1.4. All **changes of state** (for example, from liquid to gas or from liquid to solid) are physical changes.

In a **chemical change** (also called a **chemical reaction**), a substance is transformed into a chemically different substance. When hydrogen burns in air, for example, it undergoes a chemical change because it combines with oxygen to form water (**Figure 1.10**).

Chemical changes can be dramatic. In the account given in **Figure 1.11**, Ira Remsen, author of a popular chemistry text published in 1901, describes his first experiences with chemical reactions.

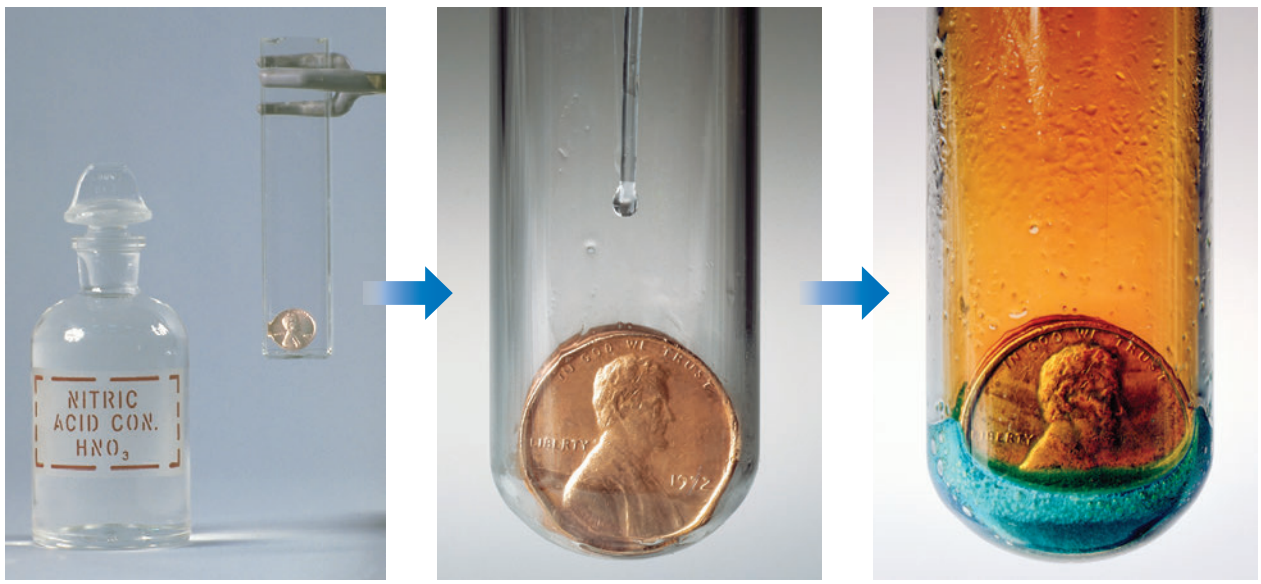
Separation of Mixtures

We can separate a mixture into its components by taking advantage of differences in their properties. For example, a heterogeneous mixture of iron filings and gold filings could be sorted by color into iron and gold. A less tedious approach would be to use a magnet to



▲ **Figure 1.10** **A chemical reaction.**

While reading a textbook of chemistry, I came upon the statement "nitric acid acts upon copper," and I determined to see what this meant. Having located some nitric acid, I had only to learn what the words "act upon" meant. In the interest of knowledge I was even willing to sacrifice one of the few copper cents then in my possession. I put one of them on the table, opened a bottle labeled "nitric acid," poured some of the liquid on the copper, and prepared to make an observation. But what was this wonderful thing which I beheld? The cent was already changed, and it was no small change either. A greenish-blue liquid foamed and fumed over the cent and over the table. The air became colored dark red. How could I stop this? I tried by picking the cent up and throwing it out the window. I learned another fact: nitric acid acts upon fingers. The pain led to another unpremeditated experiment. I drew my fingers across my trousers and discovered nitric acid acts upon trousers. That was the most impressive experiment I have ever performed. I tell of it even now with interest. It was a revelation to me. Plainly the only way to learn about such remarkable kinds of action is to see the results, to experiment, to work in the laboratory.*



▲ **Figure 1.11** **The chemical reaction between a copper penny and nitric acid.** The dissolved copper produces the blue-green solution; the reddish brown gas produced is nitrogen dioxide.

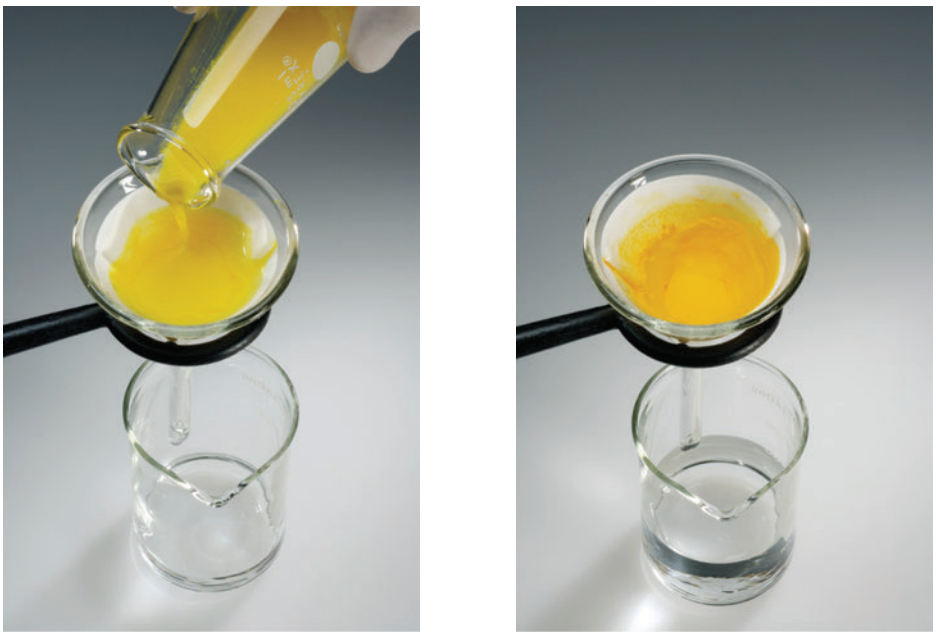
attract the iron filings, leaving the gold ones behind. We can also take advantage of an important chemical difference between these two metals: Many acids dissolve iron but not gold. Thus, if we put our mixture into an appropriate acid, the acid would dissolve the iron and the solid gold would be left behind. The two could then be separated by

*Remsen, *The Principles of Theoretical Chemistry,* 1887.

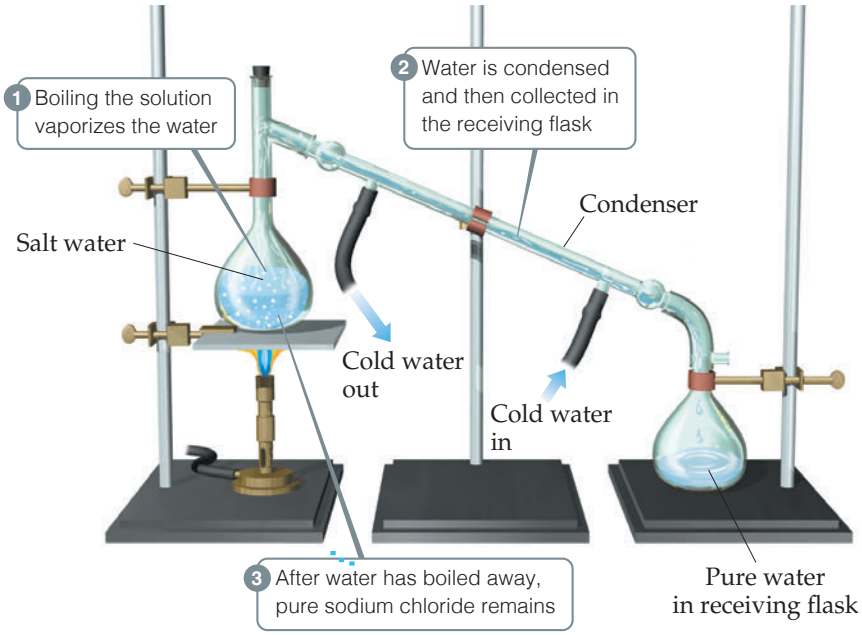
filtration (Figure 1.12). We would have to use other chemical reactions, which we will learn about later, to transform the dissolved iron back into metal.

An important method of separating the components of a homogeneous mixture is **distillation**, a process that depends on the different abilities of substances to form gases. For example, if we boil a solution of salt and water, the water evaporates, forming a gas, and the salt is left behind. The gaseous water can be converted back to a liquid on the walls of a condenser, as shown in Figure 1.13.

The differing abilities of substances to adhere to the surfaces of solids can also be used to separate mixtures. This ability is the basis of *chromatography*, a technique shown in Figure 1.14.

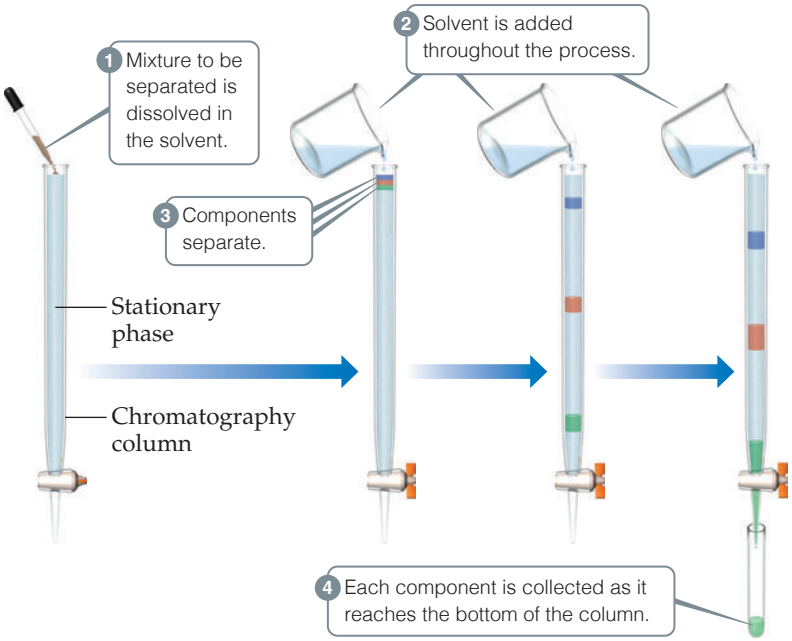


▶ **Figure 1.12 Separation by filtration.** A mixture of a solid and a liquid is poured through filter paper. The liquid passes through the paper while the solid remains on the paper.



▲ **Figure 1.13 Distillation.** Apparatus for separating a sodium chloride solution (salt water) into its components.

Go Figure Is the separation of the mixture shown here a physical or chemical process?



▲ **Figure 1.14** **Separation of three substances using column chromatography.**

Self-Assessment Exercise

1.6 When water boils in a pot, bubbles of water vapor can be seen rising through the liquid. What type of change does this represent?

(a) a physical change
(b) a chemical change

Exercises

1.7 Zirconia, an oxide of zirconium, is often used as an affordable diamond substitute. Just like diamond, it is a colorless crystal which sparkles under sunlight. Which of the following physical properties do you think would help in differentiating between diamond and Zirconia—melting point, density, or physical state?

1.8 In the process of attempting to characterize a substance, a chemist makes the following observations: The substance is a silvery white, lustrous metal. It melts at 649 °C and boils at 1105 °C. Its density at 20 °C is 1.738 g/cm^3. The substance burns in air, producing an intense white light. It reacts with chlorine to give a brittle white solid. The substance can be pounded into thin sheets or drawn into wires. It is a good conductor of electricity. Which of these characteristics are physical properties, and which are chemical properties?

1.9 Label each of the following as either a physical process or a chemical process: **(a)** crushing a metal can, **(b)** production of urine in the kidneys, **(c)** melting a piece of chocolate, **(d)** burning fossil fuel, **(e)** discharging a battery.

1.10 Which separation method is better suited for obtaining sugar from cane juice—filtration or evaporation?

Answers to Self-Assessment Exercises

1.6 (a)

1.4 The Nature of Energy



Since the earliest time, humans have recognized fire as a form of energy. In chemistry, it is convenient to distinguish between different types of energy, and, by the end of this section, you should be able to

- Recognize the difference between kinetic and potential energy

All objects in the universe are made of matter, but matter alone is not enough to describe the behavior of the world around us. The water in an alpine lake and a pot of boiling water are both made from the same substance, but your body will experience a very different sensation if you put your hand in each. The difference between the two is their energy content; boiling water has more energy than chilled water. To understand chemistry, we must also understand energy and the changes in energy that accompany chemical processes.

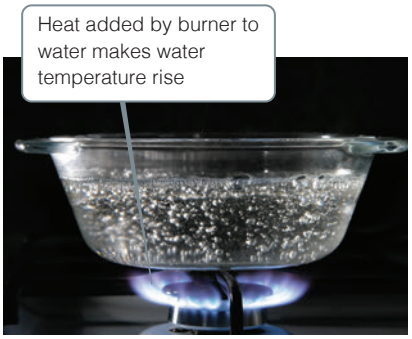
Unlike matter, energy does not have mass and cannot be held in our hands, but its effects can be observed and measured. **Energy** *is defined as the capacity to do work or transfer heat.* **Work** is *the energy transferred when a force exerted on an object causes a displacement of that object*, and **heat** is *the energy used to cause the temperature of an object to increase* (Figure 1.15). Although the temperature of an object is intuitive to most people, the definition of work is less apparent. We define work, w, as the product of the force exerted on the object, F, and the distance, d, that it moves:

$$w = F \times d \qquad [1.1]$$

where **force** is defined as any push or pull exerted on the object.* Familiar examples include gravity and the attraction between opposite poles of a bar magnet. It takes work to lift an object off of the floor, or to pull apart two magnets that have come together at the opposite poles.



(a)



(b)

▲ **Figure 1.15 Work and heat, two forms of energy.** (**a**) *Work* is energy used to cause an object to move against an opposing force. (**b**) *Heat* is energy used to increase the temperature of an object.

Kinetic Energy and Potential Energy

To understand energy, we need to grasp its two fundamental forms, kinetic energy and potential energy. Objects, whether they are automobiles, soccer balls, or molecules, can possess **kinetic energy**, the energy of *motion*. The magnitude of kinetic energy, E_k, of an object depends on its mass, m, and velocity, v:

$$E_k = \frac{1}{2}mv^2 \qquad [1.2]$$

*In using this equation, only the component of the force that is acting parallel to the distance traveled is used. That will generally be the case for problems we will encounter in this chapter.

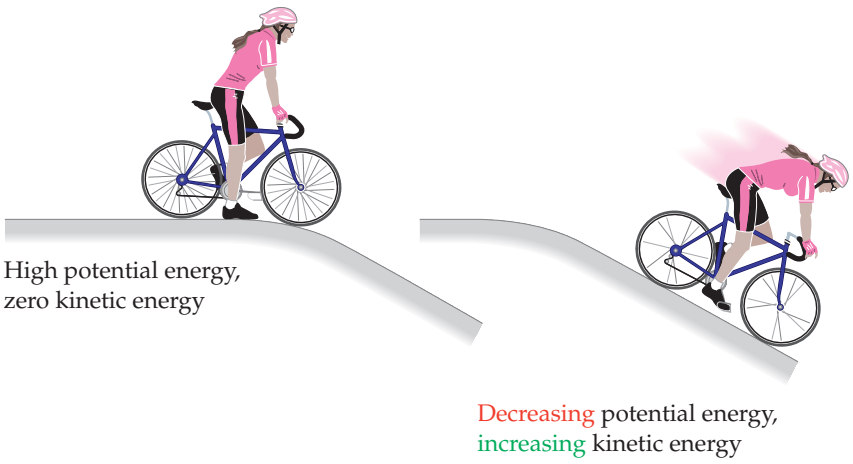
Thus, the kinetic energy of an object increases as its velocity or speed** increases. For example, a car has greater kinetic energy moving at 65 kilometers per hour (km/h) than it does at 25 km/h. For a given velocity, the kinetic energy increases with increasing mass. Thus, a large truck traveling at 65 km/h has greater kinetic energy than a motorcycle traveling at the same velocity because the truck has the greater mass.

In chemistry, we are interested in the kinetic energy of atoms and molecules. Although these particles are too small to be seen, they have mass and are in motion, and therefore, possess kinetic energy. When a substance is heated, be it a pot of water on the stove or an aluminum can sitting in the sun, the atoms and molecules in that substance gain kinetic energy and their average speed increases. Hence, we see that the transfer of heat is simply the transfer of kinetic energy at the molecular level.

All other forms of energy—the energy stored in a stretched spring, in a weight held above your head, or in a chemical bond—are classified as potential energy. An object has **potential energy** by virtue of its position relative to other objects. Potential energy is, in essence, the "stored" energy that arises from the attractions and repulsions an object experiences in relation to other objects.

We are familiar with many instances in which potential energy is converted into kinetic energy. For example, think of a cyclist poised at the top of a hill (**Figure 1.16**). Because of the attractive force of gravity, the potential energy of the bicycle is greater at the top of the hill than at the bottom. As a result, the bicycle easily rolls down the hill with increasing speed. As it does so, potential energy is converted into kinetic energy. The potential energy decreases as the bicycle rolls down the hill, while at the same time its kinetic energy increases as it picks up speed (Equation 1.2). This example illustrates that kinetic and potential energy are interconvertible.

Gravitational forces play a negligible role in the ways that atoms and molecules interact with one another. Forces that arise from electrical charges are more important when dealing with atoms and molecules. One of the most important forms of potential energy in chemistry is *electrostatic potential energy*, which arises from the interactions between charged particles. You are probably familiar with the fact that opposite charges attract each other and like charges repel. The strength of this interaction increases as the magnitude of the charges increase, and decreases as the



▲ **Figure 1.16 Potential energy and kinetic energy.** The potential energy initially stored in the motionless bicycle and rider at the top of the hill is converted to kinetic energy as the bicycle moves down the hill and loses potential energy.

**Strictly speaking, velocity is a vector quantity that has a direction; that is, it tells you how fast an object is moving and in what direction. Speed is a scalar quantity that tells you how fast an object is moving but not the direction of the motion. Unless otherwise stated, we will not be concerned with the direction of motion, and thus velocity and speed are interchangeable quantities for the treatment in this book.

distance between charges increases. We will return to electrostatic energy several times throughout the book.

One of our goals in chemistry is to relate the energy changes seen in the macroscopic world to the kinetic or potential energy of substances at the molecular level. Many substances, fuels for example, release energy when they react. The *chemical energy* of a fuel is due to the potential energy stored in the arrangements of its atoms. As we will learn in later chapters, *chemical energy is released when bonds between atoms are formed, and consumed when bonds between atoms are broken*. When a fuel burns, some bonds are broken and others are formed, but the net effect is to convert chemical potential energy to thermal energy, the energy associated with temperature. The increase in thermal energy arises from increased molecular motion and hence increased kinetic energy at the molecular level.

Self-Assessment Exercise

1.11 What happens to the chemical energy of a nickel-metal hydride battery as it is recharged after powering an electric razor?

(a) It increases
(b) It decreases
(c) It remains the same

Exercises

1.12 Two positively charged particles are first brought close together and then released. Once released, the repulsion between particles causes them to move away from each other. (**a**) This is an example of potential energy being converted into what form of energy? (**b**) Does the potential energy of the two particles prior to release increase or decrease as the distance between them is increased.

1.13 For each of the following processes, does the potential energy of the object(s) increase or decrease? (**a**) The charge of two oppositely charged particles is increased. (**b**) H_2O molecule is split into two oppositely charged ions, H^+ and OH^-. (**c**) A person skydives from a height of 600 meters.

Answers to Self-Assessment Exercises

1.11 (a)

1.5 Units of Measurement



Many properties of matter are *quantitative*, that is, associated with numbers. When a number represents a measured quantity, the units of that quantity must be specified. The volume of a soft drink expressed in different units demonstrates how important this is. To say that the length of a pencil is 17.5 is meaningless. Expressing the number with its units, 17.5 centimeters (cm), properly specifies the length. The units used for scientific measurements are those of the **metric system**.

The metric system, developed in France during the late eighteenth century, is used as the system of measurement in most countries. By the end of this section, you should be able to

- Convert between different multiples of SI units

SI Units

In 1960, an international agreement was reached specifying a particular choice of metric units for use in scientific measurements. These preferred units are called **SI units**, after the French *Système International d'Unités*. This system has seven *base units* from which all other units are derived (Table 1.3). In this section, we will consider the base units for length, mass, and temperature.

With SI units, prefixes are used to indicate decimal fractions or multiples of various units. For example, the prefix *milli-* represents a 10^{-3} fraction, one-thousandth, of a unit: A milligram (mg) is 10^{-3} gram (g), a millimeter (mm) is 10^{-3} meter (m), and so forth.

TABLE 1.3 SI Base Units

Physical Quantity	Name of Unit	Abbreviation
Length	Meter	m
Mass	Kilogram	kg
Temperature	Kelvin	K
Time	Second	s or sec
Amount of substance	Mole	mol
Electric current	Ampere	A or amp
Luminous intensity	Candela	cd

A CLOSER LOOK The Scientific Method

Where does scientific knowledge come from? How is it acquired? How do we know it is reliable? How do scientists add to it, or modify it?

There is nothing mysterious about how scientists work. The first idea to keep in mind is that scientific knowledge is gained through observations of the natural world. A principal aim of the scientist is to organize these observations by identifying patterns and regularity, making measurements, and associating one set of observations with another. The next step is to ask *why* nature behaves in the manner we observe. To answer this question, the scientist constructs a model, known as a **hypothesis**, to explain the observations. Initially, the hypothesis is likely to be pretty tentative. There could be more than one reasonable hypothesis. If a hypothesis is correct, then certain results and observations should follow from it. In this way, hypotheses can stimulate the design of experiments to learn more about the system being studied. Scientific creativity comes into play in thinking of hypotheses that are fruitful in suggesting good experiments to do, ones that will shed new light on the nature of the system.

As more information is gathered, the initial hypotheses get winnowed down. Eventually, just one may stand out as most consistent with a body of accumulated evidence. We then begin to call this hypothesis a **theory**, a model that has predictive powers and that accounts for all the available observations. A theory also generally is consistent with other, perhaps larger and more general theories. For example, a theory of what goes on inside a volcano has to be consistent with more general theories regarding heat transfer, chemistry at high temperature, and so forth.

We will be encountering many theories as we proceed through this book. Some of them have been found over and over again to be consistent with observations. However, no theory can be proven to be absolutely true. We can treat it as though it is, but there always remains a possibility that there is some respect in which a theory is wrong. A famous example is Isaac Newton's theory of mechanics, which yielded such precise results for the mechanical behavior of matter that no exceptions to it were found before the twentieth century. But Albert Einstein showed that Newton's theory of the nature of space and time is incorrect.

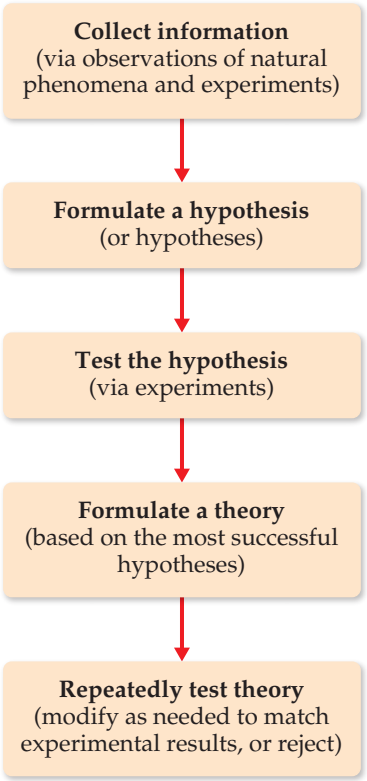
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Einstein's theory of relativity represented a fundamental shift in how we think of space and time. He predicted where the exceptions to predictions based on Newton's theory might be found. Although only small departures from Newton's theory were predicted, they *were* observed. Einstein's theory of relativity became accepted as the correct model. However, for most uses, Newton's laws of motion are quite accurate enough.

The overall process we have just considered, illustrated in Figure 1.17, is often referred to as *the scientific method*. But there is no single scientific method. Many factors play a role in advancing scientific knowledge. The one unvarying requirement is that our explanations be consistent with observations and that they depend solely on natural phenomena.

When nature behaves in a certain way over and over again, under all sorts of different conditions, we can summarize that behavior in a **scientific law**. For example, it has been repeatedly observed that in a chemical reaction there is no change in the total mass of the materials reacting as compared with the materials that are formed; we call this observation the *law of conservation of mass*. It is important to make a distinction between a theory and a scientific law. On the one hand, a scientific law is a statement of what always happens, to the best of our knowledge. A theory, on the other hand, is an *explanation* for what happens. If we discover some law fails to hold true, then we must assume the theory underlying that law is wrong in some way.

Related Exercises: 1.74, 1.96



▲ **Figure 1.17** The scientific method.

Table 1.4 presents the prefixes commonly encountered in chemistry. In using SI units and in working problems throughout this text, you must be comfortable using exponential notation. If you are unfamiliar with exponential notation or want to review it, refer to Appendix A.1.

TABLE 1.4 Prefixes Used in the Metric System and with SI Units

Prefix	Abbreviation	Meaning	Example	
Peta	P	10^{15}	1 petawatt (PW)	$= 1 \times 10^{15}$ watts[a]
Tera	T	10^{12}	1 terawatt (TW)	$= 1 \times 10^{12}$ watts
Giga	G	10^{9}	1 gigawatt (GW)	$= 1 \times 10^{9}$ watts
Mega	M	10^{6}	1 megawatt (MW)	$= 1 \times 10^{6}$ watts
Kilo	k	10^{3}	1 kilowatt (kW)	$= 1 \times 10^{3}$ watts
Deci	d	10^{-1}	1 deciwatt (dW)	$= 1 \times 10^{-1}$ watt
Centi	c	10^{-2}	1 centiwatt (cW)	$= 1 \times 10^{-2}$ watt
Milli	m	10^{-3}	1 milliwatt (mW)	$= 1 \times 10^{-3}$ watt
Micro	μ[b]	10^{-6}	1 microwatt (μW)	$= 1 \times 10^{-6}$ watt
Nano	n	10^{-9}	1 nanowatt (nW)	$= 1 \times 10^{-9}$ watt
Pico	p	10^{-12}	1 picowatt (pW)	$= 1 \times 10^{-12}$ watt
Femto	f	10^{-15}	1 femtowatt (fW)	$= 1 \times 10^{-15}$ watt
Atto	a	10^{-18}	1 attowatt (aW)	$= 1 \times 10^{-18}$ watt
Zepto	z	10^{-21}	1 zeptowatt (zW)	$= 1 \times 10^{-21}$ watt

[a]The watt (W) is the SI unit of power, which is the rate at which energy is either generated or consumed. The SI unit of energy is the joule (J); $1\,J = 1\,kg \cdot m^2/s^2$ and $1\,W = 1\,J/s$.
[b]Greek letter mu, pronounced "mew."

Although non–SI units are being phased out, some are still commonly used by scientists. Whenever we first encounter a non–SI unit in the text, the SI unit will also be given. The relations between the non–SI and SI units we will use most frequently in this text appear on the back inside cover. We will discuss how to convert from one to the other in Section 1.7.

Length and Mass

The SI base unit of *length* is the meter, a distance slightly longer than a yard. **Mass*** is a measure of the amount of material in an object. The SI base unit of mass is the kilogram (kg). This base unit is unusual because it uses a prefix, *kilo-*, instead of the word *gram* alone. We obtain other units for mass by adding prefixes to the word *gram*.

Sample Exercise 1.2

Using SI Prefixes

What is the name of the unit that equals (**a**) 10^{-9} gram, (**b**) 10^{-6} second, (**c**) 10^{-3} meter?

SOLUTION

We can find the prefix related to each power of ten in Table 1.4: (**a**) nanogram, ng; (**b**) microsecond, μs; (**c**) millimeter, mm.

Practice Exercise

(**a**) How many picometers are there in 1 m? (**b**) Express 6.0×10^3 m using a prefix to replace the power of ten. (**c**) Use exponential notation to express 4.22 mg in grams. (**d**) Use decimal notation to express 4.22 mg in grams.

Temperature

Temperature, a measure of the hotness or coldness of an object, is a physical property that determines the direction of heat flow. Heat always flows spontaneously from a substance at higher temperature to one at lower temperature. Thus, the influx of heat we feel when we touch a hot object tells us that the object is at a higher temperature than our hand.

The temperature scales commonly employed in science are the Celsius and Kelvin scales. The **Celsius scale** was originally based on the assignment of 0 °C to the freezing point of water and 100 °C to its boiling point at sea level (Figure 1.18).

The **Kelvin scale** is the SI temperature scale, and the SI unit of temperature is the *kelvin* (K). Zero on the Kelvin scale is the temperature at which all thermal motion ceases, a temperature referred to as **absolute zero**. On the Celsius scale, absolute zero has the value −273.15 °C. The Celsius and Kelvin scales have equal-sized units—that is, a kelvin is the same size as a degree Celsius. Thus, the Kelvin and Celsius scales are related according to

$$K = °C + 273.15 \qquad [1.3]$$

The freezing point of water, 0 °C, is 273.15 K (Figure 1.18). Notice that we do not use a degree sign (°) with temperatures on the Kelvin scale.

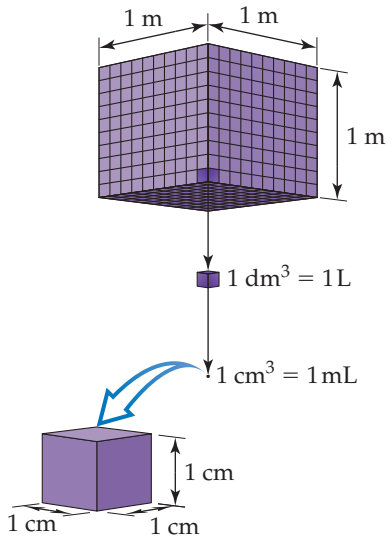
Derived SI Units

The SI base units are used to formulate *derived units*. A **derived unit** is obtained by multiplication or division of one or more of the base units. We begin with the defining

*Mass and weight are not the same. Mass is a measure of the amount of matter; weight is the force exerted on this mass by gravity. For example, an astronaut weighs less on the Moon than on Earth because the Moon's gravitational force is less than Earth's. The astronaut's mass on the Moon, however, is the same as it is on Earth.

Go Figure

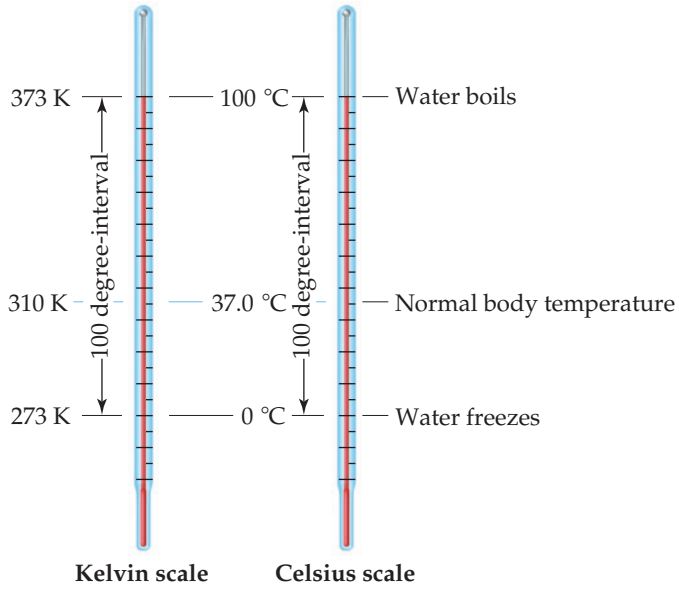
How many 1-L bottles are required to contain 1 m^3 of liquid?



▲ **Figure 1.19 Volume relationships.** The volume occupied by a cube 1 m on each edge is one cubic meter, 1 m^3. Each cubic meter contains 1000 dm^3, 1 m^3 = 1000 dm^3. One liter is the same volume as one cubic decimeter, 1 L = 1 dm^3. Each cubic decimeter contains 1000 cubic centimeters, 1 dm^3 = 1000 cm^3. One cubic centimeter equals one milliliter, 1 cm^3 = 1 mL.

Go Figure

True or false: The "size" of a degree on the Celsius scale is the same as the "size" of a degree on the Kelvin scale.



▲ **Figure 1.18 Comparison of the Kelvin and Celsius temperature scales.**

equation for a quantity and, then substitute the appropriate base units. For example, *speed* is defined as the ratio of distance traveled to elapsed time. Thus, the derived SI unit for speed is the SI unit for distance (length), m, divided by the SI unit for time, s, which gives m/s, read "meters per second." Two common derived units in chemistry are those for volume and density.

Volume

The *volume* of a cube is its length cubed, length^3. Thus, the derived SI unit of volume is the SI unit of length, m, raised to the third power. The cubic meter, m^3, is the volume of a cube that is 1 m on each edge (**Figure 1.19**). Smaller units, such as cubic centimeters, cm^3 (sometimes written cc), are frequently used in chemistry. Another volume unit used in chemistry is the *liter* (L), which equals a cubic decimeter, dm^3. (The liter is the first metric unit we have encountered that is *not* an SI unit.) There are 1000 milliliters (mL) in a liter, and 1 mL is the same volume as 1 cm^3: 1 mL = 1 cm^3.

Sample Exercise 1.3

Converting Units of Temperature

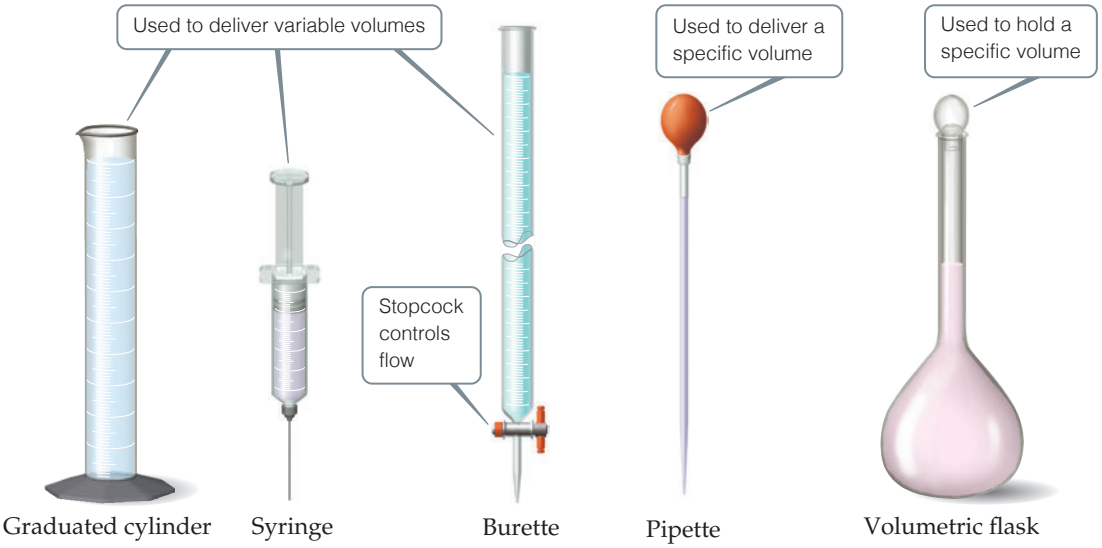
A weather forecaster predicts the temperature will reach 31 °C. What is this temperature in K?

SOLUTION

Equation 1.3, we have K = 31 + 273 = 304 K.

Practice Exercise

Using Wolfram Alpha (http://www.wolframalpha.com/) or some other reference, determine which of these elements would be liquid at 525 K (assume samples are protected from air): (**a**) bismuth, Bi; (**b**) platinum, Pt; (**c**) selenium, Se; (**d**) calcium, Ca; (**e**) copper, Cu.



▲ **Figure 1.20** **Common volumetric glassware.**

In the lab, you will likely use the devices in **Figure 1.20** to measure and deliver volumes of liquids. Syringes, burettes, and pipettes deliver amounts of liquids with more precision than graduated cylinders. Volumetric flasks are used to contain specific volumes of liquid.

Density

Density is defined as the amount of mass in a unit volume of a substance:

$$\text{density} = \frac{\text{mass}}{\text{volume}} \qquad [1.4]$$

The densities of solids and liquids are commonly expressed in either grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL). The densities of some common substances are listed in **Table 1.5**. It is no coincidence that the density of water is 1.00 g/mL; the gram was originally defined as the mass of 1 mL of water at a specific temperature. Because most substances change volume when they are heated or cooled, densities are temperature dependent, and so temperature should be specified when reporting densities. If no temperature is reported, we assume 25 °C, close to normal room temperature.

The terms *density* and *weight* are sometimes confused. A person who says that iron weighs more than air generally means that iron has a higher density than air—1 kg of air has the same mass as 1 kg of iron, but the iron occupies a smaller volume, thereby giving it a higher density. If we combine two liquids that do not mix, the less dense liquid will float on the denser liquid.

TABLE 1.5 Densities of Selected Substances at 25 °C

Substance	Density (g/cm^3)
Air	0.001
Balsa wood	0.16
Ethanol	0.79
Water	1.00
Ethylene glycol	1.09
Table sugar	1.59
Table salt	2.16
Iron	7.9
Gold	19.32

Units of Energy

The SI unit for energy is the **joule** (pronounced "jool"), J, in honor of James Joule (1818–1889), a British scientist who investigated work and heat. If we return to Equation 1.2 where kinetic energy was defined, we immediately see that joules are a derived unit, $1\ J = 1\ kg\text{-}m^2/s^2$. Numerically, a 2-kg mass moving at a velocity of 1 m/s possesses a kinetic energy of 1 J:

$$E_k = \frac{1}{2}mv^2 = \frac{1}{2}(2\ kg)(1\ m/s)^2 = 1\ kg\text{-}m^2/s^2 = 1\ J$$

Sample Exercise 1.4

Determining Density and Using Density to Determine Volume or Mass

(**a**) Calculate the density of mercury if 1.00×10^2 g occupies a volume of 7.36 cm^3.
(**b**) Calculate the volume of 65.0 g of liquid methanol if its density is 0.791 g/mL.
(**c**) What is the mass in grams of a cube of gold (density = 19.32 g/cm^3) if the length of the cube is 2.00 cm?

SOLUTION

(**a**) We are given mass and volume, so Equation 1.3 yields

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.00 \times 10^2\ \text{g}}{7.36\ \text{cm}^3} = 13.6\ \text{g/cm}^3$$

(**b**) Solving Equation 1.3 for volume and then using the given mass and density gives

$$\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{65.0\ \text{g}}{0.791\ \text{g/mL}} = 82.2\ \text{mL}$$

(**c**) We can calculate the mass from the volume of the cube and its density. The volume of a cube is given by its length cubed:

$$\text{Volume} = (2.00\ \text{cm})^3 = (2.00)^3\ \text{cm}^3 = 8.00\ \text{cm}^3$$

Solving Equation 1.3 for mass and substituting the volume and density of the cube, we have

$$\text{Mass} = \text{volume} \times \text{density} = (8.00\ \text{cm}^3)(19.32\ \text{g/cm}^3) = 155\ \text{g}$$

Practice Exercise

(**a**) Calculate the density of a 374.5-g sample of copper if it has a volume of 41.8 cm^3. (**b**) A student needs 15.0 g of ethanol for an experiment. If the density of ethanol is 0.789 g/mL, how many milliliters of ethanol are needed? (**c**) What is the mass, in grams, of 25.0 mL of mercury (density = 13.6 g/mL)?

Because a joule is not a very large amount of energy, we often use *kilojoules* (kJ) in discussing the energies associated with chemical reactions. For example, the amount of heat released when hydrogen and oxygen react to form 1 g of water is 16 kJ.

It is still quite common in chemistry, biology, and biochemistry to find energy changes associated with chemical reactions expressed in the non-SI unit of calories. A **calorie** (cal) was originally defined as the amount of energy required to raise the temperature of 1 g of water from 14.5 to 15.5 °C. It has since been defined in terms of a joule:

$$1\ \text{cal} = 4.184\ \text{J (exactly)}$$

A related energy unit that is familiar to anyone who has read a food label is the nutritional *Calorie* (note the capital C), which is 1000 times larger than calorie with a lowercase c: 1 Cal = 1000 cal = 1 kcal.

Sample Exercise 1.5

Identifying and Calculating Energy Changes

A standard propane (C_3H_8) tank used in an outdoor grill holds approximately 9.0 kg of propane. When the grill is operating, propane reacts with oxygen to form carbon dioxide and water. For every gram of propane that reacts with oxygen in this way, 46 kJ of energy is released as heat. (**a**) How much energy is released if the entire contents of the propane tank react with oxygen? (**b**) As the propane reacts, does the potential energy stored in chemical bonds increase or decrease? (**c**) If you were to store an equivalent amount of potential energy by pumping water to an elevation of 75 m above the ground, what mass of water would be needed? (Note: The force due to gravity acting on the water, which is the water's weight, is $F = m \times g$, where m Is the mass of the object and g is the gravitational constant, $g = 9.8\ \text{m/s}^2$.)

SOLUTION

(**a**) We can calculate the amount of energy released from the propane as heat by converting the mass of propane from kg to g and then using the fact that 46 kJ of heat are released per gram:

$$E = 9.0\ \text{kg} \times \frac{1000\ \text{g}}{1\ \text{kg}} \times \frac{46\ \text{kJ}}{1\ \text{g}} = 4.1 \times 10^5\ \text{kJ} = 4.1 \times 10^8\ \text{J}$$

(**b**) When propane reacts with oxygen, the potential energy stored in the chemical bonds is converted to an alternate form of energy, heat. Therefore, the potential energy stored as chemical energy must decrease.

(**c**) The amount of work done to pump the water to a height of 75 m can be calculated using Equation 1.1:

$$w = F \times d = (m \times g) \times d$$

rearranging to solve for the mass of water:

$$m = \frac{w}{g \times d} = \frac{4.1 \times 10^8\ \text{J}}{(9.8\ \text{m/s}^2)(75\ \text{m})} = \frac{4.1 \times 10^8\ \text{kg-m}^2/\text{s}^2}{(9.8\ \text{m/s}^2)(75\ \text{m})}$$

$$= 5.6 \times 10^5\ \text{kg}$$

At 25 °C, this mass of water would have a volume of 560,000 L. Thus, we see that large amounts of potential energy can be stored as chemical energy.

Practice Exercise

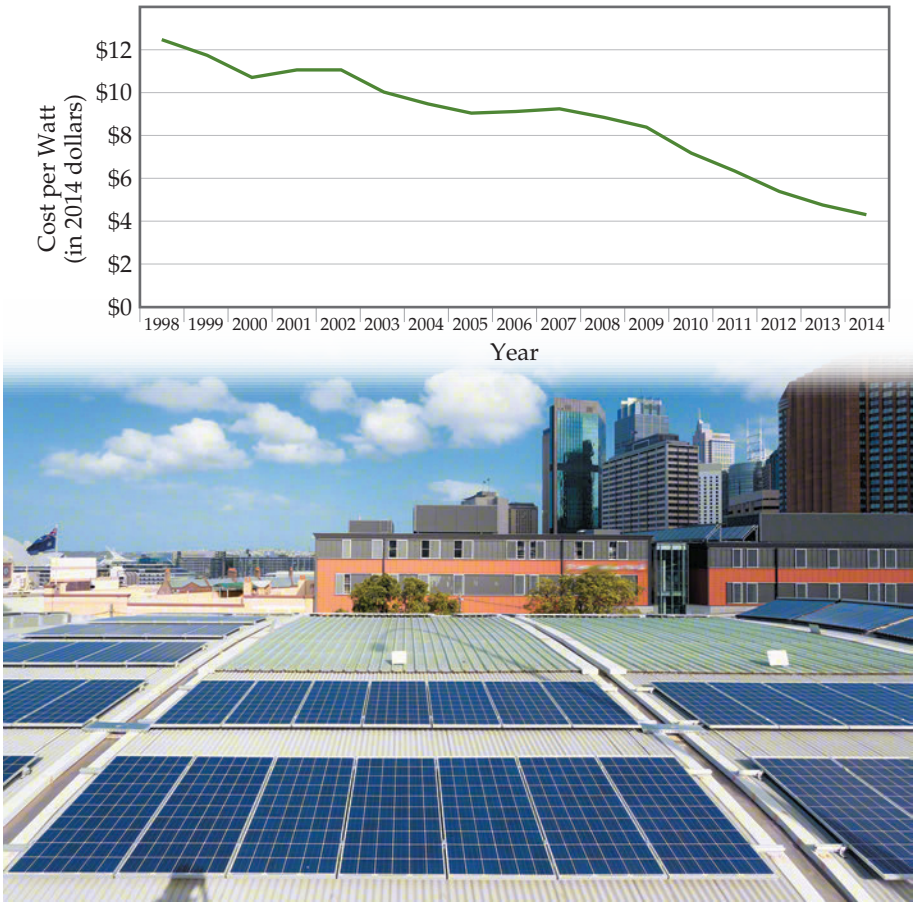
Which of the following objects has the greatest kinetic energy? (**a**) a 500-kg motorcycle moving at 100 km/h (**b**) a 1,000-kg car moving at 50 km/h (**c**) a 1500-kg car moving at 30 km/h (**d**) a 5000 kg truck moving at 10 km/h (**e**) a 10,000-kg truck moving at 5 km/h

CHEMISTRY PUT TO WORK Chemistry in the News

Solar Energy Steps Up. Given the challenges society faces in trying to mitigate the effects of climate change, the need for affordable clean energy has never been greater. Given the massive amount of energy our planet receives from the Sun, solar energy has long been touted as a technology of the future. The problem for decades has been the relatively high cost of solar power compared to energy generated from burning fossil fuels. However, in recent years the cost of solar energy has decreased more rapidly than most people thought possible, decreasing more than 50% in just the past five years (Figure 1.21).

Not surprisingly, over the last six years the number of solar panel installations worldwide has increased sixfold. Over the same period, the number of coal plants operating in the United States has decreased by 38%, from 523 to 323. China is on track to install plants capable of generating more than 18 gigawatts of solar energy in 2015, nearly equal to the entire solar energy capacity of the United States. Furthermore, with the price of solar energy dropping rapidly, there is reason to believe that developing nations may forgo building fossil fuel power plants and skip straight to green energy technologies like solar and wind.

Recently, chemists have discovered a new class of materials called halide perovskites that have the potential to bring the cost of solar energy down even further. Solar cells made with halide perovskites have been shown to be nearly as efficient as single crystal silicon solar cells, but can be prepared from inexpensive solution methods that differ from the more costly and energy-intensive methods used to produce silicon solar cells. There are still many challenges to be overcome before halide perovskite solar cells are produced commercially, but their future looks very promising.



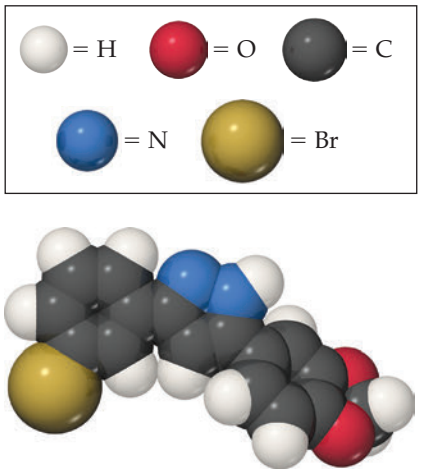
▲ **Figure 1.21 The cost of energy generated by photovoltaic modules.** The median price per watt of electricity generated has dropped by two-thirds since 1998. The cost figures here include the cost for fully installed residential solar panels.

Slowing a Progressive Disease. Proteins are very large molecules that play an essential role in biology and the functioning of living organisms. Out of the myriad different types of proteins, scientists have identified one class of proteins called *prions* that play an important role in certain neurological diseases. We all have prion proteins in our brains, and for nearly all of us, they cause no harmful effects. For a small fraction of people, though, something causes the prions to change form and to adopt an incorrectly folded molecular shape. This process, once begun, is cumulative, propagating throughout the brain; the misfolded proteins somehow trigger the same misfolding in other prion proteins. Eventually, the misfolded proteins aggregate into clusters that can destroy neurons, producing symptoms such as those seen in Alzheimer's and Parkinson's diseases.

Currently, no therapies have been developed to stop the progression of prion diseases. However, there are encouraging signs that certain small molecules could disrupt propagation of the disease. They might be able to do this by blocking the interaction between one prion protein and another that causes the misfolding to propagate. So far, the experimental work has involved studies of mice infected with prions. One such molecule, called Anle-138b, is shown in Figure 1.22. Administration of this compound more than doubled the life spans of treated mice.

Compounds such as this one are not suitable for use in treating prion disease in humans, but studies conducted thus far point the way toward discovery of molecules that might in the future provide

Continued



▲ **Figure 1.22** **Anle-138b, a promising molecule for the treatment of degenerative brain diseases.**

effective therapies. This work illustrates the complex and sometimes tortuous path that takes the scientist from promising beginnings to a much desired goal.

Chemical Approaches to Art Restoration. Works of art are made from materials that over time can undergo chemical reactions that alter their appearance or undermine their mechanical stability. Layers of dirt and pollutants can build up on the surface, discoloring statues, murals, and paintings. Plasters that serve as the base for frescoes react with gases in the atmosphere. One approach to art restoration is to use selected chemical reactions to undo or reverse the effects of detrimental reactions that have occurred over time.

One such example involves murals at the ancient Mayan ruins of Mayapan in Mexico's Yucatán peninsula. In the 1960s, polymer coatings were applied to these murals in an attempt to preserve them, but within a decade it became clear that the polymer coatings were doing more harm than good. Unfortunately, years of oxidation and cross-linking reactions had rendered the polymer coatings insoluble to nearly every type of organic solvent. In 2008, a team of Italian chemists found a way to remove the polymer coatings without damaging the underlying fresco. They treated the murals with a microemulsion, a special type of mixture where molecules called surfactants encapsulate and carry nanometer-sized droplets of organic solvents through an aqueous solution to the surface of the fresco. Once the droplets reach the surface, they can dissolve and carry away the unwanted polymer coating.

Self-Assessment Exercise

1.14 A standard Olympic-size swimming pool contains 2.5 ML of water. What volume is this in m^3?

(a) 2.5 m^3

(b) 250 m^3

(c) 2 500 m^3

(d) 2 500 000 m^3

Exercises

1.15 Convert the following expressions into exponential notation: (**a**) 3 terameters (Tm) (**b**) 2.5 femtoseconds (fs) (**c**) 57 micrometers (μm) (**d**) 8.3 megagrams (Mg).

1.16 Make the following conversions: **(a)** 25 °C to K (**b**) 110 °C to K (**c**) 300 K to °C (**d**) 1100 K to °C

1.17 **(a)** A sample of tetrachloroethene, a liquid used in dry cleaning that is being phased out because of its potential to cause cancer, has a mass of 40.55 g and a volume of 25.0 mL at 25 °C. What is its density at this temperature? Will tetrachloroethene float on water? (Materials that are less dense than water will float.) **(b)** Carbon dioxide (CO_2) is a gas at room temperature and pressure. However, carbon dioxide can be put under pressure to become a "supercritical fluid" that is a much safer dry-cleaning agent than tetrachloroethylene. At a certain pressure, the density of supercritical CO_2 is 0.469 g/cm^3. What is the mass of a 25.0-mL sample of supercritical CO_2 at this pressure?

1.18 **(a)** To identify a liquid substance, a student determined its density. Using a graduated cylinder, she measured out a 45-mL sample of the substance. She then measured the mass of the sample, finding that it weighed 38.5 g. She knew that the sub-stance had to be either isopropyl alcohol (density 0.785 g/mL) or toluene (density 0.866 g/mL). What are the calculated density and the probable identity of the substance? **(b)** An experiment requires 45.0 g of ethylene glycol, a liquid whose density is 1.114 g/mL. Rather than weigh the sample on a balance, a chemist chooses to dispense the liquid using a graduated cylinder. What volume of the liquid should he use? **(c)** Is a graduated cylinder such as that shown in Figure 1.20 likely to afford the accuracy of measurement needed? **(d)** A cubic piece of metal measures 5.00 cm on each edge. If the metal is nickel, whose density is 8.90 g/cm^3, what is the mass of the cube?

1.19 If on a certain year, an estimated amount of 4 million metric tons (1 metric ton = 1000 kg) of nitrous oxide (N_2O) was emitted worldwide due to agricultural activities, express this mass of N_2O in grams without exponential notation, using an appropriate metric prefix.

Answers to Self-Assessment Exercises

1.14 (c)

1.6 Uncertainty in Measurement



Weighing a single postage stamp on a pair of old-fashioned scales is unlikely to give you a meaningful result. As scientists, when we make measurements, we must always consider the appropriateness of the numbers we report. There are specific ways in which to do this that can give us confidence in interpreting data collected by ourselves and others. By the end of this section, you should be able to

- Determine the correct number of significant figures to report at the conclusion of an experiment

Two kinds of numbers are encountered in scientific work: *exact numbers* (those whose values are known exactly) and *inexact numbers* (those whose values have some uncertainty). Most of the exact numbers we will encounter in this book have defined values. For example, there are exactly 12 eggs in a dozen and exactly 1000 g in a kilogram. The number 1 in any conversion factor, such as 1 m = 100 cm or 1 kg = 1000 g, is an exact number. Exact numbers can also result from counting objects. For example, we can count the exact number of marbles in a jar or the exact number of people in a classroom.

Numbers obtained by measurement are always *inexact*. The equipment used to measure quantities always has inherent limitations (equipment errors), and there are differences in how different people make the same measurement (human errors). Suppose ten students with ten balances are to determine the mass of the same coin. The ten measurements will probably vary slightly for various reasons. The balances might be calibrated slightly differently, and there might be differences in how each student reads the mass from the balance. Remember: *Uncertainties always exist in measured quantities.*

Precision and Accuracy

The terms *precision* and *accuracy* are often used in discussing the uncertainties of measured values. **Precision** is a measure of how closely individual measurements agree with one another. **Accuracy** refers to how closely individual measurements agree with the correct, or "true," value. The dart analogy in **Figure 1.23** illustrates the difference between these two concepts.

In the laboratory, we often perform several "trials" of an experiment and average the results. The precision of the measurements is often expressed in terms of the *standard deviation* (Appendix A.5), which reflects how much the individual measurements differ



High precision can be achieved on a scale like this one, which has 0.1 mg accuracy.

Go Figure

How would the darts be positioned on the target for the case of "good accuracy, poor precision"?



Good accuracy
Good precision



Poor accuracy
Good precision



Poor accuracy
Poor precision

▲ **Figure 1.23** Precision and accuracy.

from the average. We gain confidence in our measurements if we obtain nearly the same value each time—that is, when the standard deviation is small. Figure 1.23 reminds us, however, that precise measurements can be inaccurate. For example, if a very sensitive balance is poorly calibrated, the masses we measure will be consistently either high or low. They will be inaccurate even if they are precise.

Significant Figures

Suppose you determine the mass of a coin on a balance capable of measuring to the nearest 0.0001 g. You could report the mass as 2.2405 ± 0.0001 g. The ± notation (read "plus or minus") expresses the magnitude of the uncertainty of your measurement. In much scientific work, we drop the ± notation with the understanding that *there is always some uncertainty in the last digit reported for any measured quantity.*

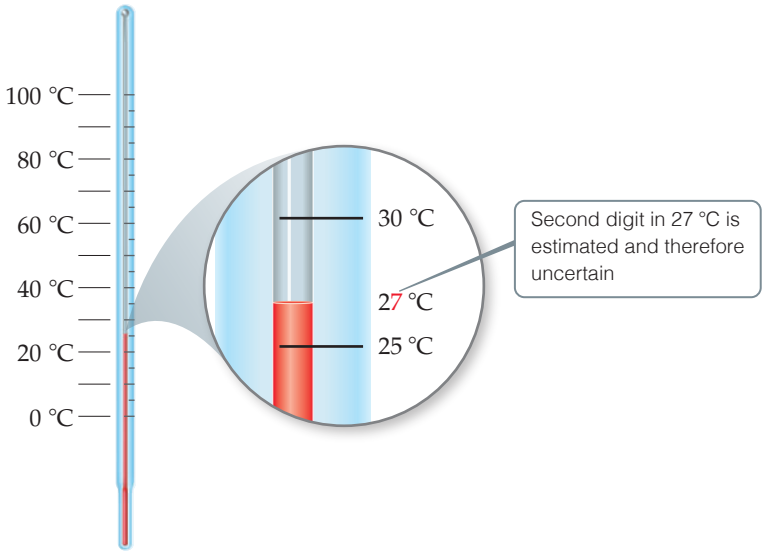
Figure 1.24 shows a thermometer with its liquid column between two scale marks. We can read the certain digits from the scale and estimate the uncertain one. Seeing that the liquid is between the 25 °C and 30 °C marks, we estimate the temperature to be 27 °C, being uncertain of the second digit of our measurement. By *uncertain* we mean that the temperature is reliably 27 °C and not 28 °C or 26 °C, but we can't say that it is *exactly* 27 °C.

All digits of a measured quantity, including the uncertain one, are called **significant figures**. A measured mass reported as 2.2 g has two significant figures, whereas one reported as 2.2405 g has five significant figures. The greater the number of significant figures, the greater the precision implied for the measurement.

To determine the number of significant figures in a reported measurement, read the number from left to right, counting the digits starting with the first digit that is not zero. *In any measurement that is properly reported, all nonzero digits are significant.* Because zeros can be used either as part of the measured value or merely to locate the decimal point, they may or may not be significant:

- Zeros *between* nonzero digits are always significant—1005 kg (four significant figures); 7.03 cm (three significant figures).
- Zeros *at the beginning* of a number are never significant; they merely indicate the position of the decimal point—0.02 g (one significant figure); 0.0026 cm (two significant figures).
- Zeros *at the end* of a number are significant if the number contains a decimal point—0.0200 g (three significant figures); 3.0 cm (two significant figures).

A problem arises when a number ends with zeros but contains no decimal point. In such cases, it is normally assumed that the zeros are not significant. Exponential notation (Appendix A.1) can be used to indicate whether end zeros are significant.



▲ **Figure 1.24** Uncertainty and significant figures in a measurement.

For example, a mass of 10 300 g can be written to show three, four, or five significant figures depending on how the measurement is obtained:

1.03×10^4 g	(three significant figures)
1.030×10^4 g	(four significant figures)
1.0300×10^4 g	(five significant figures)

In these numbers, all the zeros to the right of the decimal point are significant (rules 1 and 3). (The exponential term 10^4 does not add to the number of significant figures.)

Sample Exercise 1.6

Assigning Appropriate Significant Figures

The US state of Colorado is listed in a road atlas as having a population of 5,546,574 and an area of 269,837 square kilometers. Do the numbers of significant figures in these two quantities seem reasonable? If not, what seems to be wrong with them?

SOLUTION

The population of Colorado must vary from day to day as people move in or out, are born, or die. Thus, the reported number suggests a much higher degree of *accuracy* than is possible. Moreover, it would not be feasible to actually count every individual resident in the state at any given time. Thus, the reported number suggests far greater *precision* than is possible. A reported number of 5,500,000 would better reflect the actual state of knowledge.

The area of Colorado does not normally vary from time to time, so the question here is whether the accuracy of the measurements is good to six significant figures. It would be possible to achieve such accuracy using satellite technology, provided the legal boundaries are known with sufficient accuracy.

Practice Exercise

The back inside cover of the book tells us that there are 1000 cm^3 in 1 liter. Does this make the liter an exact volume?

Sample Exercise 1.7

Determining the Number of Significant Figures in a Measurement

How many significant figures are in each of the following numbers (assume that each number is a measured quantity): (**a**) 4.003, (**b**) 6.023×10^{23}, (**c**) 5000?

SOLUTION

(**a**) Four; the zeros are significant figures. (**b**) Four; the exponential term does not add to the number of significant figures. (**c**) One; we assume that the zeros are not significant when there is no decimal point shown. If the number has more significant figures, a decimal point should be employed or the number written in exponential notation. Thus, 5000. has four significant figures, whereas 5.00×10^3 has three.

Practice Exercise

An object is determined to have a mass of 0.01080 g. How many significant figures are there in this measurement?
(**a**) 2 (**b**) 3 (**c**) 4 (**d**) 5 (**e**) 6

Significant Figures in Calculations

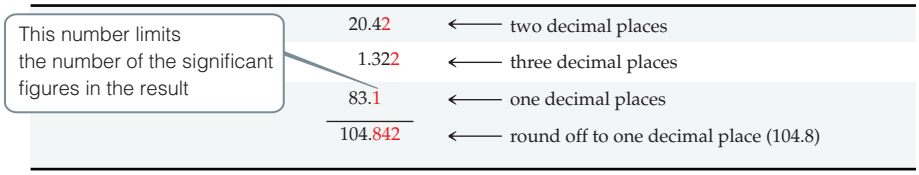
Apply the following rule when carrying measured quantities through calculations.

> *The least certain measurement limits the certainty of the calculated quantity and thereby determines the number of significant figures in the final answer.*

The final answer should be reported with only one uncertain digit. To keep track of significant figures in calculations, we will make frequent use of two rules: one for addition and subtraction, and another for multiplication and division.

1. *For addition and subtraction,* the result has the same number of decimal places as the measurement with the *fewest decimal places.* When the result contains more than the correct number of significant figures, it must be rounded off. Consider the following

example where the first three numbers are added to give the fourth and in which the uncertain digits appear in color:



We report the result as 104.8 because 83.1 has only one decimal place.

2. *For multiplication and division*, the result contains the same number of significant figures as the measurement with the *fewest significant figures*. When the result contains more than the correct number of significant figures, it must be rounded off. For example, the area of a rectangle whose measured edge lengths are 6.221 and 5.2 cm should be reported with two significant figures, 32 cm^2, even though a calculator shows the product to have more digits:

$$\text{Area} = (6.221\ \text{cm})(5.2\ \text{cm}) = 32.3492\ \text{cm}^2 \Rightarrow \text{round off to } 32\ \text{cm}^2$$

because 5.2 has two significant figures.

In determining the final answer for a calculated quantity, *exact numbers* are assumed to have an infinite number of significant figures. Thus, when we say, "There are 1000 meters in 1 kilometer," the number 1000 is exact, and we need not worry about the number of significant figures in it.

When *rounding off numbers* look at the leftmost digit to be removed:

- If the leftmost digit removed is less than 5, the preceding number is left unchanged. Thus, rounding off 7.248 to two significant figures gives 7.2.
- If the leftmost digit removed is 5 or greater, the preceding number is increased by 1. Rounding off 4.735 to three significant figures gives 4.74, and rounding 2.376 to two significant figures gives 2.4.*

Sample Exercise 1.8

Determining the Number of Significant Figures in a Calculated Quantity

The width, length, and height of a small box are 15.5, 27.3, and 5.4 cm, respectively. Calculate the volume of the box, using the correct number of significant figures in your answer.

SOLUTION

In reporting the volume, we can show only as many significant figures as given in the dimension with the fewest significant figures, which is that for the height (two significant figures):

$$\begin{aligned}\text{Volume} &= \text{width} \times \text{length} \times \text{height} \\ &= (15.5\ \text{cm})(27.3\ \text{cm})(5.4\ \text{cm}) \\ &= 2285.01\ \text{cm}^3 \Rightarrow 2.3 \times 10^3\ \text{cm}^3\end{aligned}$$

A calculator used for this calculation shows 2285.01, which we must round off to two significant figures. Because the resulting number is 2300, it is best reported in exponential notation, 2.3×10^3, to clearly indicate two significant figures.

Practice Exercise

It takes 10.5 s for a sprinter to run 100.00 m. Calculate her average speed in meters per second and express the result to the correct number of significant figures.

*Your instructor may want you to use a slight variation on the rule when the leftmost digit to be removed is exactly 5, with no following digits or only zeros following. One common practice is to round up to the next higher number if that number will be even and otherwise leave the number unchanged. Thus, 4.7350 would be rounded to 4.74, and 4.7450 would also be rounded to 4.74.

Sample Exercise 1.9

Determining the Number of Significant Figures in a Calculated Quantity

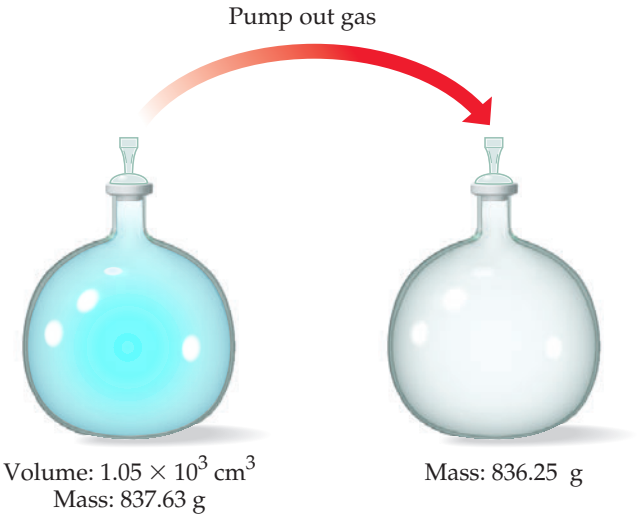
A vessel containing a gas at 25 °C is weighed, emptied, and then reweighed as depicted in Figure 1.25. From the data provided, calculate the density of the gas at 25 °C.

SOLUTION

To calculate the density, we must know both the mass and the volume of the gas. The mass of the gas is just the difference in the masses of the full and empty container:

$$\begin{array}{r} 837.63\ \text{g} \\ -836.25\ \text{g} \\ \hline 1.38\ \text{g} \end{array}$$

In subtracting numbers, we determine the number of significant figures in our result by counting decimal places in each quantity.



▲ Figure 1.25 Uncertainty and significant figures in a measurement.

In this case each quantity has two decimal places. Thus, the mass of the gas, 1.38 g, has two decimal places.

Using the volume given in the question, $1.05 \times 10^3\ \text{cm}^3$, and the definition of density, we have

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.38\ \text{g}}{1.05 \times 10^3\ \text{cm}^3}$$

$$= 1.31 \times 10^{-3}\ \text{g/cm}^3 = 0.00131\ \text{g/cm}^3$$

In dividing numbers, we determine the number of significant figures our result should contain by counting the number of significant figures in each quantity. There are three significant figures in our answer, corresponding to the number of significant figures in the two numbers that form the ratio. Notice that in this example, following the rules for determining significant figures gives an answer containing only three significant figures, even though the measured masses contain five significant figures.

Practice Exercise

You are asked to determine the mass of a piece of copper using its reported density, 8.96 g/mL, and a 150-mL graduated cylinder. First, you add 105 mL of water to the graduated cylinder; then you place the piece of copper in the cylinder and record a volume of 137 mL. What is the mass of the copper reported with the correct number of significant figures? (**a**) 287 g (**b**) 3.5×10^{-3} g/mL (**c**) 286.72 g/mL (**d**) 3.48×10^{-3} g/mL (**e**) 2.9×10^2 g/mL

When a calculation involves two or more steps and you write answers for intermediate steps, retain at least one nonsignificant digit for the intermediate answers. This procedure ensures that small errors from rounding at each step do not combine to affect the final result. When using a calculator, you may enter the numbers one after another, rounding only the final answer. Accumulated rounding-off errors may account for small differences among results you obtain and answers given in the text for numerical problems.

Self-Assessment Exercise

1.20 Do the following numbers, all representing the thickness of a typical piece of paper, have the same number of significant figures: 0.10 mm, 1.0×10^{-4} m, 100 μm?

(a) Yes

(b) No

Exercises

1.21 Indicate which of the following are exact numbers: (**a**) the mass of a 7.5 by 12.5 cm index card, (**b**) the number of grams in a kilogram, (**c**) the volume of a cup of Seattle's Best coffee, (**d**) the number of centimeters in a kilometer, (**e**) the number of microseconds in a week, (**f**) the number of pages in this book.

1.22 What is the number of significant figures in each of the following measured quantities? **(a)** 902.5 kg, **(b)** 3×10^{-6} m, **(c)** 0.0096 L, **(d)** $2.94 \times 10^3\ \text{m}^2$, **(e)** 92.03 km (**f**) 782.234 g.

1.23 Round each of the following numbers to three significant figures and express the result in standard exponential

notation: **(a)** 2048732.23 **(b)** 0.000292945 **(c)** −82454.09 **(d)** 942.057024 **(e)** −0.00000324683.

1.24 Carry out the following operations and express the answers with the appropriate number of significant numbers.

(**a**) 43.029 + 0.02348 (**b**) 952.72 − 73.4201

(**c**) $(2.93 \times 10^3)\,(0.732)$ (**d**) 0.06324/0.624

1.25 You weigh an object on a balance and read the mass in grams according to the picture. How many significant figures are in this measurement?



Answers to Self-Assessment Exercises

1.20 (b)

1.7 Dimensional Analysis



Anyone who has travelled to another country and looked at the price of fuel there will experience the need to convert from one set of units to another. Most often, this conversion is between currencies but, in some cases, the standard volume may have different units—liters or gallons for example.

The SI system of units provides a common 'language' in which to communicate measurement. However, there are still some industries and some countries in which historic units are employed. By the end of this section, you should be able to

- Convert between different units for a particular measurement

Because measured quantities have units associated with them, it is important to keep track of units as well as numerical values when using the quantities in calculations. Throughout the text we use dimensional analysis in solving problems. In **dimensional analysis**, units are multiplied together or divided into each other along with the numerical values. Equivalent units cancel each other. Using dimensional analysis helps ensure that solutions to problems yield the proper units. Moreover, it provides a systematic way of solving many numerical problems and of checking solutions for possible errors.

Conversion Factors

The key to using dimensional analysis is the correct use of *conversion factors* to change one unit into another. A **conversion factor** is a fraction whose numerator and denominator are the same quantity expressed in different units. For example, 2.54 cm and 1 inch are the same length: 2.54 cm = 1 in. This relationship allows us to write two conversion factors:

$$\frac{2.54\text{ cm}}{1\text{ in.}} \quad \text{and} \quad \frac{1\text{ in.}}{2.54\text{ cm}}$$

We use the first factor to convert inches to centimeters. For example, the length in centimeters of an object that is 8.50 in. long is

$$\text{Number of centimeters} = (8.50\ \cancel{\text{in.}})\left(\frac{2.54\text{ cm}}{1\ \cancel{\text{in.}}}\right) = 21.6\text{ cm}$$

(Desired unit: cm; Given unit: in.)

The unit inches in the denominator of the conversion factor cancels the unit inches in the given data (8.50 *inches*), so that the centimeters unit in the numerator of the conversion factor becomes the unit of the final answer. Because the numerator and denominator of a conversion factor are equal, multiplying any quantity by a conversion factor is equivalent to multiplying by the number 1 and so does not change the intrinsic value of the quantity. The length 8.50 in. is the same as the length 21.6 cm.

In general, we begin any conversion by examining the units of the given data and the units we desire. We then ask ourselves what conversion factors we have available to take us from the units of the given quantity to those of the desired one. When we multiply a quantity by a conversion factor, the units multiply and divide as follows:

$$\cancel{\text{Given unit}} \times \frac{\text{desired unit}}{\cancel{\text{given unit}}} = \text{desired unit}$$

If the desired units are not obtained in a calculation, an error must have been made somewhere. Careful inspection of units often reveals the source of the error.

Sample Exercise 1.10

Converting Units

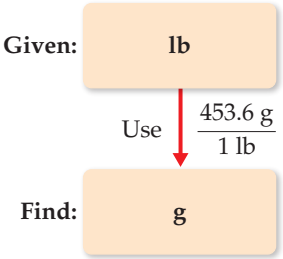
If a woman has a mass of 115 lb, what is her mass in grams? (The measurement of a 'pound' has the units 'lb'. 1 lb = 453.6 g)

SOLUTION

Because we want to change from pounds to grams, we look for a relationship between these units of mass. The conversion factor table found on the back inside cover tells us that 1 lb = 453.6 g. To cancel pounds and leave grams, we write the conversion factor with grams in the numerator and pounds in the denominator:

$$\text{Mass in grams} = (115\ \cancel{\text{lb}})\left(\frac{453.6\text{ g}}{1\ \cancel{\text{lb}}}\right) = 5.22 \times 10^4\text{ g}$$

The answer can be given to only three significant figures, the number of significant figures in 115 lb. The process we have used is diagrammed on the top right column.



Practice Exercise

At a particular instant in time, the Earth is judged to be 92,955,000 miles from the Sun. What is the distance in kilometers to four significant figures? (1 mile = 1.6093 km.)

(**a**) 5763×10^4 km (**b**) 1.496×10^8 km (**c**) 1.49596×10^8 km (**d**) 1.483×10^4 km (**e**) 57,759,000 km

STRATEGIES FOR SUCCESS Estimating Answers

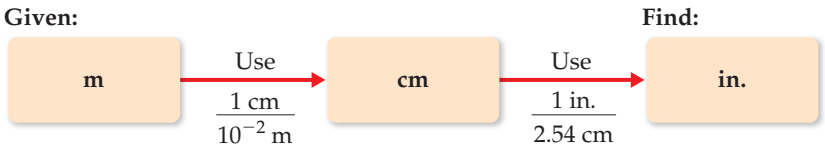
Calculators are wonderful devices; they enable you to get to the wrong answer very quickly. Of course, that's not the destination you want. You can take certain steps to avoid putting that wrong answer into your homework set or on an exam. One is to keep track of the units in a calculation and use the correct conversion factors. Second, you can do a quick mental check to be sure that your answer is reasonable: you can try to make a "ballpark" estimate.

A ballpark estimate involves making a rough calculation using numbers that are rounded off in such a way that the arithmetic can be done without a calculator. Even though this approach does not give an exact answer, it gives one that is roughly the correct size. By using dimensional analysis and by estimating answers, you can readily check the reasonableness of your calculations.

You can get better at making estimates by practicing in everyday life. How far is it from your house to the chemistry lecture hall? How many bikes are there on campus? If you respond "I have no idea" to these questions, you're giving up too easily. Try estimating familiar quantities and you'll get better at making estimates in science and in other aspects of your life where a misjudgment can be costly.

Using Two or More Conversion Factors

It is often necessary to use several conversion factors in solving a problem. As an example, let's convert the length of an 8.00 m rod to inches. We may be given the relationship between centimeters and inches (1 in. = 2.54 cm). We combine this with our knowledge of SI prefixes, ie 1 cm = 10^{-2} m. Thus, we can convert step by step, first from meters to centimeters and then from centimeters to inches:



Combining the given quantity (8.00 m) and the two conversion factors, we have

$$\text{Number of inches} = (8.00\ \text{m})\left(\frac{1\ \text{cm}}{10^{-2}\ \text{m}}\right)\left(\frac{1\ \text{in.}}{2.54\ \text{cm}}\right) = 315\ \text{in.}$$

The first conversion factor is used to cancel meters and convert the length to centimeters. Thus, meters are written in the denominator and centimeters in the numerator. The second conversion factor is used to cancel centimeters and convert the length to inches, so it has centimeters in the denominator and inches, the desired unit, in the numerator.

Note that you could have used 100 cm = 1 m as a conversion factor as well in the second parentheses. As long as you keep track of your given units and cancel them properly to obtain the desired units, you are likely to be successful in your calculations.

Sample Exercise 1.11

Converting Units Using Two or More Conversion Factors

The average speed of a nitrogen molecule in air at 25 °C is 515 m/s. Convert this speed to miles per hour.

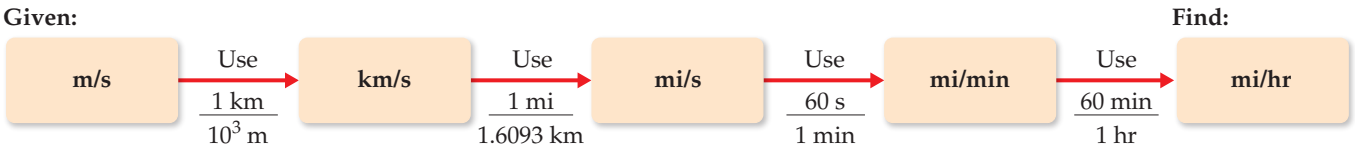
SOLUTION

To go from the given units, m/s, to the desired units, mi/hr, we must convert meters to miles and seconds to hours. From our knowledge of SI prefixes we know that 1 km = 10^3 m and we are given 1 mi = 1.6093 km. Thus, we can convert m to km and then convert km to mi. From our knowledge of time we know that 60 s = 1 min and 60 min = 1 hr. Thus, we can convert s to min and then convert min to hr. The overall process is

Applying first the conversions for distance and then those for time, we can set up one long equation in which unwanted units are canceled:

$$\text{Speed in mi/hr} = \left(515\frac{\text{m}}{\text{s}}\right)\left(\frac{1\ \text{km}}{10^3\ \text{m}}\right)\left(\frac{1\ \text{mi}}{1.6093\ \text{km}}\right)\left(\frac{60\ \text{s}}{1\ \text{min}}\right)\left(\frac{60\ \text{min}}{1\ \text{hr}}\right)$$

$$= 1.15 \times 10^3\ \text{mi/hr}$$



Our answer has the desired units. We can check our calculation, using the estimating procedure described in the "Strategies in Chemistry" box. The given speed is about 500 m/s. Dividing by 1000 converts m to km, giving 0.5 km/s. Because 1 mi is about 1.6 km, this speed corresponds to $0.5/1.6 = 0.3$ mi/s. Multiplying by 60 gives about $0.3 \times 60 = 20$ mi/min. Multiplying again by 60 gives $20 \times 60 = 1200$ mi/hr. The approximate solution (about 1200 mi/hr) and the detailed solution (1150 mi/hr) are reasonably close.

The answer to the detailed solution has three significant figures, corresponding to the number of significant figures in the given speed in m/s.

Practice Exercise

A car travels 28 mi per gallon of gasoline. What is the mileage in kilometers per liter?

Conversions Involving Volume

The conversion factors previously noted convert from one unit of a given measure to another unit of the same measure, such as from length to length. We also have conversion factors that convert from one measure to a different one. The density of a substance, for example, can be treated as a conversion factor between mass and volume. Suppose we want to know the mass in grams of 2 cubic inches ($2.00\ \text{in.}^3$) of gold, which has a density of $19.3\ \text{g/cm}^3$. The density gives us the conversion factors:

$$\frac{19.3\ \text{g}}{1\ \text{cm}^3} \quad \text{and} \quad \frac{1\ \text{cm}^3}{19.3\ \text{g}}$$

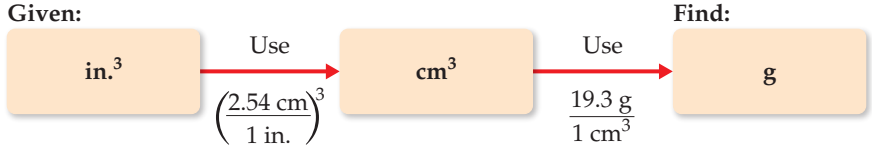
Because we want a mass in grams, we use the first factor, which has mass in grams in the numerator. To use this factor, however, we must first convert cubic inches to cubic centimeters. The relationship between in.^3 and cm^3 may not be given directly, but the relationship between inches and centimeters is given: 1 in. = 2.54 cm (exactly). Cubing both sides of this equation gives $(1\ \text{in.})^3 = (2.54\ \text{cm})^3$, from which we write the desired conversion factor:

$$\frac{(2.54\ \text{cm})^3}{(1\ \text{in.})^3} = \frac{(2.54)^3\ \text{cm}^3}{(1)^3\ \text{in.}^3} = \frac{16.39\ \text{cm}^3}{1\ \text{in.}^3}$$

Notice that both the numbers and the units are cubed. Also, because 2.54 is an exact number, we can retain as many digits of $(2.54)^3$ as we need. We have used four, one more than the number of digits in the density ($19.3\ \text{g/cm}^3$). Applying our conversion factors, we can now solve the problem:

$$\text{Mass in grams} = (2.00\ \text{in.}^3)\left(\frac{16.39\ \text{cm}^3}{1\ \text{in.}^3}\right)\left(\frac{19.3\ \text{g}}{1\ \text{cm}^3}\right) = 633\ \text{g}$$

The procedure is diagrammed here. The final answer is reported to three significant figures, the same number of significant figures as in $2.00\ \text{in.}^3$ and 19.3 g.



Sample Exercise 1.12

Converting Volume Units

Earth's oceans contain approximately $1.36 \times 10^9\ km^3$ of water. Calculate the volume in liters.

SOLUTION

We know $1\ L = 10^{-3}\ m^3$ (Figure 1.19), but there is no relationship listed involving km^3. From our knowledge of SI prefixes, however, we know $1\ km = 10^3\ m$ and we can use this relationship between lengths to write the desired conversion factor between volumes:

$$\left(\frac{10^3\ m}{1\ km}\right)^3 = \frac{10^9\ m^3}{1\ km^3}$$

Thus, converting from km^3 to m^3 to L, we have

$$\text{Volume in liters} = (1.36 \times 10^9\ \cancel{km^3})\left(\frac{10^9\ \cancel{m^3}}{1\ \cancel{km^3}}\right)\left(\frac{1\ L}{10^{-3}\ \cancel{m^3}}\right)$$

$$= 1.36 \times 10^{21}\ L$$



How many liters of water do Earth's oceans contain?

Practice Exercise

A barrel of oil as measured on the oil market is equal to 1.333 U.S. barrels. A U.S. barrel is equal to 31.5 gal. If oil is on the market at $94.0 per barrel, what is the price in dollars per gallon?

(**a**) $2.24/gal (**b**) $3.98/gal (**c**) $2.98/gal (**d**) $1.05/gal (**e**) $8.42/gal

STRATEGIES FOR SUCCESS The Importance of Practice

If you have ever played a musical instrument or participated in athletics, you know that the keys to success are practice and discipline. You cannot learn to play a piano merely by listening to music, and you cannot learn how to play basketball merely by watching games on television. Likewise, you cannot learn chemistry by merely watching your instructor give lectures. Simply reading this book, listening to lectures, or reviewing notes will not usually be sufficient when exam time comes around. Your task is to master chemical concepts to a degree that you can put them to use in solving problems and answering questions. Solving problems correctly takes practice—actually, a fair amount of it. You will do well in your chemistry course if you embrace the idea that you need to master the materials presented and then learn how to apply them in solving problems. Even if you're a brilliant student, this will take time; it's what being a student is all about. Almost no one fully absorbs new material on a first reading, especially when new concepts are being presented. You are sure to master the content of the chapters more fully by reading them through at least twice, even more for passages that present you with difficulties in understanding.

Throughout the book, we have provided sample exercises in which the solutions are shown in detail. For practice exercises, we supply only the answer, at the back of the book. It is important that you use these exercises to test yourself.

The practice exercises in this text and the homework assignments given by your instructor provide the minimal practice that you will need to succeed in your chemistry course. Only by working all the assigned problems will you face the full range of difficulty and coverage that your instructor expects you to master for exams. There is no substitute for a determined and perhaps lengthy effort to work problems on your own. If you are stuck on a problem, however, ask for help from your instructor, a teaching assistant, a tutor, or a fellow student. Spending an inordinate amount of time on a single exercise is rarely effective unless you know that it is particularly challenging and is expected to require extensive thought and effort.

STRATEGIES FOR SUCCESS The Features of This Book

If, like most students, you haven't yet read the part of the Preface to this text entitled TO THE STUDENT, *you should do it now*. In less than two pages of reading you will encounter valuable advice on how to navigate your way through this book and through the course. We're serious! This is advice you can use.

The TO THE STUDENT section describes how text features such as "What's Ahead," Key Terms, Learning Outcomes, and Key Equations will help you remember what you have learned. If you have registered for MasteringChemistry®, you will have access to many helpful animations, tutorials, and additional problems correlated to specific topics and sections of each chapter. An eBook is also available online. In addition, the Pearson eText brings to life the content of each chapter with animations and videos. Interactive end-of-section Self-Assessment Exercises are featured with specific wrong-answer feedback.

As previously mentioned, working exercises is very important—in fact, essential. You will find a large variety of exercises at the end of each section and chapter that are designed to test your problem-solving skills in chemistry. Your instructor will very likely assign some of these exercises as homework.

- The first few exercises called "Visualizing Concepts" are meant to test how well you understand a concept without plugging a lot of numbers into a formula.
- Additional Exercises appear after the regular exercises; the chapter sections that they cover are not identified.
- Integrative Exercises, which start appearing in Chapter 3, are problems that require skills learned in previous chapters.

- Also first appearing in Chapter 3 are Design an Experiment exercises consisting of problem scenarios that challenge you to design experiments to test hypotheses.

Many chemical databases are available, usually on the Web.

- The *CRC Handbook of Chemistry and Physics* is the standard reference for many types of data and is available in libraries.
- The *Merck Index* is a standard reference for the properties of many organic compounds, especially those of biological interest.
- WebElements (http://www.webelements.com/) is a good website for looking up the properties of the elements.
- Wolfram Alpha (http://www.wolframalpha.com/) can also be a source of useful information on substances, numerical values, and other data.

Self-Assessment Exercise

1.26 A soft drink indicates that it contain 21 kJ of energy. Given 1 J = 0.2390 calories, what is the energy content in calories (hint: mind the significant figures)?

(a) 5.0 cal

(b) 88 cal

(c) 5.0 kcal

(d) 5019 cal

Exercises

1.27 Using your knowledge of metric units and the information given in the chapter, write down the conversion factors needed to convert **(a)** in. to cm **(b)** lb to g **(c)** μg to g **(d)** ft^2 to cm^2.

1.28 **(a)** A bumblebee flies with a ground speed of 15.2 m/s. Calculate its speed in km/hr. **(b)** The lung capacity of the blue whale is 5.0×10^3 L. Convert this volume into gallons. **(c)** The Statue of Liberty is 151 ft tall. Calculate its height in meters. **(d)** Bamboo can grow up to 60.0 cm/day. Convert this growth rate into inches per hour.

1.29 Perform the following conversions: **(a)** 5.00 days to s, **(b)** 0.0550 miles to m, **(c)** \$1.89/gal to dollars per liter, **(d)** 0.510 in/ms to km/h, **(e)** 22.50 gal/min to L/s, **(f)** 0.02500 ft^3 to cm^3.

1.30 **(a)** How many liters of wine can be held in a wine barrel whose capacity is 31 gal? **(b)** The recommended adult dose of Elixophyllin®, a drug used to treat asthma, is 6 mg/kg of body mass. Calculate the dose in milligrams for a 185 lb person. **(c)** If an automobile is able to travel 400 km on 47.3 L of fuel, what is the gas mileage in miles per gallon? **(d)** When the coffee is brewed according to directions, a pound of coffee beans yields 50 cups of coffee. How many kg of coffee are required to produce 200 cups of coffee?

1.31 The density of air at ordinary atmospheric pressure and 25 °C is 1.19 g/L. What is the mass, in kilograms, of the air in a room that measures 4.5 m × 5.0 m × 2.5 m?

1.32 Gold can be hammered into extremely thin sheets called gold leaf. An architect wants to cover a 30 m × 25 m ceiling with gold leaf that is twelve-millionths of a centimeter thick. The density of gold is 19.32 g/cm^3, and gold costs \$1654 per troy ounce (1 troy ounce = 31.1034768 g). How much will it cost the architect to buy the necessary gold?

Answers to Self-Assessment Exercises

1.26 (c)

Chapter Summary and Key Terms

THE STUDY OF CHEMISTRY (SECTION 1.1) **Chemistry** is the study of the composition, structure, properties, and changes of **matter**. The composition of matter relates to the kinds of **elements** it contains. The structure of matter relates to the ways the **atoms** of these elements are arranged. A **property** is any characteristic that gives a sample of matter its unique identity. A **molecule** is an entity composed of two or more atoms, with the atoms attached to one another in a specific way.

The **scientific method** is a dynamic process used to answer questions about the physical world. Observations and experiments lead to tentative explanations or **hypotheses**. As a hypothesis is tested and refined, a **theory** may be developed that can predict the results of future observations and experiments. When observations repeatedly lead to the same consistent results, we speak of a **scientific law**, a general rule that summarizes how nature behaves.

CLASSIFICATIONS OF MATTER (SECTION 1.2) Matter exists in three physical states, **gas**, **liquid**, and **solid**, which are known as the **states of matter**. There are two kinds of **pure substances: elements** and **compounds**. Each element has a single kind of atom and is represented by a chemical symbol consisting of one or two letters, with the first letter capitalized. Compounds are composed of two or more elements joined chemically. The **law of constant composition**, also called the **law of definite proportions**, states that the elemental composition of a pure compound is always the same. Most matter consists of a mixture of substances. **Mixtures** have variable compositions and can be either homogeneous or heterogeneous; homogeneous mixtures are called **solutions**.

PROPERTIES OF MATTER (SECTION 1.3) Each substance has a unique set of **physical properties** and **chemical properties** that can be used to identify it. During a **physical change**, matter does not change its composition. **Changes of state** are physical changes. In a **chemical change (chemical reaction)**, a substance is transformed into a chemically different substance. **Intensive properties** are independent of the amount of matter examined and are used to identify substances. **Extensive properties** relate to the amount of substance present. Differences in physical and chemical properties are used to separate substances.

THE NATURE OF ENERGY (SECTION 1.4) **Energy** is defined as the capacity to do work or transfer heat. **Work** is the energy transferred when a force exerted on an object causes a displacement of that object, and **heat** is the energy used to cause the temperature of an object to increase. An object can possess energy in two forms: **kinetic energy**,

which is the energy associated with the motion of an object, and **potential energy**, which is the energy that an object possesses by virtue of its position relative to other objects. Important forms of potential energy include gravitational energy and electrostatic energy.

UNITS OF MEASUREMENT (SECTION 1.5) Measurements in chemistry are made using the **metric system**. Special emphasis is placed on **SI units**, which are based on the meter, the kilogram, and the second as the basic units of length, **mass**, and time, respectively. SI units use prefixes to indicate fractions or multiples of base units. The SI **temperature** scale is the **Kelvin scale**, although the **Celsius scale** is frequently used as well. **Absolute zero** is the lowest temperature attainable. It has the value 0 K. A **derived unit** is obtained by multiplication or division of SI base units. Derived units are needed for defined quantities such as speed or volume. **Density** is an important derived unit that equals mass divided by volume.

UNCERTAINTY IN MEASUREMENT (SECTION 1.6) All measured quantities are inexact to some extent. The **precision** of a measurement indicates how closely different measurements of a quantity agree with one another. The **accuracy** of a measurement indicates how well a measurement agrees with the accepted or "true" value. The **significant figures** in a measured quantity include one estimated digit, the last digit of the measurement. The significant figures indicate the extent of the uncertainty of the measurement. Certain rules must be followed so that a calculation involving measured quantities is reported with the appropriate number of significant figures.

DIMENSIONAL ANALYSIS (SECTION 1.7) In the **dimensional analysis** approach to problem solving, we keep track of units as we carry measurements through calculations. The units are multiplied together, divided into each other, or canceled like algebraic quantities. Obtaining the proper units for the final result is an important means of checking the method of calculation. When converting units and when carrying out several other types of problems, **conversion factors** can be used. These factors are ratios constructed from valid relations between equivalent quantities.

Learning Outcomes After studying this chapter, you should be able to:

- Distinguish among elements, compounds, and mixtures. (Section 1.2) *Related Exercises: 1.3, 1.5, 1.45*
- Identify symbols of common elements. (Section 1.2) *Related Exercises: 1.4, 1.46*
- Distinguish between chemical and physical changes. (Section 1.3) *Related Exercises: 1.8, 1.9, 1.47, 1.48*
- Distinguish between kinetic and potential energy. (Section 1.4) *Related Exercises: 1.12, 1.13*
- Calculate the kinetic energy of an object. (Section 1.4). *Related Exercises: 1.50, 1.51, 1.52, 1.53*
- Identify common metric prefixes. (Section 1.5) *Related Exercises: 1.15, 1.54*
- Demonstrate the use of significant figures, scientific notation, and SI units in calculations. (Section 1.6) *Related Exercises: 1.22, 1.24, 1.63, 1.65*
- Use appropriate SI units for defined quantities, and employ dimensional analysis in calculations. (Sections 1.5 and 1.7) *Related Exercises: 1.28, 1.30, 1.68, 1.70*

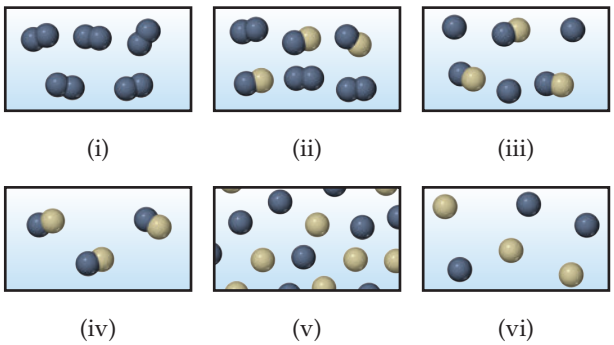
Key Equations

• $w = F \times d$	[1.1]	Work done by a force in the direction of displacement
• $E_k = \frac{1}{2}mv^2$	[1.2]	Kinetic energy
• $\text{K} = {}^\circ\text{C} + 273.15$	[1.3]	Converting between Celsius (°C) and Kelvin (K) temperature scales
• $\text{Density} = \frac{\text{mass}}{\text{volume}}$	[1.4]	Definition of density

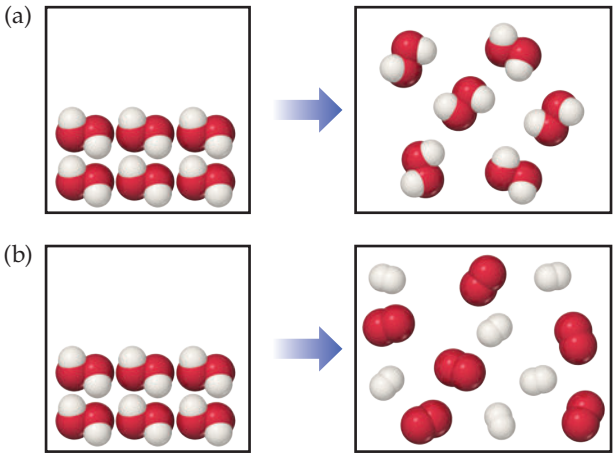
Exercises

Visualizing Concepts

1.33 Which of the following figures represents (**a**) a pure element, (**b**) a mixture of two elements, (**c**) a pure compound, (**d**) a mixture of an element and a compound? (More than one picture might fit each description.) [Section 1.2]



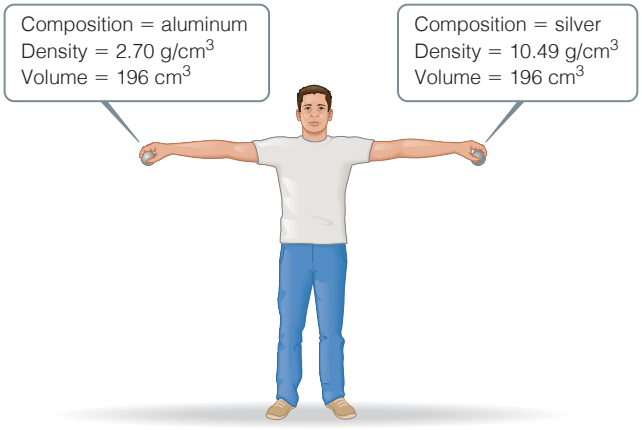
1.34 Which of the following diagrams represents a chemical change? [Section 1.3]



1.35 Musical instruments like trumpets and trombones are made from an alloy called brass. Brass is composed of copper and zinc atoms and appears homogeneous under an optical microscope. The approximate composition of most brass objects is a 2:1 ratio of copper to zinc atoms, but the exact ratio varies somewhat from one piece of brass to another. (**a**) Would you classify brass as an element, a compound, a homogeneous mixture, or a heterogeneous mixture? (**b**) Would it be correct to say that brass is a solution? [Section 1.2]



1.36 Consider the two spheres shown here, one made of silver and the other of aluminum. (**a**) What is the mass of each sphere in kg? (**b**) The force of gravity acting on an object is $F = mg$, where m is the mass of an object and g is the acleration of gravity (9.8 m/s^2). How much work do you do on each sphere it you raise it from the floor to a height of 2.2 m? (**c**) Does the act of lifting the sphere off the ground increase the potential energy of the aluminum sphere by a larger, smaller, or same amount as the silver sphere? (**d**) If you release the spheres simultaneously, they will have the same velocity when they hit the ground. Will they have the same kinetic energy? If not, which sphere will have more kinetic energy? [Section 1.4]



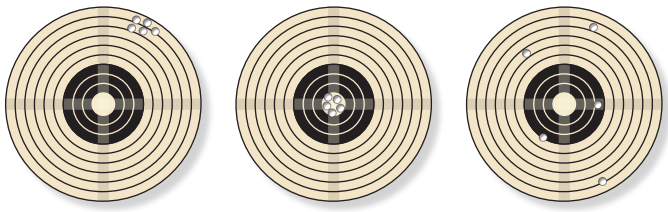
1.37 Is the separation method used in brewing a cup of coffee best described as distillation, filtration, or chromatography? [Section 1.3]



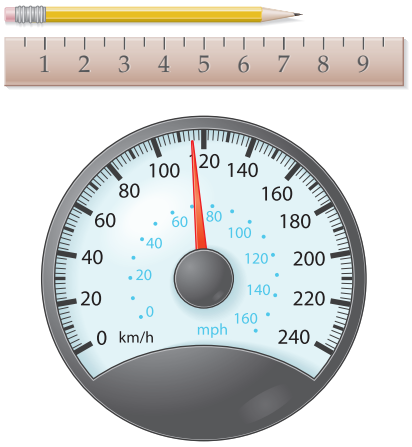
1.38 Identify each of the following as measurements of length, area, volume, mass, density, time, or temperature: (**a**) 25 ps, (**b**) 374.2 mg, (**c**) 77 K, (**d**) 100,000 km^2, (**e**) 1.06 μm, (**f**) 16 nm^2, (**g**) −78 °C, (**h**) 2.56 g/cm^3, **(i)** 28 cm^3. [Section 1.5]

1.39 (**a**) Three spheres of equal size are composed of aluminum (density = 2.70 g/cm^3), silver (density = 10.49 g/cm^3), and nickel (density = 8.90 g/cm^3). List the spheres from lightest to heaviest. (**b**) Three cubes of equal mass are composed of gold (density = 19.32 g/cm^3), platinum (density = 21.45 g/cm^3), and lead (density = 11.35 g/cm^3). List the cubes from smallest to largest. [Section 1.5]

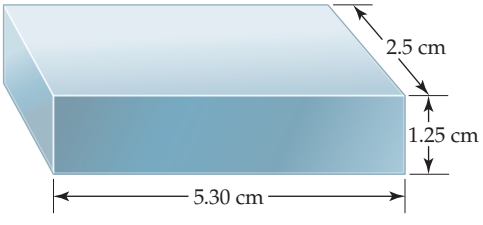
1.40 The three targets from a rifle range shown here were produced by: (**A**) the instructor firing a newly acquired target rifle; (**B**) the instructor firing his personal target rifle; and (**C**) a student who has fired his target rifle only a few times. (**a**) Comment on the accuracy and precision for each of these three sets of results. (**b**) For the A and C results in the future to look like those in B, what needs to happen? [Section 1.6]



1.41 (**a**) What is the length of the pencil in the following figure if the ruler reads in centimeters? How many significant figures are there in this measurement? (**b**) An automobile speedometer with circular scales reading both miles per hour and kilometers per hour is shown. What speed is indicated, in both units? How many significant figures are in the measurements? [Section 1.6]



1.42 (**a**) How many significant figures should be reported for the volume of the metal bar shown here? (**b**) If the mass of the bar is 104.72 g, how many significant figures should be reported when its density is determined using the calculated volume? [Section 1.6]



1.43 Consider the jar of jelly beans in the photo. To get an estimate of the number of beans in the jar you weigh six beans and obtain masses of 3.15, 3.12, 2.98, 3.14, 3.02, and 3.09 g. Then you weigh the jar with all the beans in it, and obtain a mass of 2082 g. The empty jar has a mass of 653 g. Based on these data, estimate the number of beans in the jar. Justify the number of significant figures you use in your estimate. [Section 1.6]



1.44 This photo shows a picture of an agate stone. Jack, who picked up the stone on the Lake Superior shoreline and polished it, insists that agate is a chemical compound. Ellen argues that it cannot be a compound. Discuss the relative merits of their positions. [Section 1.2]

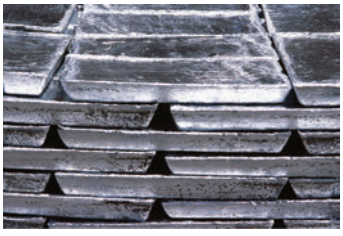


Classification and Properties of Matter (Sections 1.2 and 1.3)

1.45 Classify each of the following as a pure substance or a mixture. If a mixture, indicate whether it is homogeneous or heterogeneous: (**a**) milk, (**b**) beer, (**c**) diamond, (**d**) mayonnaise.

1.46 Give the chemical symbol or name for each of the following elements, as appropriate: (**a**) rhenium, (**b**) tungsten, (**c**) caesium, (**d**) hydrogen, (**e**) indium, (**f**) As, (**g**) Xe, (**h**) Kr, (**i**) Te, (**j**) Ge.

1.47 (**a**) Read the following description of the element zinc and indicate which are physical properties and which are chemical properties.



Zinc melts at 420 °C. When zinc granules are added to dilute sulfuric acid, hydrogen is given off and the metal dissolves. Zinc has a hardness on the Mohs scale of 2.5 and a density of 7.13 g/cm^3 at 25 °C. It reacts slowly with oxygen gas at elevated temperatures to form zinc oxide, ZnO.

(**a**) Which properties of zinc can you describe from the photo? Are these physical or chemical properties?

1.48 A match is lit to light a candle. The following observations are made: (**a**) The candle burns. (**b**) Some wax melts. (**c**) Melted wax solidifies on the candleholder. (**d**) Soot (carbon) is produced by the burning of the match and the candle. Which of these occurrences are due to physical changes, and which are due to chemical changes?

1.49 A silvery metal is put inside a beaker of water. Bubbles form on the surface of the metal and it dissolves gradually. (**a**) Is this an example of a chemical or a physical change? (**b**) Do you expect the remaining solution to be a pure substance or a mixture?

The Nature of Energy (Section 1.4)

1.50 (**a**) Calculate the kinetic energy, in joules, of a 15-g bullet moving at 120 m/s. (**b**) When the bullet is stopped by a bulletproof vest, which form of energy does the kinetic energy of the bullet convert to?

1.51 (**a**) A baseball weighs 145.4 g. What is the kinetic energy, in joules, of this baseball when it is thrown by a major league pitcher at 150 km/h? (**b**) By what factor will the kinetic energy change if the speed of the baseball is decreased to 90 km/h? (**c**) What happens to the kinetic energy when the baseball is caught by the catcher? Is it converted mostly to heat or to some form of potential energy?

1.52 What is the kinetic energy and velocity of the aluminum sphere in Problem 1.36 at the moment it hits the ground? (Assume that energy is conserved during the fall and that 100% of the sphere's initial potential energy is converted to kinetic energy by the time impact occurs.)

1.53 What is the kinetic energy and velocity of the silver sphere in Problem 1.36 at the moment it hits the ground? (Assume that energy is conserved during the fall and that 100% of the sphere's initial potential energy is converted to kinetic energy by the time impact occurs.)

Units of Measurement (Section 1.5)

1.54 Use appropriate metric prefixes to write the following measurements without use of exponents: (**a**) 7.29×10^6 g (**b**) 6.1×10^{-10} m (**c**) 1.828×10^{-3} s (**d**) 3.523×10^9 m^3 (**e**) 9.62×10^2 m/s (**f**) 8.923×10^{-12} kg (**g**) 3.552×10^{12} L.

1.55 Make the following conversions: (**a**) 83 °F to °C (**b**) 29 °C to °F (**c**) 294 °C to K (**d**) 832 K to °C (**e**) 721 K to °F (**f**) 35 °F to K.

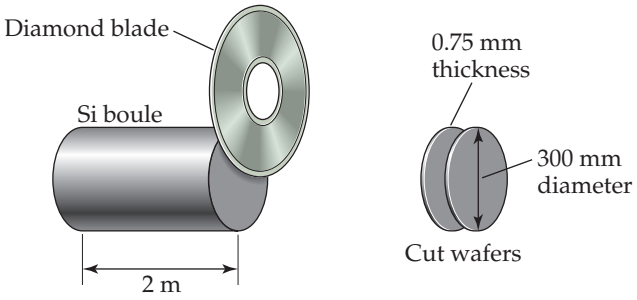
1.56 (**a**) A child has a fever of 101 °F. What is the temperature in °C? (**b**) In a desert, the temperature can be as high as 45 °C, what is the temperature in °F? (**c**) During winter, the temperature of the Arctic region can drop below −50 °C, what is the temperature in degree Fahrenheit and in Kelvin? (**d**) The sublimation temperature of dry ice is −78.5 °C. Convert this temperature to degree Fahrenheit and Kelvin. **(e)** Ethanol boils at 351 K. Convert this temperature to degree Fahrenheit and degree Celsius.

1.57 (**a**) What is the mass of a silver cube whose edges measure 2.00 cm each at 25 °C? The density of silver is 10.49 g/cm^3 at 25 °C. (**b**) The density of aluminum is 2.70 g/cm^3 at 25 °C. What is the weight of the aluminum foil with an area of 0.5 m^2 and a thickness of 0.5 mm? (**c**) The density of hexane is 0.655 g/mL at 25 °C. Calculate the mass of 1.5 L of hexane at this temperature.

1.58 (**a**) After the label fell off a bottle containing a clear liquid believed to be benzene, a chemist measured the density of the liquid to verify its identity. A 25.0-mL portion of the liquid

had a mass of 21.95 g. A chemistry handbook lists the density of benzene at 15 °C as 0.8787 g/mL. Is the calculated density in agreement with the tabulated value? (**b**) An experiment requires 15.0 g of cyclohexane, whose density at 25 °C is 0.7781 g/mL. What volume of cyclohexane should be used? (**c**) A spherical ball of lead has a diameter of 5.0 cm. What is the mass of the sphere if lead has a density of 11.34 g/cm^3? (The volume of a sphere is $(4/3)\pi r^3$, where r is the radius.)

1.59 Silicon for computer chips is grown in large cylinders called "boules" that are 300 mm in diameter and 2 m in length, as shown. The density of silicon is 2.33 g/cm^3. Silicon wafers for making integrated circuits are sliced from a 2.0 m boule and are typically 0.75 mm thick and 300 mm in diameter. (**a**) How many wafers can be cut from a single boule? (**b**) What is the mass of a silicon wafer? (The volume of a cylinder is given by $\pi r^2 h$, where r is the radius and h is its height.)



1.60 Use of the British thermal unit (Btu) is common in some types of engineering work. A Btu is the amount of heat required to raise the temperature of 1 lb of water by 1°F. Calculate the number of joules in a Btu.

1.61 A watt is a measure of power (the rate of energy change) equal to 1 J/s. (**a**) Calculate the number of joules in a kilowatt-hour. (**b**) An adult person radiates heat to the surroundings at about the same rate as a 100-watt electric incandescent light bulb. What is the total amount of energy in kcal radiated to the surroundings by an adult over a 24 h period?

Uncertainty in Measurement (Section 1.6)

1.62 Indicate which of the following are exact numbers: (**a**) the mass of a 945-mL can of coffee, (**b**) the number of students in your chemistry class, (**c**) the temperature of the surface of the Sun, (**d**) the mass of a postage stamp, (**e**) the number of milliliters in a cubic meter of water, (**f**) the average height of NBA basketball players.

1.63 Indicate the number of significant figures in each of the following measured quantities: (**a**) 62.65 km/hr, (**b**) 78.00 K, (**c**) 36.9 mL, (**d**) 250 mm, (**e**) 89.2 metric tons, (**f**) 6.4224×10^2 m^3.

1.64 (**a**) The diameter of Earth at the equator is 12756.27 km. Round this number to three significant figures and express it in standard exponential notation. (**b**) The circumference of Earth through the poles is 40,008 km. Round this number to four significant figures and express it in standard exponential notation.

1.65 Carry out the following operations and express the answers with the appropriate number of significant numbers.

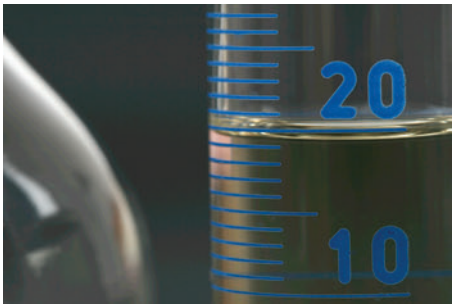
(**a**) $(6.234 + 8.72) \times 0.6746$

(**b**) $732.1 - (892.5/8.2)$

(**c**) $[(3.696 \times 10^5) - (6.234 \times 10^3)] \times 0.0742$

(**d**) $0.006438 \times 108 - (8.639 + 8.52)$

1.66 You have a graduated cylinder that contains a liquid (see photograph). Write the volume of the liquid, in milliliters, using the proper number of significant figures.



Dimensional Analysis (Section 1.7)

Note: 12 inches = 1 foot

1 m = 39.37 inches

1 mile = 1.609 km

1 pound = 454 g

1 gallon = 3.7854 L

1 m^3 = 264 gallon

1.67 Using your knowledge of metric units and the given information, write down the conversion factors needed to convert (**a**) km/h to m/s (**b**) mL to μL (**c**) ps to s (**d**) m^3 to gal.

1.68 (**a**) The speed of light in a vacuum is 2.998×10^8 m/s. Calculate its speed in miles per hour. (**b**) The Sears Tower in Chicago is 1454 ft tall. Calculate its height in meters. (**c**) The Vehicle Assembly Building at the Kennedy Space Center in Florida has a volume of 3,666,500 m^3. Convert this volume to liters and express the result in standard exponential notation. (**d**) An individual suffering from a high cholesterol level in her blood has 242 mg of cholesterol per 100 mL of blood. If the total blood volume of the individual is 5.2 L, how many grams of total blood cholesterol does the individual's body contain?

1.69 Carry out the following conversions: (**a**) 0.105 in. to mm, (**b**) 8.75 mm/s to km/h, (**c**) \$3.99/lb to dollars per kg, (**d**) 8.75 lb/ft^3 to g/mL.

1.70 (**a**) In March 1989, the *Exxon Valdez* ran aground and spilled 240,000 barrels of crude petroleum off the coast of Alaska. One barrel of petroleum is equal to 42 gal. How many liters of petroleum were spilled?

1.71 The indoor concentration of ozone above 300 μg/m^3 is considered to be unhealthy. What mass of ozone in grams is present in a room measuring 3.2 m $\times$ 2.8 m $\times$ 4.1 m?

1.72 A copper refinery produces a copper ingot weighing 70 kg. If the copper is drawn into wire whose diameter is 7.50 mm, how many meters of copper can be obtained from the ingot? The density of copper is 8.94 g/cm^3. (Assume that the wire is a cylinder whose volume $V = \pi r^2 h$, where r is its radius and h is its height or length.)

Additional Exercises

1.73 Classify each of the following as a pure substance, a solution, or a heterogeneous mixture: (**a**) a leaf, (**b**) a 999 gold bar, (**c**) stainless steel.

1.74 (**a**) Which is more likely to eventually be shown to be incorrect: an hypothesis or a theory? (**b**) A(n) _____ reliably predicts the behavior of matter, while a(n) _____ provides an explanation for that behavior.

1.75 A sample of ascorbic acid (vitamin C) is synthesized in the laboratory. It contains 1.50 g of carbon and 2.00 g of oxygen. Another sample of ascorbic acid isolated from citrus fruits contains 6.35 g of carbon. According to the law of constant composition, how many grams of oxygen does it contain?

1.76 Ethyl chloride is sold as a liquid (see photo) under pressure for use as a local skin anesthetic. Ethyl chloride boils at 12 °C at atmospheric pressure. When the liquid is sprayed onto the skin, it boils off, cooling and numbing the skin as it vaporizes. (**a**) What changes of state are involved in this use of ethyl chloride? (**b**) What is the boiling point of ethyl chloride in degrees Fahrenheit? (**c**) The bottle shown contains 103.5 mL of ethyl chloride. The density of ethyl chloride at 25 °C is 0.765 g/cm^3. What is the mass of ethyl chloride in the bottle?



1.77 Two students determine the percentage of lead in a sample as a laboratory exercise. The true percentage is 22.52%. The students' results for three determinations are as follows:

(**1**) 22.52, 22.48, 22.54

(**2**) 22.64, 22.58, 22.62

(**a**) Calculate the average percentage for each set of data and state which set is the more accurate based on the average. (**b**) Precision can be judged by examining the average of the deviations from the average value for that data set. (Calculate the average value for each data set; then calculate the average value of the absolute deviations of each measurement from the average.) Which set is more precise?

1.78 Is the use of significant figures in each of the following statements appropriate? (**a**) The 2005 circulation of *National Geographic* was 7,812,564. (**b**) On July 1, 2005, the population of Cook County, Illinois, was 5,303,683. (**c**) In the United States, 0.621% of the population has the surname Brown. (**d**) You calculate your grade point average to be 3.87562.

1.79 What type of quantity (for example, length, volume, density) do the following units indicate? (**a**) m^3, (**b**) ns, (**c**) mm, (**d**) g/dm^3, (**e**) °C, (**f**) ms^{-1}, (**g**) Pa.

1.80 Give the derived SI units for each of the following quantities in base SI units:

(**a**) acceleration = distance/time^2

(**b**) force = mass × acceleration

(**c**) work = force × distance

(**d**) pressure = force/area

(**e**) power = work/time

(**f**) velocity = distance/time

(**g**) energy = mass × (velocity)^2

1.81 The distance from Earth to the Moon is approximately 240,000 mi. (**a**) What is this distance in meters? (**b**) The peregrine falcon has been measured as traveling up to 350 km/hr in a dive. If this falcon could fly to the Moon at this speed, how many seconds would it take? (**c**) The speed of light is 3.00×10^8 m/s. How long does it take for light to travel from Earth to the Moon and back again? (**d**) Earth travels around the Sun at an average speed of 29.783 km/s. Convert this speed to miles per hour.

1.82 Which of the following would you characterize as pure or nearly pure substance? (**a**) stomach acid; (**b**) dry ice; (**c**) ice-cream; (**d**) stainless steel; (**e**) petroleum; (**f**) distilled water; (**g**) carbon monoxide gas; (**h**) compressed air in balloon.

1.83 The U.S. quarter has a mass of 5.67 g and is approximately 1.55 mm thick. (**a**) How many quarters would have to be stacked to reach 575 ft, the height of the Washington Monument? (**b**) How much would this stack weigh? (**c**) How much money would this stack contain? (**d**) The U.S. National Debt Clock showed the outstanding public debt to be $16,213,166,914,811 on October 28, 2012. How many stacks like the one described would be necessary to pay off this debt?

1.84 In the United States, water used for irrigation is measured in acre-feet. An acre-foot of water covers an acre to a depth of exactly 1 ft. An acre is 4840 yd^2. An acre-foot is enough water to supply two typical households for 1.00 yr. (**a**) If desalinated water costs $1950 per acre-foot, how much does desalinated water cost per liter? (**b**) How much would it cost one household per day if it were the only source of water?

1.85 By using estimation technique, determine which of the following is the heaviest and which is the lightest: a 10-lb bag of fertilizer, a 10-kg bag of rice, or 2 gal of olive oil (density = 0.918 g/cm^3).

1.86 Suppose you decide to define your own temperature scale with units of O, using the freezing point (13 °C) and boiling point (360 °C) of oleic acid, the main component of olive oil. If you set the freezing point of oleic acid as 0 °O and the boiling point as 100 °O, what is the freezing point of water on this new scale?

1.87 Hexane (density = 0.659 g/mL) and acetic acid (density = 1.0446 g/mL) do not form a solution when mixed but are separate in distinct layers. A piece of oak wood (density = 900 kg/m^3) is placed inside a test tube containing hexane and acetic acid solution; sketch how the three substances would position themselves.

1.88 Two spheres of equal volume are placed on the scales as shown. Which one is more dense?



1.89 Water has a density of 0.997 g/cm^3 at 25 °C; ice has a density of 0.917 g/cm^3 at −10 °C. (**a**) If a soft-drink bottle whose volume is 1.50 L is completely filled with water and then frozen to −10 °C, what volume does the ice occupy? (**b**) Can the ice be contained within the bottle?

1.90 A 32.65-g sample of a solid is placed in a flask. Toluene, in which the solid is insoluble, is added to the flask so that the total volume of solid and liquid together is 50.00 mL. The solid and toluene together weigh 58.58 g. The density of toluene at the temperature of the experiment is 0.864 g/mL. What is the density of the solid?

1.91 A thief plans to steal a cylindrical platinum medal with a radius of 2.3 cm and a thickness of 0.8 cm from a jewellery store. If the platinum has a density of 21.45 g/cm^3, what is the mass of the medal in kg? [The volume of a cylinder is $V = \pi r^2 h$.]

1.92 Saline solution used in hospital contains 0.9% sodium chloride by mass. Calculate the number of grams of sodium chloride in 0.5 gal of saline solution if the solution has a density of 1.01 g/mL.

1.93 A 40-lb container of peat moss measures 14 × 20 × 30 in. A 40-lb container of topsoil has a volume of 1.9 gal. (**a**) Calculate the average densities of peat moss and topsoil in units of g/cm^3. Would it be correct to say that peat moss is "lighter" than topsoil? (**b**) How many bags of peat moss are needed to cover an area measuring 15.0 ft × 20.0 ft to a depth of 3.0 in.?

1.94 A 10.0 g block of gold is hammered into a thin gold sheet which has an area of 150 cm^2. Given the density of gold is 19.3 g/cm^3, what is the approximate thickness of the gold sheet in millimeters?

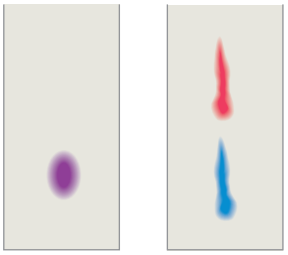
1.95 The total rate at which power is used by humans worldwide is approximately 15 TW (terawatts). The solar flux averaged over the sunlit half of Earth is 680 W/m^2 (assuming no clouds). The area of Earth's disc as seen from the Sun is 1.28×10^{14} m^2. The surface area of Earth is approximately 197,000,000 square miles. How much of Earth's surface would we need to cover with solar energy collectors to power the planet for use by all humans? Assume that the solar energy collectors can convert only 10% of the available sunlight into useful power.

1.96 In 2005, J. Robin Warren and Barry J. Marshall shared the Nobel Prize in Medicine for discovering the bacterium *Helicobacter pylori* and for establishing experimental proof that it plays a major role in gastritis and peptic ulcer disease. The story began when Warren, a pathologist, noticed that bacilli were associated with the tissues taken from patients suffering from ulcers. Look up the history of this case and describe Warren's first hypothesis. What sorts of evidence did it take to create a credible theory based on it?

1.97 A 30.0-cm-long cylindrical plastic tube, sealed at one end, is filled with acetic acid. The mass of acetic acid needed to fill the tube is found to be 89.24 g. The density of acetic acid is 1.05 g/mL. Calculate the inner diameter of the tube in centimeters.

1.98 Gold is alloyed (mixed) with other metals to increase its hardness in making jewelry. (**a**) Consider a piece of gold jewelry that weighs 9.85 g and has a volume of 0.675 cm^3. The jewelry contains only gold and silver, which have densities of 19.3 and 10.5 g/cm^3, respectively. If the total volume of the jewelry is the sum of the volumes of the gold and silver that it contains, calculate the percentage of gold (by mass) in the jewelry. (**b**) The relative amount of gold in an alloy is commonly expressed in units of carats. Pure gold is 24 carat, and the percentage of gold in an alloy is given as a percentage of this value. For example, an alloy that is 50% gold is 12 carat. State the purity of the gold jewelry in carats.

1.99 Paper chromatography is a simple but reliable method for separating a mixture into its constituent substances. You have a mixture of two vegetable dyes, one red and one blue, that you are trying to separate. You try two different chromatography procedures and achieve the separations shown in the figure. Which procedure worked better? Can you suggest a method to quantify how good or poor the separation was?



1.100 Judge the following statements as true or false. If you believe a statement to be false, provide a corrected version.

(**a**) Air and water are both elements.

(**b**) All mixtures contain at least one element and one compound.

(**c**) Compounds can be decomposed into two or more other substances; elements cannot.

(**d**) Elements can exist in any of the three states of matter.

(**e**) When yellow stains in a kitchen sink are treated with bleach water, the disappearance of the stains is due to a physical change.

(**f**) A hypothesis is more weakly supported by experimental evidence than a theory.

(**g**) The number 0.0033 has more significant figures than 0.033.

(**h**) Conversion factors used in converting units always have a numerical value of one.

(**i**) Compounds always contain at least two different elements.

1.101 You are assigned the task of separating a desired granular material with a density of 3.62 g/cm^3 from an undesired granular material that has a density of 2.04 g/cm^3. You want to do this by shaking the mixture in a liquid in which the heavier material will fall to the bottom and the lighter material will float. A solid will float on any liquid that is more dense. Using an Internet-based source or a handbook of chemistry, find the densities of the following substances: carbon tetrachloride, hexane, benzene, and diiodomethane. Which of these

liquids will serve your purpose, assuming no chemical interaction takes place between the liquid and the solids?

1.102 In 2009, a team from Northwestern University and Western Washington University reported the preparation of a new "spongy" material composed of nickel, molybdenum, and sulfur that excels at removing mercury from water. The density of this new material is 0.20 g/cm^3, and its surface area is 1242 m^2 per gram of material. (**a**) Calculate the volume of a 10.0-mg sample of this material. (**b**) Calculate the surface area for a 10.0-mg sample of this material. (**c**) A 10.0-mL sample of contaminated water had 7.748 mg of mercury in it. After treatment with 10.0 mg of the new spongy material, 0.001 mg of mercury remained in the contaminated water. What percentage of the mercury was removed from the water? (**d**) What is the final mass of the spongy material after the exposure to mercury?

2

ATOMS, MOLECULES, AND IONS

WHAT'S AHEAD

2.1 The Atomic Theory of Matter
2.2 The Discovery of Atomic Structure
2.3 The Modern View of Atomic Structure
2.4 Atomic Weights
2.5 The Periodic Table
2.6 Molecules and Molecular Compounds
2.7 Ions and Ionic Compounds
2.8 Naming Inorganic Compounds
2.9 Some Simple Organic Compounds

2.1 | The Atomic Theory of Matter



Take a moment to appreciate the great variety of colors, textures, and other properties in the materials that surround you—the array of colors in a flower, the texture of the fabric in your clothes, the solubility of sugar in a cup of coffee or the transparency and beauty of a diamond. How can we explain the striking and seemingly infinite variety of properties of the materials that make up our world? What makes diamond transparent

and hard whereas table salt is brittle and dissolves in water? Aluminum conducts electricity, but aluminum oxide does not. Paper burns in the presence of oxygen gas but not in the presence of nitrogen gas. What accounts for these differences? The answers to all such questions lie in the structures of atoms, which determine the physical and chemical properties of matter.

Although materials vary greatly in their properties, everything is formed from only about 100 different kinds of atoms. In a sense, these different atoms are like the 26 letters of the English alphabet that join in different combinations to form the immense number of words in our language. But what rules govern the ways in which atoms combine? How do the properties of a substance relate to the kinds of atoms it contains? Indeed, what is an atom like, and what makes the atoms of one element different from those of another?

A helicopter engine is composed of many smaller parts, just as any substance on Earth is composed of countless atoms and molecules to give it its unique characteristics.

In this chapter, we introduce the basic structure of atoms and discuss the formation of molecules and ions. This knowledge provides you with the foundation you need to understand the chapters that follow.

By the end of this section, you should be able to

- Understand Dalton's postulates.

Philosophers from the earliest times speculated about the nature of the fundamental "stuff" from which the world is made. Democritus (460–370 BCE) and other early Greek philosophers described the material world as made up of tiny indivisible particles that they called *atomos*, meaning "indivisible" or "uncuttable." Later, however, Plato and Aristotle formulated the notion that there can be no ultimately indivisible particles, and the "atomic" view of matter faded for many centuries during which Aristotelean philosophy dominated Western culture.

The notion of **atoms** reemerged in Europe during the seventeenth century. As chemists learned to measure the amounts of elements that reacted with one another to form new substances, the ground was laid for an atomic theory that linked the idea of elements with the idea of atoms. That theory came from the work of John Dalton during the period from 1803 to 1807. Dalton's atomic theory was based on four postulates (see Figure 2.1).

A good theory explains known facts; Dalton's theory explained several laws of chemical combination known at the time.

- The *law of constant composition*, based on postulate 4:

  In a given compound, the relative numbers and kinds of atoms are constant.

- The **law of conservation of mass,** based on postulate 3:

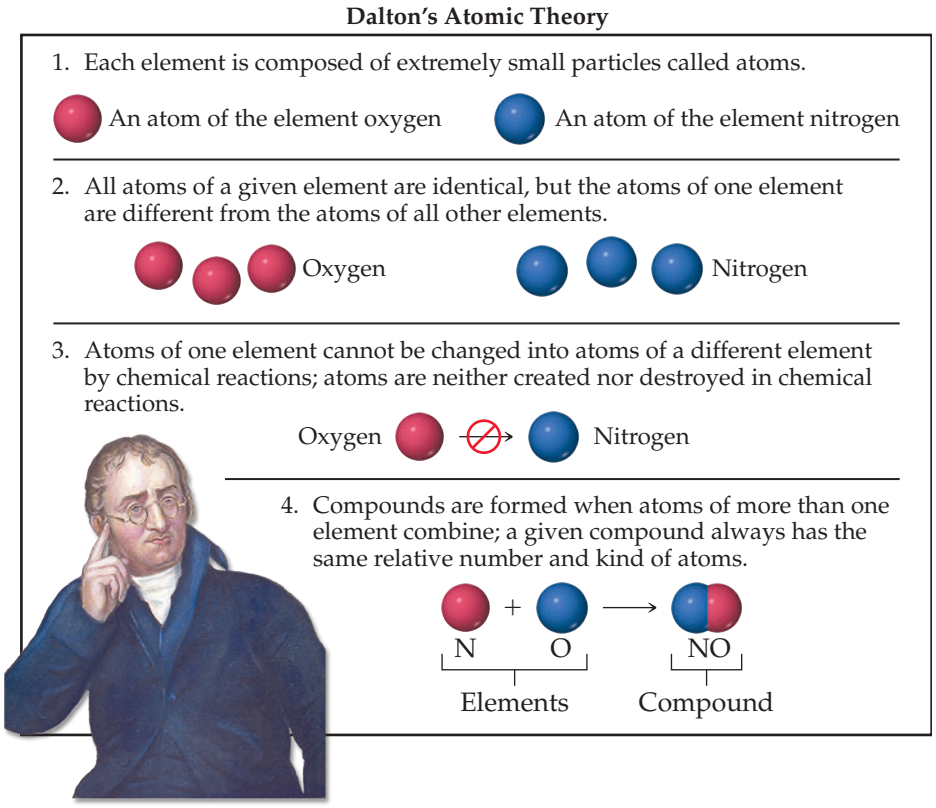
  The total mass of materials present after a chemical reaction is the same as the total mass present before the reaction.

A good theory also predicts new facts; Dalton used his theory to deduce

- The **law of multiple proportions:**

  If two elements A and B combine to form more than one compound, the masses of B that can combine with a given mass of A are in the ratio of small whole numbers.

We can illustrate this law by considering water and hydrogen peroxide, both of which consist of the elements hydrogen and oxygen. In forming water, 8.0 g of oxygen combines with 1.0 g of hydrogen. In forming hydrogen peroxide, 16.0 g of oxygen combines with 1.0 g of hydrogen. Thus, the ratio of the masses of oxygen per gram of hydrogen in the two compounds is 2:1. Using Dalton's atomic theory, we conclude that hydrogen peroxide contains twice as many atoms of oxygen per hydrogen atom than does water.



◀ **Figure 2.1 Dalton's atomic theory.*** John Dalton (1766–1844), the son of a poor English weaver, began teaching at age 12. He spent most of his years in Manchester, where he taught both grammar school and college. His lifelong interest in meteorology led him to study gases, then chemistry, and eventually atomic theory. Despite his humble beginnings, Dalton gained a strong scientific reputation during his lifetime.

Self-Assessment Exercise

2.1 In an experiment, 7.0 g of nitrogen reacted with exactly 16.0 g of oxygen to form a single compound. What would be the total mass of the compound?

(a) 7.0 g

(b) 16 g

(c) 23 g

Exercises

2.2 A 1.0-g sample of carbon dioxide (CO_2) is fully decomposed into its elements, yielding 0.273 g of carbon and 0.727 g of oxygen. (**a**) What is the ratio of the mass of O to C? (**b**) If a sample of a different compound decomposes into 0.429 g of carbon and 0.571 g of oxygen, what is its ratio of the mass of O to C? (**c**) According to Dalton's atomic theory, what is the empirical formula of the second compound?

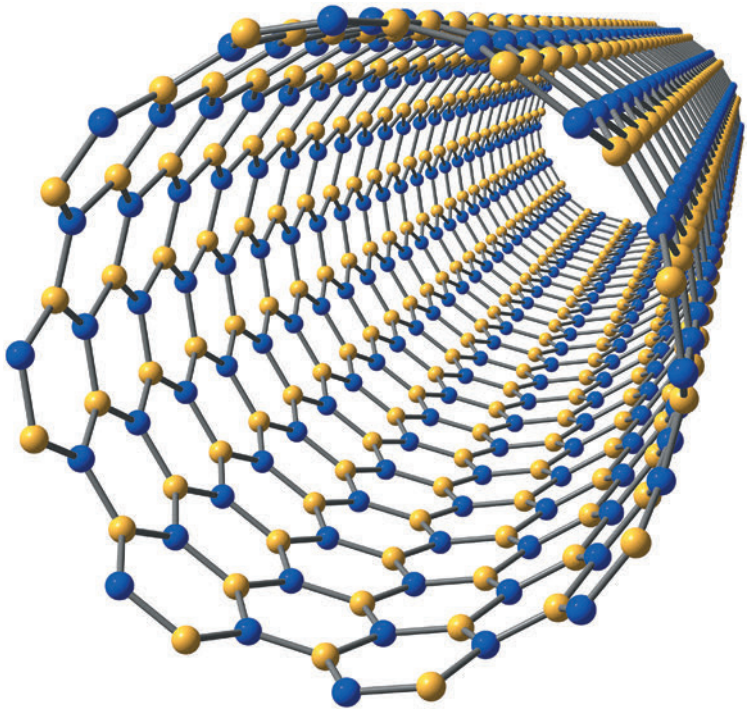
2.3 A chemist finds that 30.82 g of nitrogen will react with 17.60, 35.20, 70.40, or 88.00 g of oxygen to form four different compounds. (**a**) Calculate the mass of oxygen per gram of nitrogen in each compound. (**b**) How do the numbers in part (a) support Dalton's atomic theory?

Answers to Self-Assessment Exercises

2.1 (c)

*Dalton, "Atomic Theory" 1844.

2.2 The Discovery of Atomic Structure



Dalton based his conclusions about atoms on chemical observations made in the laboratory. By assuming the existence of atoms, he was able to account for the laws of constant composition and of multiple proportions. But neither Dalton nor those who followed him during the century after his work was published had any direct evidence for the existence of atoms. Today, however, we can measure the properties of individual atoms and even provide images of them. The picture was obtained by a technique called scanning tunneling microscopy. The color was added to the image by computer to help distinguish its features. Each gold sphere is a silicon atom.

By the end of this section, you should be able to

- Describe the main experiments that led to the discovery of the electron and to the nuclear model of the atom

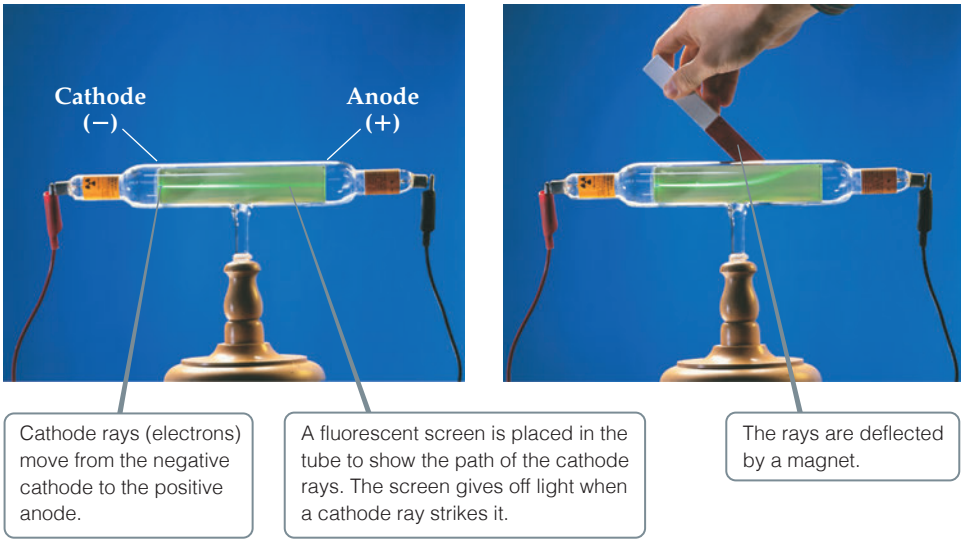
As scientists developed methods for probing the nature of matter, the supposedly indivisible atom began to show signs of a more complex structure, and today we know that the atom is composed of **subatomic particles**. Before we summarize the current model, we briefly consider a few of the landmark discoveries that led to that model. We will see that the atom is composed in part of electrically charged particles, some with a positive charge and some with a negative charge. As we discuss the development of our current model of the atom, keep in mind this fact: *Particles with the same charge repel one another, whereas particles with opposite charges attract one another.*

Cathode Rays and Electrons

During the mid-1800s, scientists began to study electrical discharge through a glass tube pumped almost empty of air (**Figure 2.2**). When a high voltage was applied to the electrodes in the tube, radiation was produced between the electrodes. This radiation, called **cathode rays**, originated at the negative electrode and traveled to the positive electrode. Although the rays could not be seen, their presence was detected because they cause certain materials to *fluoresce,* or to give off light.

Experiments showed that cathode rays are deflected by electric or magnetic fields in a way consistent with there being a stream of negative electrical charge. The British scientist J. J. Thomson (1856–1940) observed that cathode rays are the same regardless of the identity of the cathode material. In a paper published in 1897, Thomson described cathode rays as streams of negatively charged particles that we now call **electrons**.

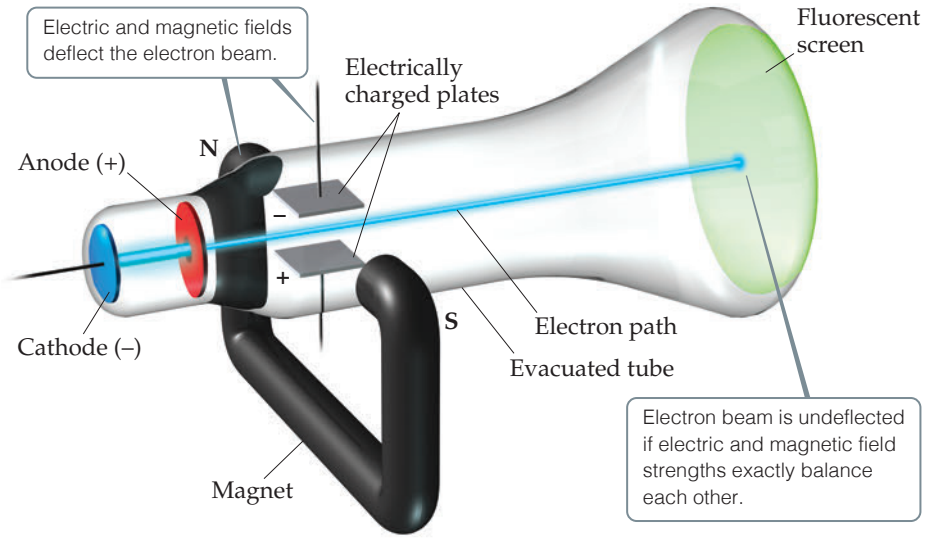
Go Figure If the fluorescent screen were removed from the tube, would cathode rays still be generated? Would you be able to see them?



▲ **Figure 2.2** **Cathode-ray tube.**

Thomson constructed a cathode-ray tube having a hole in the anode through which the cathode rays could pass. Electrically charged plates and a magnet were positioned perpendicular to the beam, and a fluorescent screen that would give off light when struck with a cathode ray was located at one end (**Figure 2.3**). Because the electron is a negatively charged particle, the electric field deflected the rays in one direction, and the magnetic field deflected them in the opposite direction. Thomson adjusted the strengths of the fields so that the effects balanced each other, allowing the electrons to travel in a straight path to the screen. Knowing the strengths that resulted in the straight path made it possible to calculate a value of 1.76×10^8 coulombs* per gram for the ratio of the electron's electrical charge to its mass.

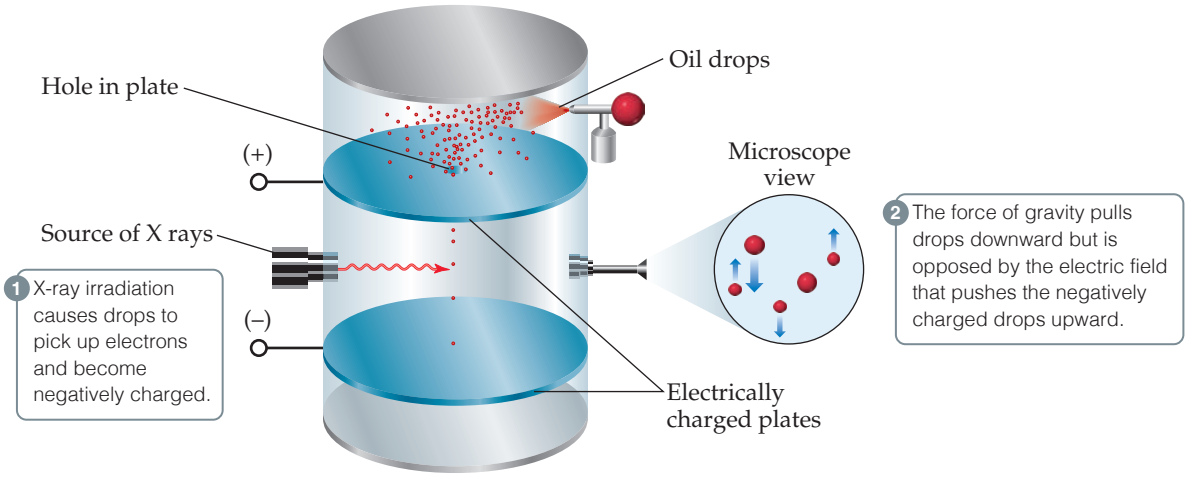
Go Figure If no magnetic field were applied, would you expect the electron beam to be deflected upward or downward by the electric field?



▲ **Figure 2.3** **Cathode-ray tube with perpendicular magnetic and electric fields.** The cathode rays (electrons) originate at the cathode and are accelerated toward the anode, which has a hole in its center. A narrow beam of electrons passes through the hole and travels to the fluorescent screen that glows when struck by a cathode ray.

*The coulomb (C) is the SI unit for electrical charge.

Go Figure Are the masses of the oil drops changed significantly when electrons accumulate on them?



▲ **Figure 2.4 Millikan's oil-drop experiment to measure the charge of the electron.** Small drops of oil are allowed to fall between electrically charged plates. Millikan measured how varying the voltage between the plates affected the rate of fall. From these data he calculated the negative charge on the drops. Because the charge on any drop was always some integral multiple of 1.602×10^{-19} C, Millikan deduced this value to be the charge of a single electron.

Once the charge-to-mass ratio of the electron was known, measuring either quantity allowed scientists to calculate the other. In 1909, Robert Millikan (1868–1953) of the University of Chicago succeeded in measuring the charge of an electron by performing the experiment described in Figure 2.4. He then calculated the mass of the electron by using his experimental value for the charge, 1.602×10^{-19} C, and Thomson's charge-to-mass ratio, 1.76×10^{8} C/g:

$$\text{Electron mass} = \frac{1.602 \times 10^{-19}\,\cancel{\text{C}}}{1.76 \times 10^{8}\,\cancel{\text{C}}/\text{g}} = 9.10 \times 10^{-28}\,\text{g}$$

This result agrees well with the currently accepted value for the electron mass, 9.10938×10^{-28} g. This mass is about 2000 times smaller than that of hydrogen, the lightest atom.



▲ **Figure 2.5 Marie Sklodowska Curie (1867–1934).** In 1903, Henri Becquerel, Marie Curie, and her husband, Pierre, were jointly awarded the Nobel Prize in Physics for their pioneering work on radioactivity (a term she introduced). In 1911, Marie Curie won a second Nobel Prize, this time in chemistry for her discovery of the elements polonium and radium.

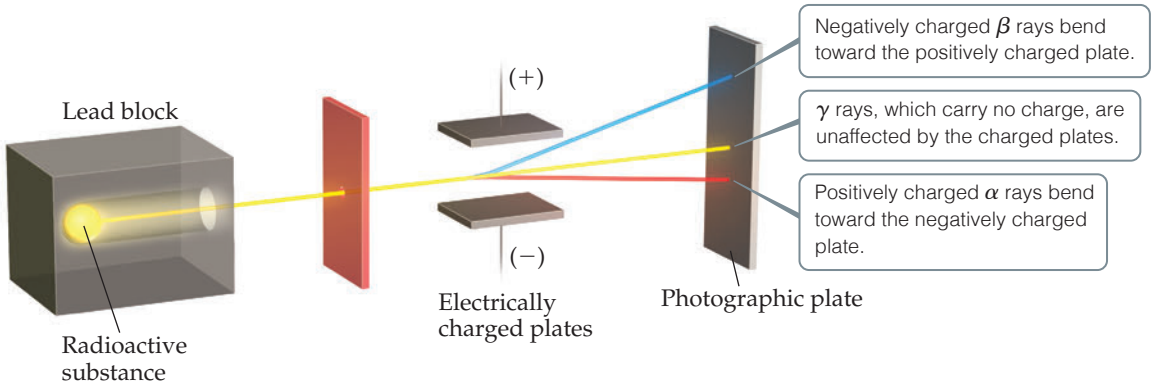
Radioactivity

In 1896 the French scientist Henri Becquerel (1852–1908) discovered that a compound of uranium spontaneously emits high-energy radiation. This spontaneous emission of radiation is called **radioactivity**. At Becquerel's suggestion, Marie Curie (Figure 2.5) and her husband, Pierre, began experiments to identify and isolate the source of radioactivity in the compound. They concluded that it was the uranium atoms.

Further study of radioactivity, principally by the British scientist Ernest Rutherford, revealed three types of radiation: alpha (α), beta (β), and gamma (γ). Rutherford (1871–1937) was a very important figure in this period of atomic science. After working at Cambridge University with J. J. Thomson, he moved to McGill University in Montreal, where he did research on radioactivity that led to his 1908 Nobel Prize in Chemistry. In 1907 he returned to England as a faculty member at Manchester University, where he did his famous α-particle scattering experiments, described further in this chapter.

Rutherford showed that the paths of α and β radiation are bent by an electric field, although in opposite directions; while γ radiation is unaffected by the field (Figure 2.6). From this finding he concluded that α and β rays consist of fast-moving electrically

Go Figure Which subatomic particle—proton, neutron, or electron—is equivalent to a β ray? β rays are deflected to a greater extent than α rays because (**a**) they are lighter, or (**b**) they are more highly charged.

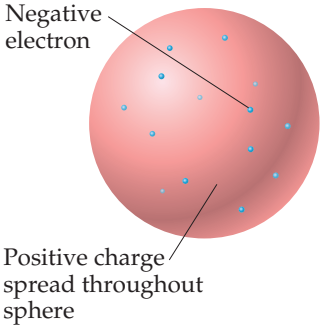


▲ **Figure 2.6 Behavior of alpha (α), beta (β), and gamma (γ) rays in an electric field.**

charged particles. In fact, β particles are nothing more than high-speed electrons that can be considered the radioactive equivalent of cathode rays. Because of their negative charge, they are attracted to a positively charged plate. The α particles have a positive charge and are attracted to a negative plate. In units of the charge of the electron, β particles have a charge of 1– and α particles a charge of 2+. Each α particle has a mass about 7400 times that of an electron. Gamma radiation is high-energy electromagnetic radiation similar to X rays; it does not consist of particles and it carries no charge.

The Nuclear Model of the Atom

With growing evidence that the atom is composed of smaller particles, scientists gave attention to how the particles fit together. During the early 1900s, Thomson reasoned that because electrons contribute only a very small fraction of an atom's mass, they probably are responsible for an equally small fraction of the atom's size. He proposed that the atom consists of a uniform positive sphere of matter in which the mass is evenly distributed and in which the electrons are embedded like raisins in a pudding or seeds in a watermelon (**Figure 2.7**). This *plum-pudding model,* named after a traditional English dessert, was very short-lived.



▲ **Figure 2.7 J. J. Thomson's plum-pudding model of the atom.** Ernest Rutherford and Ernest Marsden proved this model wrong.

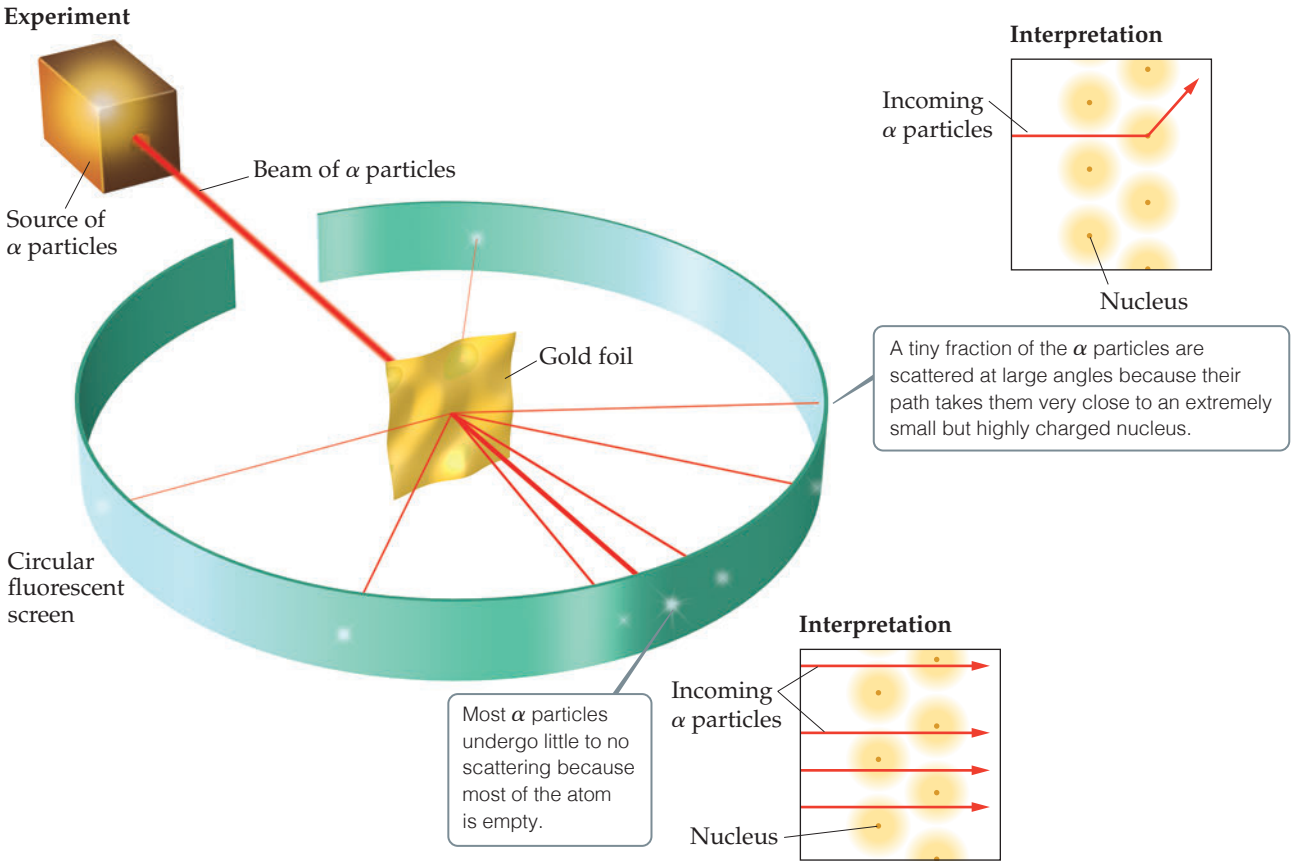
In 1910, Rutherford was studying the angles at which α particles were deflected, or *scattered*, as they passed through a thin sheet of gold foil (**Figure 2.8**). He discovered that almost all the particles passed directly through the foil without deflection, with a few particles deflected about 1°, consistent with Thomson's plum-pudding model. For the sake of completeness, Rutherford suggested that Ernest Marsden (1889–1970), an undergraduate student working in the laboratory, look for scattering at large angles. To everyone's surprise, a small amount of scattering was observed at large angles, with some particles scattered back in the direction from which they had come. The explanation for these results was not immediately obvious, but they were clearly inconsistent with Thomson's plum-pudding model.

Rutherford explained the results by postulating the **nuclear model** of the atom, in which most of the mass of each gold atom and all of its positive charge reside in a very small, extremely dense region that he called the **nucleus**. He postulated further that most of the volume of an atom is empty space in which electrons move around the nucleus. In the α-scattering experiment, most of the particles passed through the foil unscattered because they did not encounter the minute nucleus of any gold atom. Occasionally, however, an α particle came close to a gold nucleus. In such

encounters, the repulsion between the highly positive charge of the gold nucleus and the positive charge of the α particle was strong enough to deflect the particle, as shown in Figure 2.8.

Subsequent experiments led to the discovery of positive particles (**protons**) and neutral particles (**neutrons**) in the nucleus. Protons were discovered in 1919 by Rutherford and neutrons in 1932 by British scientist James Chadwick (1891–1972). Thus, the atom is composed of electrons, protons, and neutrons.

Go Figure What is the charge on the particles that form the beam? Will they be attracted to or repelled from the positively charged gold nuclei?



▲ **Figure 2.8 Rutherford's α-scattering experiment.** When α particles pass through a gold foil, most pass through undeflected but some are scattered, a few at very large angles. According to the plum-pudding model of the atom, the particles should experience only very minor deflections. The nuclear model of the atom explains why a few α particles are deflected at large angles. Although the nuclear atom has been depicted here as a yellow sphere, it is important to realize that most of the space around the nucleus contains only the low-mass electrons.

Self-Assessment Exercise

2.4 Which experiment enabled the mass of an electron to be calculated?

(a) J J Thompson's cathode ray tube experiment

(b) R Millikan's oil drop experiment

(c) E Rutherford's gold foil experiment

Exercises

2.5 An unknown particle is caused to move between two electrically charged plates, as illustrated in Figure 2.6. You hypothesize that the particle is a proton. (**a**) If your hypothesis is correct, would the particle be deflected in the same or opposite direction as the β rays? (**b**) Would it be deflected by a smaller or larger amount than the β rays?

2.6 What fraction of the α particles in Rutherford's gold foil experiment are scattered at large angles? Assume the gold foil is two layers thick, as shown in Figure 2.8, and that the approximate diameters of a gold atom and its nucleus are 270 pm and 1.0×10^{-2} pm, respectively. *Hint:* Calculate the cross sectional area occupied by the nucleus as a fraction of that occupied by the atom. Assume that the gold nuclei in each layer are offset from each other.

Answers to Self-Assessment Exercises

2.4 (b)

2.3 The Modern View of Atomic Structure



Ernest Rutherford (1871–1937), whom Einstein called 'the second Newton', was born and educated in New Zealand. In 1895, he was the first overseas student ever to be awarded a position at the Cavendish Laboratory at Cambridge University in England, where he worked with J J Thompson. In 1898, he joined the faculty of McGill University in Canada, where he did the research on radioactivity that led to his being awarded the 1908 Nobel Prize in Chemistry. In 1907, he moved back to England to join Manchester University where, in 1910, he performed his famous α-particle scattering experiments that led to the nuclear model of the atom. In 1992, his native New Zealand honored Rutherford by putting his likeness, along with his Nobel Prize medal, on its $100 currency note. Element 104 is named in his honor.

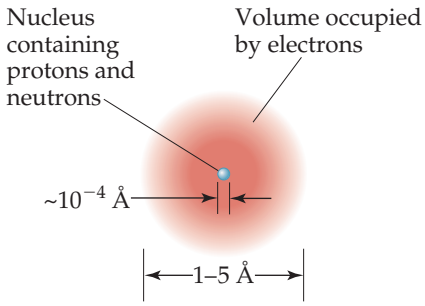
By the end of this section, you should be able to

- Describe the structure of the atom in terms of its subatomic particles
- Use symbols to indicate the composition of an isotope

Since Rutherford's time, as physicists have learned more and more about atomic nuclei, the list of particles that make up nuclei has grown and continues to increase. As chemists, however, we can take a simple view of the atom because only three subatomic particles—the proton, neutron, and electron—have a bearing on chemical behavior.

Go Figure

What is the approximate diameter of the nucleus in units of pm?



▲ **Figure 2.9 The structure of the atom.** A cloud of rapidly moving electrons occupies most of the volume of the atom. The nucleus occupies a tiny region at the center of the atom and is composed of the protons and neutrons. The nucleus contains virtually all the mass of the atom.

As noted earlier, the charge of an electron is -1.602×10^{-19} C. The charge of a proton is opposite in sign but equal in magnitude to that of an electron: $+1.602 \times 10^{-19}$ C. The quantity 1.602×10^{-19} C is called the **electronic charge**. For convenience, the charges of atomic and subatomic particles are usually expressed as multiples of this charge rather than as coulombs. Thus, the charge of an electron is 1− and that of a proton is 1+. Neutrons are electrically neutral (which is how they received their name). *Every atom has an equal number of electrons and protons, so atoms have no net electrical charge.*

Protons and neutrons reside in the tiny nucleus of the atom. The vast majority of an atom's volume is the space in which the electrons reside (Figure 2.9). Most atoms have diameters between 30 pm and 300 pm. The diameter of a chlorine atom, for example, is 175 pm.

Electrons are attracted to the protons in the nucleus by the electrostatic force that exists between particles of opposite electrical charge. In later chapters, we will see that the strength of the attractive forces between electrons and nuclei can be used to explain many of the differences among different elements.

Atoms have extremely small masses. The mass of the heaviest known atom, for example, is approximately 4×10^{-22} g. Because it would be cumbersome to express such small masses in grams, we use the **atomic mass unit** (u), where $1\text{ u} = 1.66054 \times 10^{-24}$ g. A proton has a mass of 1.0073 u, a neutron 1.0087 u, and an electron 5.486×10^{-4} u (Table 2.1). Because it takes 1836 electrons to equal the mass of one proton, and 1839 electrons to equal the mass of a single neutron, the nucleus accounts for nearly the entire mass of an atom.

TABLE 2.1 Comparison of the Proton, Neutron, and Electron

Particle	Charge	Mass (u)
Proton	Positive (1+)	1.0073
Neutron	None (neutral)	1.0087
Electron	Negative (1−)	5.486×10^{-4}

The diameter of an atomic nucleus is approximately 1^{-10} fm, only a small fraction of the diameter of the atom as a whole. You can appreciate the relative sizes of the atom and its nucleus by imagining that if the hydrogen atom were as large as a football stadium, the nucleus would be the size of a small marble. Because the tiny nucleus carries most of the mass of the atom in such a small volume, it has an incredibly high density—on the order of 10^{13}–10^{14} g/cm^3. A matchbox full of material of such density would weigh over 2.5 billion tons!

Figure 2.9 incorporates the features we have just discussed. Electrons play the major role in chemical reactions. The significance of representing the region containing electrons as an indistinct cloud will become clear in later chapters when we consider the energies and spatial arrangements of the electrons. For now, however, we have all the information we need to discuss many topics that form the basis of everyday uses of chemistry.

Atomic Numbers, Mass Numbers, and Isotopes

What makes an atom of one element different from an atom of another element? The atoms of each element have a *characteristic number of protons.* The number of protons in an atom of any particular element is called that element's **atomic number**. Because an atom has no net electrical charge, the number of electrons it contains must equal the number of protons. All atoms of carbon, for example, have six protons and six electrons, whereas all atoms of oxygen have eight protons and eight electrons. Thus, carbon has atomic number 6, and oxygen has atomic number 8. The atomic number of each element is listed with the name and symbol of the element on the front inside cover of the text.

Atoms of a given element can differ in the number of neutrons they contain and, consequently, in mass. For example, while most atoms of carbon have six neutrons, some have more and some have less. The symbol $^{12}_{6}$C (read "carbon twelve," carbon-12) represents the carbon atom containing six protons and six neutrons, whereas carbon atoms

Sample Exercise 2.1

Atomic Size

The diameter of a small coin is 17.9 mm, and the diameter of a silver atom is 288 pm. How many silver atoms could be arranged side by side across the diameter of the coin?

SOLUTION

The unknown is the number of silver (Ag) atoms. Using the relationship 1 Ag atom = 288 pm as a conversion factor relating number of atoms and distance, we start with the diameter of the coin, first converting this distance into picometers and then using the diameter of the Ag atom to convert distance to number of Ag atoms:

$$\text{Ag atoms} = (17.9\ \cancel{\text{mm}})\left(\frac{10^{-3}\ \cancel{\text{m}}}{1\ \cancel{\text{mm}}}\right)\left(\frac{1\ \text{pm}}{10^{-12}\ \cancel{\text{m}}}\right)\left(\frac{1\ \text{Ag atom}}{288\ \text{pm}}\right)$$

$$= 6.22 \times 10^{7}\ \text{Ag atoms}$$

That is, 62.2 million silver atoms could sit side by side across the coin!

Practice Exercise

The diameter of a carbon atom is 1.54 Å. (**a**) Express this diameter in picometers. (**b**) How many carbon atoms could be aligned side by side across the width of a pencil line that is 0.20 mm wide?

A CLOSER LOOK Basic Forces

Four basic forces are known in nature: (1) gravitational, (2) electromagnetic, (3) strong nuclear, and (4) weak nuclear. *Gravitational forces* are attractive forces that act between all objects in proportion to their masses. Gravitational forces between atoms or between subatomic particles are so small that they are of no chemical significance.

Electromagnetic forces are attractive or repulsive forces that act between either electrically charged or magnetic objects. The magnitude of the electric force between two charged particles is given by *Coulomb's law:* $F = kQ_1Q_2/d^2$, where Q_1 and Q_2 are the magnitudes of the charges on the two particles, d is the distance between their centers, and k is a constant determined by the units for Q and d. A negative value for the force indicates attraction, whereas a positive value indicates repulsion. Electric forces are of primary importance in determining the chemical properties of elements.

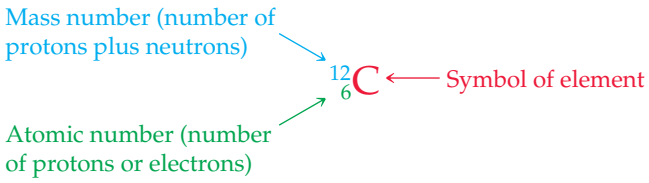
All nuclei except those of hydrogen atoms contain two or more protons. Because like charges repel, electrical repulsion would cause the protons to fly apart if the *strong nuclear force* did not keep them together. As the name implies, this force can be quite strong but only when particles are extremely close together, as are the protons and neutrons in a nucleus. At this distance, the attractive strong nuclear force is stronger than the positive–positive repulsive electric force and holds the nucleus together.

The *weak nuclear force* is weaker than the electric force and the strong nuclear force but stronger than the gravitational force. We are aware of its existence only because it shows itself in certain types of radioactivity.

Related Exercise: 2.124

that contain six protons and eight neutrons have mass number 14, are represented as $^{14}_{6}\text{C}$ and are referred to as carbon-14.

The atomic number is indicated by the subscript; the superscript, called the **mass number**, is the number of protons plus neutrons in the atom:



Because all atoms of a given element have the same atomic number, the subscript is redundant and is often omitted. Thus, the symbol for carbon-12 can be represented simply as ^{12}C.

Atoms with identical atomic numbers but different mass numbers (that is, the same number of protons but different numbers of neutrons) are called **isotopes** of one another. Several isotopes of carbon are listed in **Table 2.2**. We will generally use the notation with superscripts only when referring to a particular isotope of an element. It is important to keep in mind that the isotopes of any given element are all alike chemically. A carbon dioxide molecule that contains a ^{13}C atom behaves for all practical purposes identically to one that contains a ^{12}C atom.

TABLE 2.2 Some Isotopes of Carbon[a]

Symbol	Number of Protons	Number of Electrons	Number of Neutrons
^{11}C	6	6	5
^{12}C	6	6	6
^{13}C	6	6	7
^{14}C	6	6	8

[a] Almost 99% of the carbon found in nature is ^{12}C.

Sample Exercise 2.2

Determining the Number of Subatomic Particles in Atoms

How many protons, neutrons, and electrons are in an atom of (**a**) ^{197}Au, (**b**) strontium-90?

SOLUTION

(**a**) The superscript 197 is the mass number (protons + neutrons). According to the list of elements given on the front inside cover, gold has atomic number 79. Consequently, an atom of ^{197}Au has 79 protons, 79 electrons, and 197 − 79 = 118 neutrons. (**b**) The atomic number of strontium is 38. Thus, all atoms of this element have 38 protons and 38 electrons. The strontium-90 isotope has 90 − 38 = 52 neutrons.

Practice Exercise

Which of these atoms has the largest number of neutrons?
(**a**) ^{148}Eu (**b**) ^{157}Dy (**c**) ^{149}Nd (**d**) ^{162}Ho (**e**) ^{159}Gd

Sample Exercise 2.3

Writing Symbols for Atoms



Magnesium has three isotopes with mass numbers 24, 25, and 26. (**a**) Write the complete chemical symbol (superscript and subscript) for each. (**b**) How many neutrons are in an atom of each isotope?

SOLUTION

(**a**) Magnesium has atomic number 12, so all atoms of magnesium contain 12 protons and 12 electrons. The three isotopes are therefore represented by $^{24}_{12}Mg$, $^{25}_{12}Mg$, and $^{26}_{12}Mg$. (**b**) The number of neutrons in each isotope is the mass number minus the number of protons. The numbers of neutrons in an atom of each isotope are therefore 12, 13, and 14, respectively.

Practice Exercise

Give the complete chemical symbol for the atom that contains 82 protons, 82 electrons, and 126 neutrons.

Self-Assessment Exercises

2.7 What subatomic particle(s) account for the vast majority of the mass of an atom of helium?

(a) Electrons

(b) Protons

(c) Neutrons

(d) Electrons and protons

(e) Protons and neutrons

2.8 What is the symbol for the isotope of oxygen-18?

(a) $^{10}_{8}O$

(b) $^{18}_{8}O$

(c) $^{10}_{18}O$

Exercises

2.9 The radius of an atom of tungsten (W) is about 2.10 units. (**a**) Express this distance in nanometers (nm) and in picometers (pm). (**b**) How many tungsten atoms would have to be lined up to create a wire of 2.0 mm? (**c**) If the atom is assumed to be a sphere, what is the volume in m^3 of a single W atom?

2.10 Answer the following questions without referring to Table 2.1: (**a**) What are the main subatomic particles that make up the atom? (**b**) What is the relative charge (in multiples of the electronic charge) of each of the particles? (**c**) Which of the particles is the most massive? (**d**) Which is the least massive?

2.11 Consider an atom of ^{32}P. (**a**) How many protons, neutrons, and electrons does this atom contain? (**b**) What is the symbol of the atom obtained by adding one proton to ^{32}P? (**c**) What is the symbol of the atom obtained by adding one neutron to ^{32}P? (**d**) Are either of the atoms obtained in parts (b) and (c) isotopes of ^{32}P? If so which one?

2.12 (**a**) Define atomic number and mass number. (**b**) Which of these can vary without changing the identity of the element?

2.13 How many protons, neutrons, and electrons are in the following atoms? (**a**) ^{84}Kr, (**b**) ^{200}Hg, (**c**) ^{59}Co, (**d**) ^{55}Mn, (**e**) ^{239}U, (**f**) ^{181}Ta.

2.14 Fill in the gaps in the following table, assuming each column represents a neutral atom.

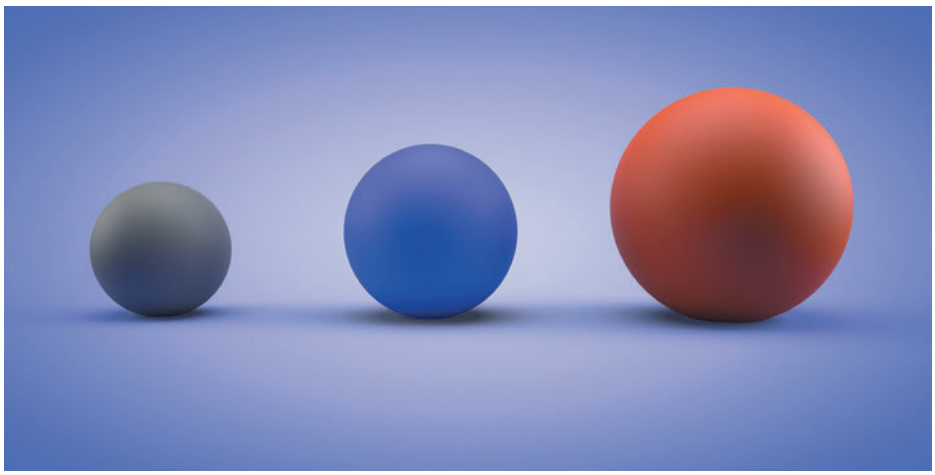
Symbol	^{159}Tb				
Protons		29			37
Neutrons		34	53		
Electrons			42	34	
Mass no.				79	85

2.15 Write the correct symbol, with both superscript and subscript, for each of the following. Use the list of elements in the front inside cover as needed: (**a**) the isotope of hafnium that contains 106 neutrons, (**b**) the isotope of mercury with mass number 201, (**c**) the isotope of rhenium with mass number 187, (**d**) the isotope of calcium that has an equal number of protons and neutrons.

Answers to Self-Assessment Exercises

2.7 (e) 2.8 (b)

2.4 | Atomic Weights



We are quite used to objects of the same shape but of different sizes—a golf ball, a tennis ball, and a soccer ball for example. Atoms of different elements also have a different size and weight. By the end of this section, you should be able to

- Calculate the atomic weight of an element from its isotopic composition.

Atoms are small pieces of matter, so they have mass. In this section, we discuss the mass scale used for atoms and introduce the concept of *atomic weights*.

The Atomic Mass Scale

Scientists of the nineteenth century were aware that atoms of different elements have different masses. They found, for example, that each 100.0 g of water contains 11.1 g of hydrogen and 88.9 g of oxygen. Thus, water contains $88.9/11.1 = 8$ times as much oxygen, by mass, as hydrogen. Once scientists understood that water contains two hydrogen atoms for each oxygen atom, they concluded that an oxygen atom must have $2 \times 8 = 16$ times as much mass as a hydrogen atom. Hydrogen, the lightest atom, was arbitrarily assigned a relative mass of 1 (no units). Atomic masses of other elements were at first determined relative to this value. Thus, oxygen was assigned an atomic mass of 16.

Today we can determine the masses of individual atoms with a high degree of accuracy. For example, we know that the ^{1}H atom has a mass of 1.6735×10^{-24} g and the ^{16}O atom has a mass of 2.6560×10^{-23} g. As we noted in Section 2.3, it is convenient to use the **atomic mass unit** when dealing with these extremely small masses:

$$1\text{ u} = 1.66054 \times 10^{-24}\text{ g} \quad \text{and} \quad 1\text{ g} = 6.02214 \times 10^{23}\text{ u}$$

The atomic mass unit is presently defined by assigning a mass of exactly 12 u to a chemically unbound atom of the ^{12}C isotope of carbon. In these units, an ^{1}H atom has a mass of 1.0078 u and an ^{16}O atom has a mass of 15.9949 u.

Atomic Weight

Most elements occur in nature as mixtures of isotopes. We can determine the *average atomic mass* of an element, usually called the element's **atomic weight**, by summing (indicated by the Greek sigma, Σ) over the masses of its isotopes multiplied by their relative abundances:

$$\text{Atomic weight} = \sum_{\substack{\text{over all}\\ \text{isotopes of}\\ \text{the element}}} [(\text{isotope mass}) \times (\text{fractional isotope abundance})] \qquad [2.1]$$

Naturally occurring carbon, for example, is composed of 98.93% ^{12}C and 1.07% ^{13}C. The masses of these isotopes are 12 u (exactly) and 13.00335 u, respectively, making the atomic weight of carbon

$$(0.9893)(12\text{ u}) + (0.0107)(13.00335\text{ u}) = 12.01\text{ u}$$

The atomic weights of the elements are listed in both the periodic table and the table of elements on the front inside cover of this text.

Sample Exercise 2.4



Calculating the Atomic Weight of an Element from Isotopic Abundances

Naturally occurring chlorine is 75.78% ^{35}Cl (atomic mass 34.969 u) and 24.22% ^{37}Cl (atomic mass 36.966 u). Calculate the atomic weight of chlorine.

SOLUTION

We can calculate the atomic weight by multiplying the abundance of each isotope by its mass and summing these products. Because 75.78% = 0.7578 and 24.22% = 0.2422, we have

$$\begin{aligned}\text{Atomic weight} &= (0.7578)(34.969\text{ u}) + (0.2422)(36.966\text{ u})\\ &= 26.50\text{ u} + 8.953\text{ u}\\ &= 35.45\text{ u}\end{aligned}$$

This answer makes sense: The atomic weight, which is actually the average atomic mass, is between the masses of the two isotopes and is closer to the value of ^{35}Cl, the more abundant isotope.

Practice Exercise

Three isotopes of silicon occur in nature: ^{28}Si (92.23%), atomic mass 27.97693 u; ^{29}Si (4.68%), atomic mass 28.97649 u; and ^{30}Si (3.09%), atomic mass 29.97377 u. Calculate the atomic weight of silicon.

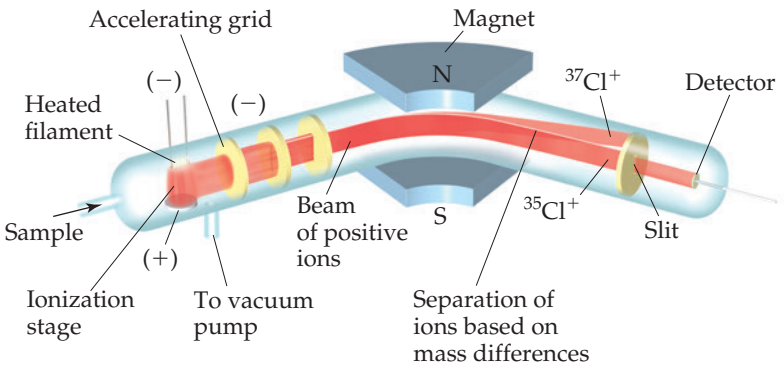
A CLOSER LOOK The Mass Spectrometer

The most accurate means for determining atomic weights is provided by the **mass spectrometer** (Figure 2.10). There are various designs of mass spectrometers, but they all operate on similar principles. The first step is to get atoms or molecules into the gas phase. Sometimes the sample to be analyzed is already a gas, whereas in other cases heating, application of an electric field, or a pulse of laser light may be needed to create gas-phase atoms or molecules. Next, the gas-phase species must be converted to positively charged particles called *ions*. There are many approaches to creating ions, including bombardment with beams of high-energy electrons or chemical reactions with other gas-phase molecules. Once gas-phase ions have been produced, they are accelerated toward a negatively charged grid. After the ions pass through the grid, they encounter two slits that allow only a narrow beam of ions to pass. This beam then passes between the poles of a magnet, which deflects the ions into a curved path. For ions with the same charge, the extent of deflection depends on mass—the more massive the ion, the less the deflection. The ions are thereby separated according to their masses. By changing the strength of the magnetic field or the accelerating voltage on the grid, ions of various masses can be selected to enter the detector.

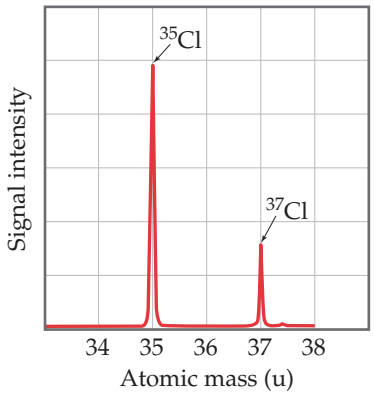
A graph of the intensity of the detector signal versus ion atomic mass is called a *mass spectrum* (Figure 2.11). Analysis of a mass spectrum gives both the masses of the ions reaching the detector and their relative abundances, which are obtained from the signal intensities. Knowing the atomic mass and the abundance of each isotope allows us to calculate the atomic weight of an element, as shown in Sample Exercise 2.4.

Mass spectrometers are used extensively today to identify chemical compounds and analyze mixtures of substances. Any molecule that loses electrons can fall apart, forming an array of positively charged fragments. The mass spectrometer measures the masses of these fragments, producing a chemical "fingerprint" of the molecule and providing clues about how the atoms were connected in the original molecule. Thus, a chemist might use this technique to determine the molecular structure of a newly synthesized compound, to analyze proteins in the human genome, or to identify a pollutant in the environment.

Related Exercises: 2.19, 2.73, 2.74, 2.99, 2.109, 2.110



▲ **Figure 2.10 A mass spectrometer.** Cl atoms are first ionized to form Cl^+ ions, accelerated with an electric field, and finally their path is directed by a magnetic field. The paths of the ions of the two Cl isotopes diverge as they pass through the field.



▲ **Figure 2.11 Mass spectrum of atomic chlorine.** The fractional abundances of the isotopes ^{35}Cl and ^{37}Cl are indicated by the relative signal intensities of the beams reaching the detector of the mass spectrometer.

Self-Assessment Exercise

2.16 Bromine has two main isotopes of similar abundance: ^{79}Br and ^{81}Br. Estimate (without using a calculator) the atomic weight of bromine.

(a) ~79 u
(b) ~80 u
(c) ~81 u

Exercises

2.17 (**a**) What isotope is used as the standard in establishing the atomic mass scale? (**b**) The atomic weight of boron is reported as 10.81, yet no atom of boron has the mass of 10.81 u. Explain.

2.18 Iron has three major isotopes: ^{54}Fe (atomic mass = 53.9396 u; abundance 5.85%), ^{56}Fe (atomic mass = 55.9349 u; abundance 91.75%), and ^{57}Fe (atomic mass = 56.9354 u; abundance 2.12 %). Calculate the atomic weight of iron.

2.19 (**a**) Thomson's cathode-ray tube (Figure 2.3) and the mass spectrometer (Figure 2.10) both involve the use of electric or magnetic fields to deflect charged particles. What are the charged particles involved in each of these experiments? (**b**) What are the labels on the axes of a mass spectrum? (**c**) To measure the mass spectrum of an atom, the atom must first lose one or more electrons. Which would you expect to be deflected more by the same setting of the electric and magnetic fields, a Cl^+ or a Cl^{2+} ion?

2.20 Naturally occurring lead has the following isotopic abundances:

Isotope	Abundance (%)	Atomic mass (u)
^{204}Pb	1.4	203.9730
^{206}Pb	24.1	205.9744
^{207}Pb	22.1	206.9759
^{208}Pb	52.4	207.9766

(**a**) What is the average atomic mass of Pb? (**b**) Sketch the mass spectrum of Pb.

Answers to Self-Assessment Exercises

2.16 (b)

2.5 The Periodic Table



The shininess of metals is an obvious similarity that they share, but many elements show pattens in their reactivity that are not so evident from their physical appearance. One triumph of classification was the ordering of the elements into the Periodic Table. It enables us to understand trends in the properties of the elements, make predictions about their chemical reactivity and even suggest the characteristics of elements that are yet to be discovered.

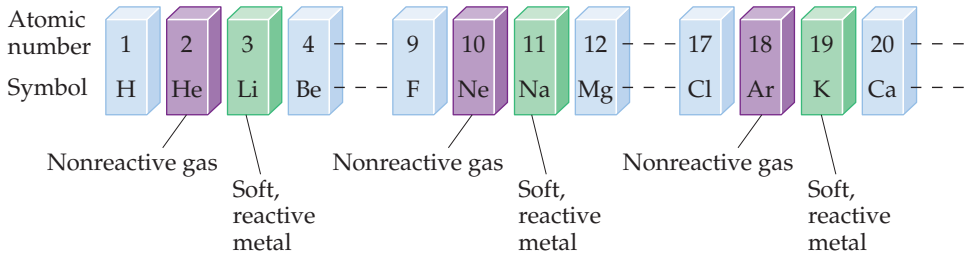
By the end of this section, you should be able to

- Describe the general features of the periodic table

As the list of known elements expanded during the early 1800s, attempts were made to find patterns in chemical behavior. These efforts culminated in the development of the periodic table in 1869. We will have much to say about the periodic table in later chapters, but it is so important and useful that you should become acquainted with it now. You will quickly learn that *the periodic table is the most significant tool that chemists use for organizing and remembering chemical facts*.

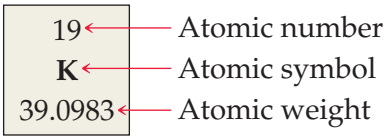
Many elements show strong similarities to one another. The elements lithium (Li), sodium (Na), and potassium (K) are all soft, very reactive metals, for example. The elements helium (He), neon (Ne), and argon (Ar) are all nonreactive gases. If the elements are arranged in order of increasing atomic number, their chemical and physical properties show a repeating, or *periodic*, pattern. For example, each of the soft, reactive metals—lithium, sodium, and potassium—comes immediately after one of the nonreactive gases—helium, neon, and argon, respectively—as shown in **Figure 2.12**.

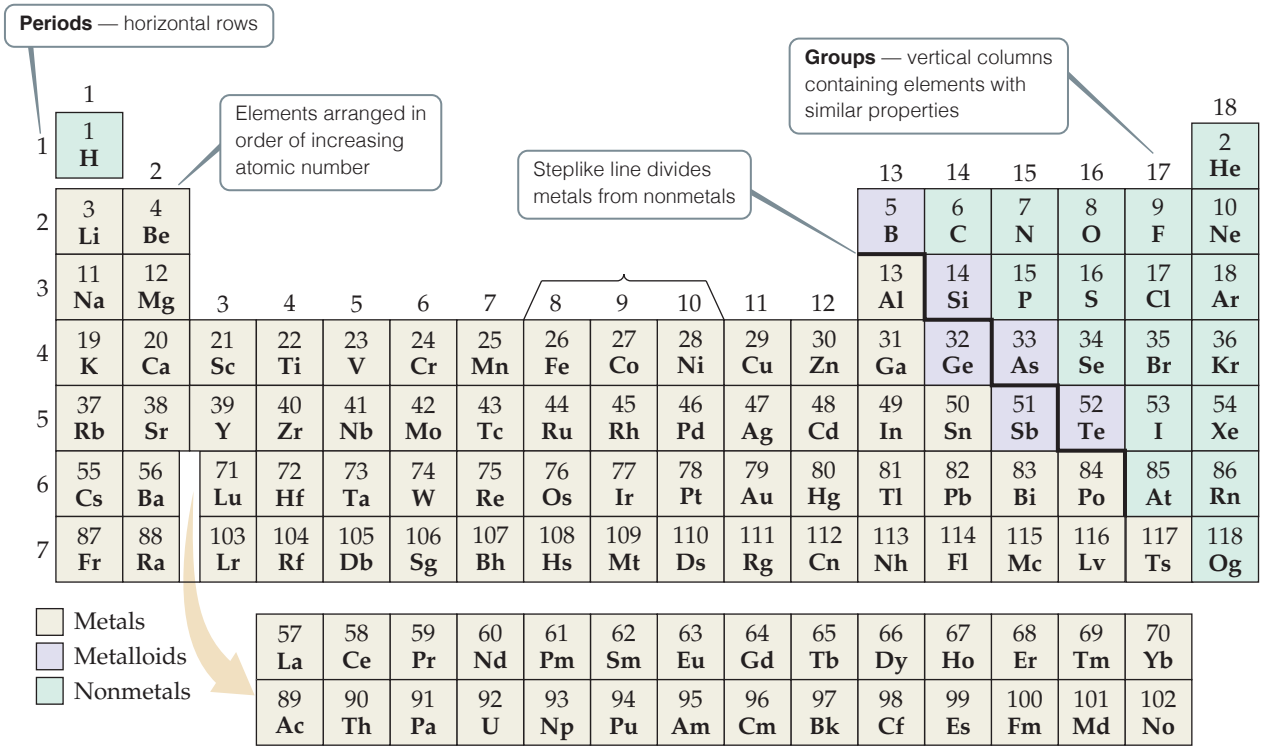
Go Figure If F is a reactive nonmetal, which other element or elements shown here are likely to be reactive nonmetals?



▲ **Figure 2.12** **Arranging elements by atomic number reveals a periodic pattern of properties.** This pattern is the basis of the periodic table.

The arrangement of elements in order of increasing atomic number, with elements having similar properties placed in vertical columns, is known as the **periodic table** (Figure 2.13). The table shows the atomic number and atomic symbol for each element, and the atomic weight is often given as well, as in this typical entry for potassium:





▲ **Figure 2.13** **Periodic table of elements.**

You might notice slight variations in periodic tables from one book to another or between those in the lecture hall and in the text. These are simply matters of style, or they might concern the particular information included. There are no fundamental differences.

The horizontal rows of the periodic table are called **periods**. The first period consists of only two elements, hydrogen (H) and helium (He). The second and third periods consist of eight elements each. The fourth and fifth periods contain 18 elements. The sixth and seventh periods have 32 elements each, but, in order to fit on a page, 14 of the elements from each period (atomic numbers 57–70 and 89–102) appear at the bottom of the table.

The vertical columns are **groups**. These are numbered from 1 to 18, as shown in Figure 2.13.

We will use the IUPAC's proposed convention and number the groups from 1 through 18.

Elements in a group often exhibit similarities in physical and chemical properties. For example, the "coinage metals"—copper (Cu), silver (Ag), and gold (Au)—belong to Group 11. These elements are less reactive than most metals, which is why they have been traditionally used throughout the world to make coins. Many other groups in the periodic table also have names, listed in Table 2.3.

We will learn in Chapters 6 and 7 that elements in a group have similar properties because they have the same arrangement of electrons at the periphery of their atoms. However, we need not wait until then to make good use of the periodic table; after all, the chemists who developed the table knew nothing about electrons! We can use the table, as they intended, to correlate behaviors of elements and to help us remember many facts.

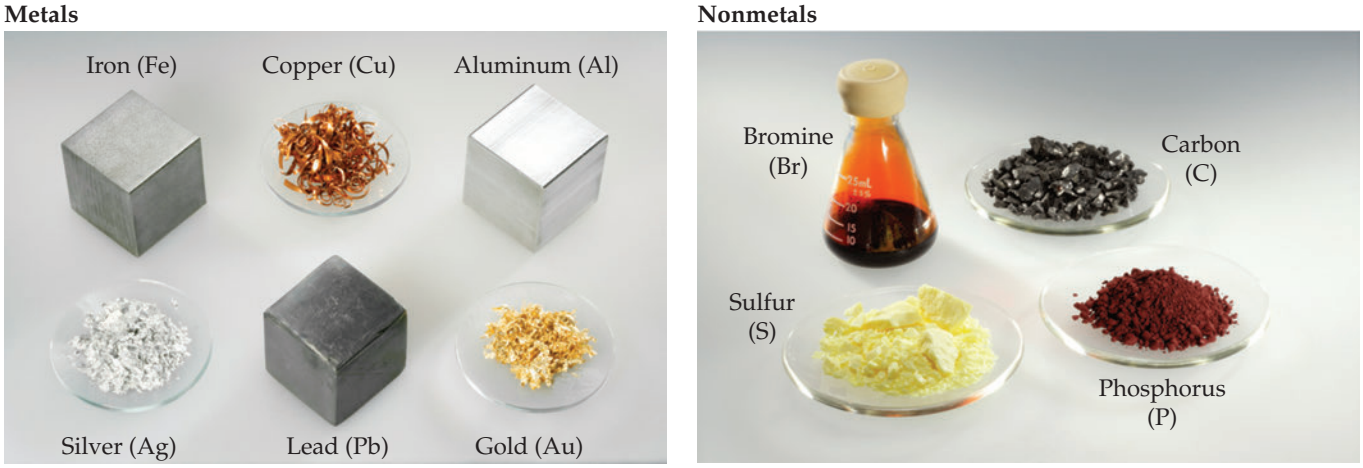
The color code of Figure 2.13 shows that, except for hydrogen, all the elements on the left and in the middle of the table are **metallic elements**, or **metals**. All the metallic elements share characteristic properties, such as luster and high electrical and heat conductivity, and all of them except mercury (Hg) are solid at room temperature.* The metals are separated from the **nonmetallic elements**, or **nonmetals**, by a stepped line that runs from boron (B) to astatine (At). (Note that hydrogen, although on the left side of the table, is a nonmetal.) At room temperature and pressure, some of the nonmetals are gaseous, some are solid, and one is liquid. Nonmetals generally differ from metals in appearance (Figure 2.14) and in other physical properties. Many of the elements that lie along the line that separates metals from nonmetals have properties that fall between those of metals and nonmetals. These elements are often referred to as **metalloids**.

TABLE 2.3 Names of Some Groups in the Periodic Table

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases	He, Ne, Ar, Kr, Xe, Rn

*All metals become liquids if heated sufficiently. Hg simply has the lowest melting point of any metallic element. Although sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and gallium (Ga) are solids at room temperature, they all melt at temperatures below 100 °C.

Go Figure Name two ways in which the metals shown here differ in general appearance from the nonmetals.



▲ **Figure 2.14** **Examples of metals and nonmetals.**

Sample Exercise 2.5

Using the Periodic Table

Which two of these elements would you expect to show the greatest similarity in chemical and physical properties: B, Ca, F, He, Mg, P?

SOLUTION

Elements in the same group of the periodic table are most likely to exhibit similar properties. We therefore expect Ca and Mg to be most alike because they are in the same group (2, the alkaline earth metals).

Practice Exercise

Locate Na (sodium) and Br (bromine) in the periodic table. Give the atomic number of each and classify each as metal, metalloid, or nonmetal.

Self-Assessment Exercise

2.21 The halogens are a group of elements, two of which are gases, one of which is a liquid, and two solid at room temperature. In spite of these obvious physical differences, there are many chemical similarities between the elements. What are the elements that are classed as halogens?

(a) Li, Be, B, C, N, O, F, Ne
(b) Be, Mg, Ca, Sr, Ba, Ra
(c) F, Cl, Br, I, At

Exercises

2.22 For each of the following elements, write its chemical symbol, locate it in the periodic table, give its atomic number, and indicate whether it is a metal, metalloid, or nonmetal: (**a**) radon, (**b**) tellurium, (**c**) cadmium, (**d**) chromium, (**e**) barium, (**f**) selenium, (**g**) sulphur.

2.23 The elements of Group 14 show an interesting change in properties moving down the group. Give the name and chemical symbol of each element in the group and label it as a nonmetal, metalloid, or metal.

Answers to Self-Assessment Exercises

2.21 (c)

2.6 | Molecules and Molecular Compounds



DNA, responsible for carrying the genetic instructions of all organisms, is one of the most complex molecules, yet it is composed of just five elements: C, H, O, N, and P. Knowing how the elements join together is fundamental to our understanding of chemistry. By the end of this section, you should be able to

- Recognize the different types of formula used to describe molecules

Even though the atom is the smallest representative sample of an element, only the noble-gas elements are normally found in nature as isolated atoms. Most matter is composed of molecules or ions. We examine molecules here and ions in Section 2.7.

Molecules and Chemical Formulas

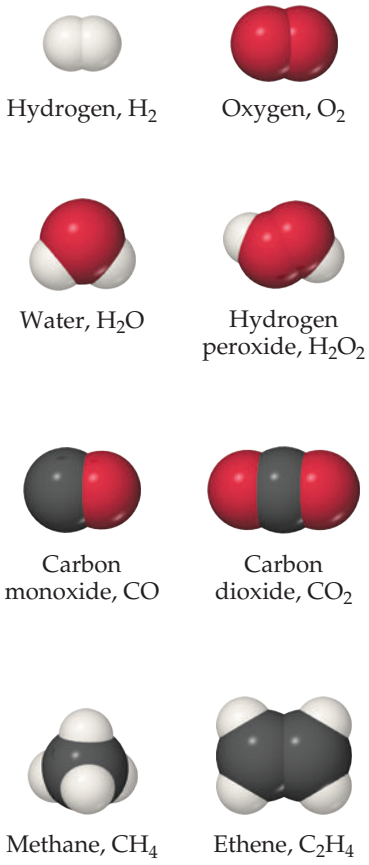
Several elements are found in nature in molecular form—two or more of the same type of atom bound together. For example, most of the oxygen in air consists of molecules that contain two oxygen atoms. As we saw in Section 1.2, we represent this molecular oxygen by the **chemical formula** O_2 (read "oh two"). The subscript tells us that two oxygen atoms are present in each molecule. A molecule made up of two atoms is called a **diatomic molecule**.

Oxygen also exists in another molecular form known as *ozone*. Molecules of ozone consist of three oxygen atoms, making the chemical formula O_3. Even though "normal" oxygen (O_2) and ozone (O_3) are both composed only of oxygen atoms, they exhibit very different chemical and physical properties. For example, O_2 is essential for life, but O_3 is toxic; O_2 is odorless, whereas O_3 has a sharp, pungent smell.

The elements that normally occur as diatomic molecules are hydrogen, oxygen, nitrogen, and the halogens (H_2, O_2, N_2, F_2, Cl_2, Br_2, and I_2). Except for hydrogen, these diatomic elements are clustered on the right side of the periodic table.

Compounds composed of molecules contain more than one type of atom and are called **molecular compounds**. A molecule of the compound methane, for example, consists of one carbon atom and four hydrogen atoms and is therefore represented by the chemical formula CH_4. Lack of a subscript on the C indicates one atom of C per methane molecule. Several common molecules of both elements and compounds are shown in **Figure 2.15**. Notice how the composition of each substance is given by its chemical formula. Notice also that these substances are composed only of nonmetallic elements.

Most of the molecular substances we will encounter contain only nonmetals.



▲ **Figure 2.15 Molecular models.** Notice how the chemical formulas of these simple molecules correspond to their compositions.

Molecular and Empirical Formulas

Chemical formulas that indicate the actual numbers of atoms in a molecule are called **molecular formulas.** (The formulas in Figure 2.17 are molecular formulas.) Chemical formulas that give only the relative number of atoms of each type in a molecule are called **empirical formulas**. The subscripts in an empirical formula are always the smallest possible whole-number ratios. The molecular formula for hydrogen peroxide is H_2O_2, for example, whereas its empirical formula is HO. The molecular formula for ethene is C_2H_4, and its empirical formula is CH_2. For many substances, the molecular formula and the empirical formula are identical, as in the case of water, H_2O.

Whenever we know the molecular formula of a compound, we can determine its empirical formula. The converse is not true, however. If we know the empirical formula of a substance, we cannot determine its molecular formula unless we have more information. So why do chemists bother with empirical formulas? As we will see in Chapter 3, certain common methods of analyzing substances lead to the empirical formula only. For example, if you decomposed hydrogen peroxide H_2O_2 into its elements and weighed them, you could determine that there were equal numbers of hydrogen and oxygen atoms, but you would not know if the molecular formula was HO, H_2O_2, H_3O_3, or the like. Once the empirical formula is known, additional experiments can give the information needed to convert the empirical formula to the molecular one. In addition, there are many substances that do not exist as isolated molecules, one example being ionic compounds that are discussed later in this chapter. For these substances, we must rely on empirical formulas.

Sample Exercise 2.6

Relating Empirical and Molecular Formulas

Write the empirical formulas for (**a**) glucose, a substance also known as either blood sugar or dextrose—molecular formula $C_6H_{12}O_6$; (**b**) nitrous oxide, a substance used as an anesthetic and commonly called laughing gas—molecular formula N_2O.

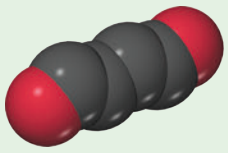
SOLUTION

(**a**) The subscripts of an empirical formula are the smallest whole-number ratios. The smallest ratios are obtained by dividing each subscript by the largest common factor, in this case 6. The resultant empirical formula for glucose is CH_2O.

(**b**) Because the subscripts in N_2O are already the lowest integral numbers, the empirical formula for nitrous oxide is the same as its molecular formula, N_2O.

Practice Exercise

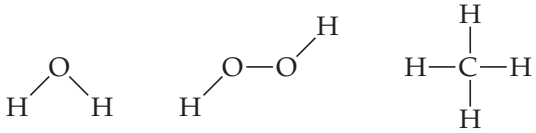
Tetracarbon dioxide is an unstable oxide of carbon with the following molecular structure:



What are the molecular and empirical formulas of this substance? (**a**) C_2O_2, CO_2 (**b**) C_4O, CO (**c**) CO_2, CO_2 (**d**) C_4O_2, C_2O (**e**) C_2O, CO_2

Picturing Molecules

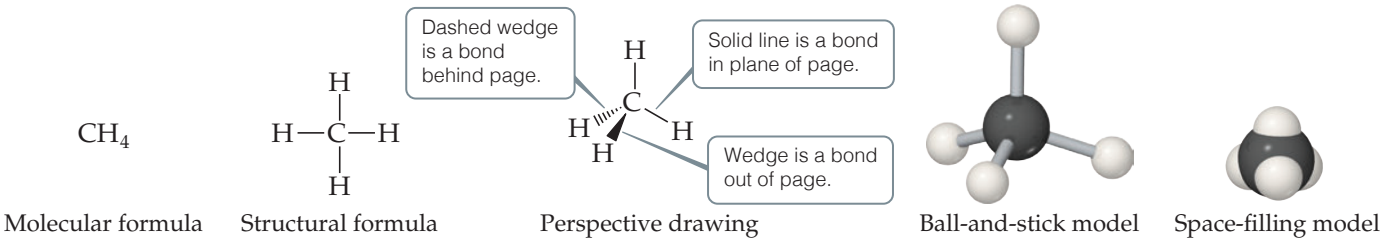
The molecular formula of a substance does not show how its atoms are joined together. A **structural formula** is needed to convey that information, as in the following examples:



Water Hydrogen peroxide Methane

The atoms are represented by their chemical symbols, and lines are used to represent the bonds that hold the atoms together.

Go Figure Which model, the ball-and-stick or the space-filling, more effectively shows the angles between bonds around a central atom?



▲ **Figure 2.16 Different representations of the methane (CH_4) molecule.** Structural formulas, perspective drawings, ball-and-stick models, and space-filling models.

A structural formula does not typically depict the actual geometry of the molecule, that is, the actual angles at which atoms are joined; for that, more sophisticated representations are needed (**Figure 2.16**).

- **Perspective drawings** use wedges and dashed lines to depict bonds that are not in the plane of the paper. This gives a crude sense of the three-dimensional shape of a molecule.
- **Ball-and-stick models** show atoms as spheres and bonds as sticks. This type of model has the advantage of accurately representing the angles at which the atoms are attached to one another in a molecule (Figure 2.16). Sometimes the chemical symbols of the elements are superimposed on the balls, but often the atoms are identified simply by color.
- **Space-filling models** depict what a molecule would look like if the atoms were scaled up in size (Figure 2.16). These models show the relative sizes of the atoms, but the angles between atoms, which help define their molecular geometry, are often more difficult to see than in ball-and-stick models. Because space-filling models give a good representation of the true size of a molecule, they are useful for picturing how two molecules might fit together or pack in the solid state. As with ball-and-stick models, the identities of the atoms are typically indicated by color.

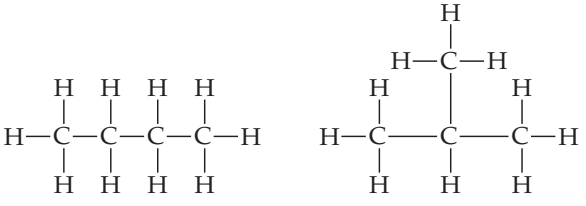
Self-Assessment Exercise

2.24 Lactic acid can build up in muscle tissue during strenuous exercise, sometimes leading to painful 'cramps'. The molecular formula of lactic acid is $C_3H_6O_3$. What is its empirical formula?

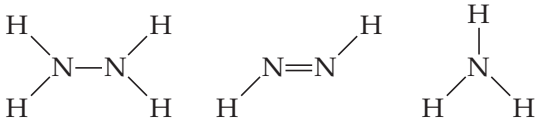
(a) CHO
(b) CH_2O
(c) $C_3H_6O_3$

Exercises

2.25 The structural formulas of the compounds *n*-butane and isobutane are shown here. (**a**) Determine the molecular formula of each. (**b**) Determine the empirical formula of each. (**c**) Which formulas—empirical, molecular, or structural—allow you determine these are different compounds?



2.26 What are the molecular and empirical formulas for each of the following compounds?



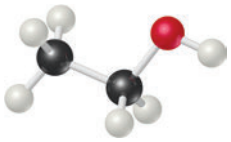
2.27 Write the empirical formula corresponding to each of the following molecular formulas: (**a**) Al_2Br_6, (**b**) C_8H_{10}, (**c**) $C_4H_8O_2$, (**d**) P_4O_{10}, (**e**) $C_6H_4Cl_2$, (**f**) $B_3N_3H_6$.

2.28 How many hydrogen atoms are in each of the following: (**a**) C_2H_5OH, (**b**) $Ca(C_2H_5COO)_2$, (**c**) $(NH_4)_3PO_4$?

2.29 Write the molecular and structural formulas for the compounds represented by the following molecular models:



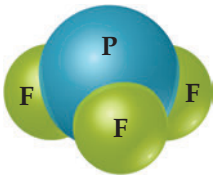
(a)



(b)



(c)



(d)

Answers to Self-Assessment Exercises

2.24 (b)

2.7 | Ions and Ionic Compounds

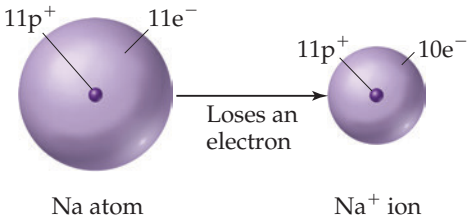


Salt has always been an essential part of our diet. In regions where it is scarce, it commands a high price. During the Roman Empire, soldiers were paid, in part, with an allocation of salt (*sal* being the Latin word for salt) and this is the origin of our word 'salary'. By the end of this section, you should be able to

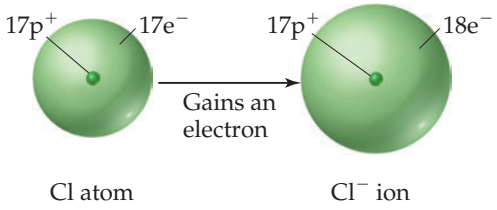
- Predict the charge on the ion formed by elements of Group 1, 2, 15, 16, and 17.
- Write the formula of an ionic compound given the charges of the ions

If electrons are removed from or added to an atom, a charged particle called an **ion** is formed. An ion with a positive charge is a **cation** (pronounced CAT-ion); a negatively charged ion is an **anion** (AN-ion).

To see how ions form, consider the sodium atom, which has 11 protons and 11 electrons. If this atom loses one electron, the resulting cation has 11 protons and 10 electrons, which means it has a net charge of 1+.



The net charge on an ion is represented by a superscript. The superscripts +, 2+, and 3+, for instance, mean a net charge resulting from the *loss* of one, two, and three electrons, respectively. The superscripts −, 2−, and 3− represent net charges resulting from the *gain* of one, two, and three electrons, respectively. Chlorine, with 17 protons and 17 electrons, for example, can gain an electron in chemical reactions, producing the Cl^- ion:



In general, metal atoms tend to lose electrons to form cations and nonmetal atoms tend to gain electrons to form anions. Thus, ionic compounds tend to be composed of both metal cations and nonmetal anions, as in NaCl.

Sample Exercise 2.7

Writing Chemical Symbols for Ions

Give the chemical symbol, including superscript indicating mass number, for (**a**) the ion with 22 protons, 26 neutrons, and 19 electrons; and (**b**) the ion of sulfur that has 16 neutrons and 18 electrons.

SOLUTION

(**a**) The number of protons is the atomic number of the element. A periodic table or list of elements tells us that the element with atomic number 22 is titanium (Ti). The mass number (protons plus neutrons) of this isotope of titanium is 22 + 26 = 48. Because the ion has three more protons than electrons, it has a net charge of 3+ and is designated $^{48}Ti^{3+}$.

(**b**) The periodic table tells us that sulfur (S) has an atomic number of 16. Thus, each atom or ion of sulfur contains 16 protons. We are told that the ion also has 16 neutrons, meaning the mass number is 16 + 16 = 32. Because the ion has 16 protons and 18 electrons, its net charge is 2− and the ion symbol is $^{32}S^{2-}$.

In general, we will focus on the net charges of ions and ignore their mass numbers unless the circumstances dictate that we specify a certain isotope.

Practice Exercise

In which of the following species is the difference between the number of protons and the number of electrons largest? (**a**) Ti^{2+} (**b**) P^{3-} (**c**) Mn (**d**) Se^{2-} (**e**) Ce^{4+}

In addition to simple ions such as Na^+ and Cl^-, there are **polyatomic ions**, such as NH_4^+ (ammonium ion) and SO_4^{2-} (sulfate ion), which consist of atoms joined as in a molecule, but carrying a net positive or negative charge. Polyatomic ions will be discussed in Section 2.8.

It is important to realize that the chemical properties of ions are very different from the chemical properties of the atoms from which the ions are derived. The addition or removal of one or more electrons produces a charged species with behavior very different from that of its associated atom or group of atoms. For example, sodium metal reacts violently with water, but an ionic compound containing sodium ions, such as NaCl, does not.

Predicting Ionic Charges

As noted in Table 2.3, the elements of Group 18 are called the noble-gas elements. The noble gases are chemically nonreactive elements that form very few compounds. Many atoms gain or lose electrons to end up with the same number of electrons as the noble gas closest to them in the periodic table. We might deduce that atoms tend to acquire the

electron arrangements of the noble gases because these electron arrangements are very stable. Nearby elements can obtain these same stable arrangements by losing or gaining electrons. For example, the loss of one electron from an atom of sodium leaves it with the same number of electrons as in a neon atom (10). Similarly, when chlorine gains an electron, it ends up with 18, the same number of electrons as in argon. This simple observation will be helpful for now to account for the formation of ions. A deeper explanation awaits us in Chapter 8, where we discuss chemical bonding.

Sample Exercise 2.8

Predicting Ionic Charge

Predict the charge expected for the most stable ion of barium and the most stable ion of oxygen.

SOLUTION

We will assume that barium and oxygen form ions that have the same number of electrons as the nearest noble-gas atom. From the periodic table, we see that barium has atomic number 56. The nearest noble gas is xenon, atomic number 54. Barium can attain a stable arrangement of 54 electrons by losing two electrons, forming the Ba^{2+} cation.

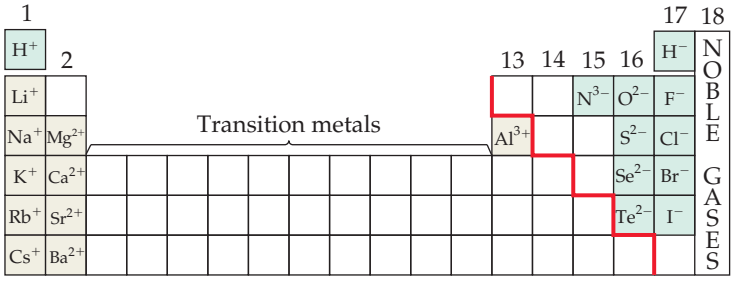
Oxygen has atomic number 8. The nearest noble gas is neon, atomic number 10. Oxygen can attain this stable electron arrangement by gaining two electrons, forming the O^{2-} anion.

Practice Exercise

Although it is helpful to know that many ions have the electron arrangement of a noble gas, many elements, especially among the metals, form ions that do not have a noble-gas electron arrangement. Use the periodic table, Figure 2.13, to determine which of the following ions has a noble-gas electron arrangement, and which do not. For those that do, indicate the noble-gas arrangement they match: (**a**) Ti^{4+}, (**b**) Mn^{2+}, (**c**) Pb^{2+}, (**d**) Te^{2-}, (**e**) Zn^{2+}.

The periodic table is very useful for remembering ionic charges, especially those of elements on the left and right sides of the table. As **Figure 2.17** shows, the charges of these ions relate in a simple way to their positions in the table: The Group 1 elements (alkali metals) form 1+ ions, the Group 2 elements (alkaline earth metals) form 2+ ions, the Group 17 elements (halogens) form 1− ions, and the Group 16 elements form 2− ions. As noted in the Practice Exercise of Sample Exercise 2.8, many of the other groups do not lend themselves to such simple rules.

Go Figure The most common ions for silver, zinc, and scandium are Ag^{+}, Zn^{2+}, and Sc^{3+}. Locate the boxes in which you would place these ions in this table. Which of these ions has the same number of electrons as a noble-gas element?



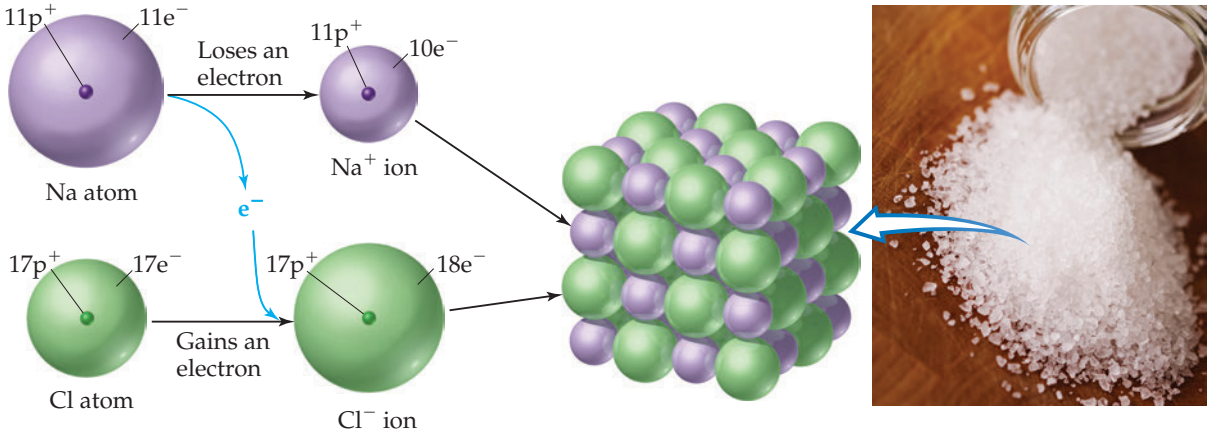
▲ **Figure 2.17 Predictable charges of some common ions.** Notice that the red stepped line that divides metals from nonmetals also separates cations from anions. Hydrogen forms both 1+ and 1− ions.

Ionic Compounds

A great deal of chemical activity involves the transfer of electrons from one substance to another. **Figure 2.18** shows that when elemental sodium is allowed to react with elemental chlorine, an electron transfers from a sodium atom to a chlorine atom, forming a Na^{+} ion and a Cl^{-} ion. Because objects of opposite charges attract, the Na^{+} and the Cl^{-} ions bind together to form the compound sodium chloride (NaCl). Sodium chloride,

which we know better as common table salt, is an example of an **ionic compound**, a compound made up of cations and anions.

Go Figure Is it possible to pick out a unique cluster of atoms that can be thought of as a sodium chloride molecule?



▲ **Figure 2.18 Formation of an ionic compound.** The transfer of an electron from a sodium atom to a chlorine atom leads to the formation of a Na^+ ion and a Cl^- ion. These ions are arranged in a lattice in solid sodium chloride, NaCl.

We can often tell whether a compound is ionic (consisting of ions) or molecular (consisting of molecules) from its composition. As a general rule, cations are metal ions and anions are nonmetal ions. Consequently,

Ionic compounds are generally combinations of metals and nonmetals, as in NaCl.

Sample Exercise 2.9

Identifying Ionic and Molecular Compounds

Which of these compounds would you expect to be ionic: N_2O, Na_2O, $CaCl_2$, SF_4?

SOLUTION

We predict that Na_2O and $CaCl_2$ are ionic compounds because they are composed of a metal combined with a nonmetal. We predict (correctly) that N_2O and SF_4 are molecular compounds because they are composed entirely of nonmetals.

Practice Exercise

Give a reason why each of the following statements is a safe prediction:

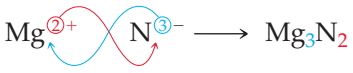
(**a**) Every compound of Rb with a nonmetal is ionic in character.
(**b**) Every compound of nitrogen with a halogen element is a molecular compound.
(**c**) The compound $MgKr_2$ does not exist.
(**d**) Na and K are very similar in the compounds they form with nonmetals.
(**e**) If contained in an ionic compound, calcium (Ca) will be in the form of the doubly charged ion, Ca^{2+}.

The ions in ionic compounds are arranged in three-dimensional structures, as Figure 2.18 shows for NaCl. Because there is no discrete "molecule" of NaCl, we are able to write only an empirical formula for this substance. This is true for most other ionic compounds.

We can write the empirical formula for an ionic compound if we know the charges of the ions. Because chemical compounds are always electrically neutral, the ions in an ionic compound always occur in such a ratio that the total positive charge equals the total negative charge. Thus, there is one Na^+ to one Cl^- in NaCl, one Ba^{2+} to two Cl^- in $BaCl_2$, and so forth.

As you consider these and other examples, you will see that if the charges on the cation and anion are equal, the subscript on each ion is 1. If the charges are not equal,

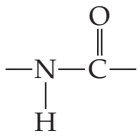
the charge on one ion (without its sign) will become the subscript on the other ion. For example, the ionic compound formed from Mg (which forms Mg^{2+} ions) and N (which forms N^{3-} ions) is Mg_3N_2:



There is one caveat to using this approach. Remember that the empirical formula should be the smallest possible whole-number ratio of the two elements. So the empirical formula for the ionic compound formed between Ti^{4+} and O^{2-} is TiO_2 rather than Ti_2O_4.

CHEMISTRY AND LIFE Elements Required by Living Organisms

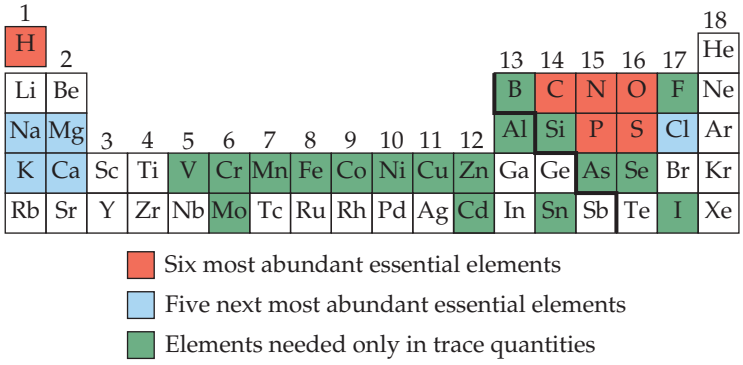
The elements essential to life are highlighted in color in **Figure 2.19**. More than 97% of the mass of most organisms is made up of just six of these elements—oxygen, carbon, hydrogen, nitrogen, phosphorus, and sulfur. Water is the most common compound in living organisms, accounting for at least 70% of the mass of most cells. In the solid components of cells, carbon is the most prevalent element by mass. Carbon atoms are found in a vast variety of organic molecules, bonded either to other carbon atoms or to atoms of other elements. Nearly all proteins, for example, contain the carbon-based group



which occurs repeatedly in the molecules.

In addition, 23 other elements have been found in various living organisms. Five are ions required by all organisms: Ca^{2+}, Cl^-, Mg^{2+}, K^+, and Na^+. Calcium ions, for example, are necessary for the formation of bone and transmission of nervous system signals. Many other elements are needed in only very small quantities and consequently are called *trace* elements. For example, trace quantities of copper are required in the diet of humans to aid in the synthesis of hemoglobin.

Related Exercise: 2.113



▲ **Figure 2.19** **Elements essential to life.**

Sample Exercise 2.10

Using Ionic Charge to Write Empirical Formulas for Ionic Compounds

Write the empirical formula of the compound formed by (**a**) Al^{3+} and Cl^- ions, (**b**) Al^{3+} and O^{2-} ions, (**c**) Mg^{2+} and NO_3^- ions.

SOLUTION

(**a**) Three Cl^- ions are required to balance the charge of one Al^{3+} ion, making the empirical formula $AlCl_3$.

(**b**) Two Al^{3+} ions are required to balance the charge of three O^{2-} ions. A 2:3 ratio is needed to balance the total positive charge of 6+ and the total negative charge of 6–. The empirical formula is Al_2O_3.

(**c**) Two NO_3^- ions are needed to balance the charge of one Mg^{2+}, yielding $Mg(NO_3)_2$. Note that the formula for the polyatomic ion, NO_3^-, must be enclosed in parentheses so that it is clear that the subscript 2 applies to all the atoms of that ion.

Practice Exercise

Which of the following nonmetals will form an ionic compound with Sc^{3+} that has a 1:1 ratio of cations to anions?
(**a**) Ne (**b**) F (**c**) O (**d**) N

Self-Assessment Exercises

2.30 Which group in the periodic table contains elements that form a 2- anion?

(a) Group 2

(b) Group 12

(c) Group 16

2.31 Which is the formula of the ionic compound formed from sodium cations and sulfur anion?

(a) Na_2S

(b) NaS

(c) NaS_2

Exercises

2.32 Predict whether each of the following compounds is molecular or ionic: (**a**) $HClO_4$ (**b**) CH_3OCH_3 (**c**) $Mg(NO_3)_2$ (**d**) H_2S (**e**) $TiCl_4$ (**f**) K_2O_2 (**g**) PCl_5 (**h**) $P(OH)_3$.

2.33 Fill in the gaps in the following table:

Symbol	$^{58}Fe^{2+}$			
Protons		50		40
Neutrons		68	78	50
Electrons			54	38
Net charge		4+	2−	

2.34 Each of the following elements is capable of forming an ion in chemical reactions. By referring to the periodic table, predict the charge of the most stable ion of each: (**a**) Be, (**b**) Rb, (**c**) As, (**d**) In, (**e**) At.

2.35 Using the periodic table to guide you, predict the chemical formula of the compound formed by the following elements: (**a**) Ga and F, (**b**) Li and H, (**c**) Al and I, (**d**) K and S.

2.36 Predict the chemical formulas of the ionic compound formed by (**a**) Fe^{3+} and OH^-, (**b**) Cs^+ and NO_3^-, (**c**) V^{2+} and CH_3COO^-, (**d**) Li^+ and PO_4^{3-}, (**e**) In^{3+} and O^{2-}.

2.37 Complete the table by filling in the formula for the ionic compound formed by each pair of cations and anions, as shown for the first pair.

Ion	K^+	NH_4^+	Mg^{2+}	Fe^{3+}
Cl^-	KCl			
OH^-				
CO_3^{2-}				
PO_4^{3-}				

Answers to Self-Assessment Exercises

2.30 (c) **2.31** (a)

2.8 | Naming Inorganic Compounds



The names and chemical formulas of compounds are essential vocabulary in chemistry. The system used in naming substances is called **chemical nomenclature**, from the Latin words *nomen* (name) and *calare* (to call). By the end of this section, you should be able to

- Convert between the name and formula of an inorganic compound

There are more than 50 million known chemical substances. Naming them all would be a hopelessly complicated task if each had a name independent of all others. Many important substances that have been known for a long time, such as water (H_2O) and ammonia (NH_3), do have traditional names (called *common names*). For most substances, however, we rely on a set of rules that leads to an informative and unique name that conveys the composition of the substance.

The rules for chemical nomenclature are based on the division of substances into categories. The major division is between organic and inorganic compounds. *Organic compounds* contain carbon and hydrogen, often in combination with oxygen, nitrogen, or other elements. All others are *inorganic compounds*. Early chemists associated organic compounds with plants and animals and inorganic compounds with the nonliving portion of our world, for example minerals and water. Although this distinction is no longer pertinent, the classification between organic and inorganic compounds continues to be useful. In this section, we consider the basic rules for naming three categories of inorganic compounds: ionic compounds, acids, and molecular compounds.

Names and Formulas of Ionic Compounds

Recall from Section 2.7 that ionic compounds usually consist of metal ions combined with nonmetal ions. The metals form the cations, and the nonmetals form the anions.

1. Cations

a. *Cations formed from metal atoms have the same name as the metal:*

Na^+	sodium ion	Zn^{2+}	zinc ion	Al^{3+}	aluminum ion

b. *If a metal can form cations with different charges, the positive charge is indicated by a Roman numeral in parentheses following the name of the metal:*

Fe^{2+}	iron(II) ion	Cu^+	copper(I) ion
Fe^{3+}	iron(III) ion	Cu^{2+}	copper(II) ion

Ions of the same element that have different charges have different chemical and physical properties, such as color (**Figure 2.20**).

Most metals that form cations with different charges are *transition metals*, elements that occur in the middle of the periodic table, from Group 3 to Group 12. The metals that form only one cation (only one possible charge) are those of Group 1 and Group 2, as well as Al^{3+} (Group 13) and two transition-metal ions: Ag^+ (Group 12) and Zn^{2+} (Group 11). Charges are not expressed when naming these ions. However, if there is any doubt in your mind whether a metal forms more than one cation, use a Roman numeral to indicate the charge. It is never wrong to do so, even though it may be unnecessary.

An older method still widely used for distinguishing between differently charged ions of a metal uses the endings *-ous* and *-ic* added to the root of the element's Latin name:

Fe^{2+}	ferrous ion	Cu^+	cuprous ion
Fe^{3+}	ferric ion	Cu^{2+}	cupric ion

Although we will only rarely use these older names in this text, you might encounter them elsewhere.



▲ **Figure 2.20 Different ions of the same element have different properties.** Both substances shown are compounds of iron. The grey substance on the left is Fe_3O_4, which contains Fe^{2+} and Fe^{3+} ions. The red substance on the right is Fe_2O_3, which contains Fe^{3+} ions.

c. *Cations formed from molecules composed of nonmetal atoms have names that end in* -ium:

NH_4^+	ammonium ion	H_3O^+	hydronium ion

These two ions are the only ions of this kind that we will encounter frequently in the text.

The names and formulas of some common cations are shown in **Table 2.4** and on the back inside cover of the text. The ions on the left side in Table 2.4 are the monatomic ions that do not have more than one possible charge. Those on the right side are either polyatomic cations or cations with more than one possible charge. The Hg_2^{2+} ion is unusual because, even though it is a metal ion, it is not monatomic. It is called the mercury(I) ion because it can be thought of as two Hg^+ ions bound together. The cations that you will encounter most frequently in this text are shown in boldface. You should learn these cations first.

TABLE 2.4 Common Cations[a]

Charge	Formula	Name	Formula	Name
1+	**H^+**	**hydrogen ion**	**NH_4^+**	**ammonium ion**
	Li^+	lithium ion	Cu^+	copper(I) or cuprous ion
	Na^+	**sodium ion**		
	K^+	**potassium ion**		
	Cs^+	cesium ion		
	Ag^+	**silver ion**		
2+	**Mg^{2+}**	**magnesium ion**	Co^{2+}	cobalt(II) or cobaltous ion
	Ca^{2+}	**calcium ion**	**Cu^{2+}**	**copper(II)** or cupric ion
	Sr^{2+}	strontium ion	**Fe^{2+}**	**iron(II)** or ferrous ion
	Ba^{2+}	barium ion	Mn^{2+}	manganese(II) or manganous ion
	Zn^{2+}	**zinc ion**	Hg_2^{2+}	mercury(I) or mercurous ion
	Cd^{2+}	cadmium ion	Hg^{2+}	mercury(II) or mercuric ion
			Ni^{2+}	nickel(II) or nickelous ion
			Pb^{2+}	**lead(II)** or plumbous ion
			Sn^{2+}	tin(II) or stannous ion
3+	**Al^{3+}**	**aluminum ion**	Cr^{3+}	chromium(III) or chromic ion
			Fe^{3+}	**iron(III)** or ferric ion

[a]The ions we use most often in this course are in boldface. Learn them first.

2. Anions

a. *The names of monatomic anions are formed by replacing the ending of the name of the element with* -ide*:*

H^-	hydride ion	O^{2-}	oxide ion	N^{3-}	nitride ion

A few polyatomic anions also have names ending in *-ide*:

OH^-	hydroxide ion	CN^-	cyanide ion	O_2^{2-}	peroxide ion

b. *Polyatomic anions containing oxygen have names ending in either* -ate *or* -ite *and are called* **oxyanions**. The *-ate* is used for the most common or representative

oxyanion of an element, and *-ite* is used for an oxyanion that has the same charge but one O atom fewer:

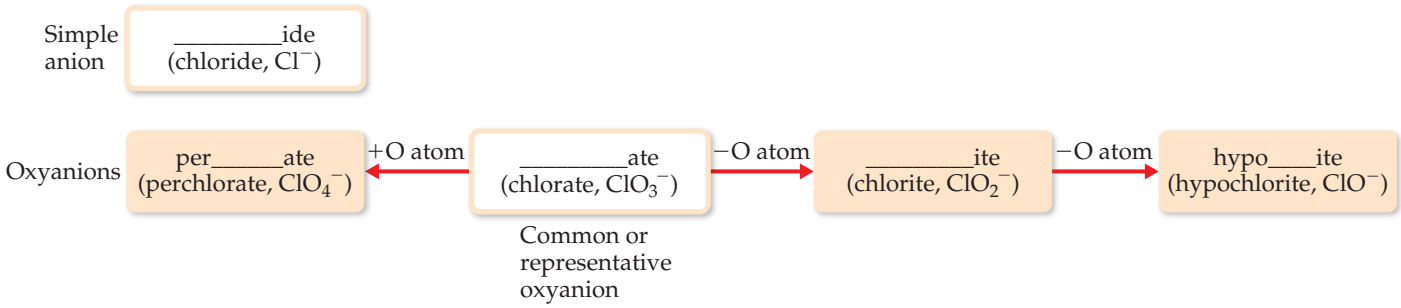
NO_3^-	nitrate ion	SO_4^{2-}	sulfate ion
NO_2^-	nitrite ion	SO_3^{2-}	sulfite ion

Prefixes are used when the series of oxyanions of an element extends to four members, as with the halogens. The prefix *per-* indicates one more O atom than the oxyanion ending in *-ate; hypo-* indicates one O atom fewer than the oxyanion ending in *-ite*:

ClO_4^-	perchlorate ion (one more O atom than chlorate)
ClO_3^-	chlorate ion
ClO_2^-	chlorite ion (one O atom fewer than chlorate)
ClO^-	hypochlorite ion (one O atom fewer than chlorite)

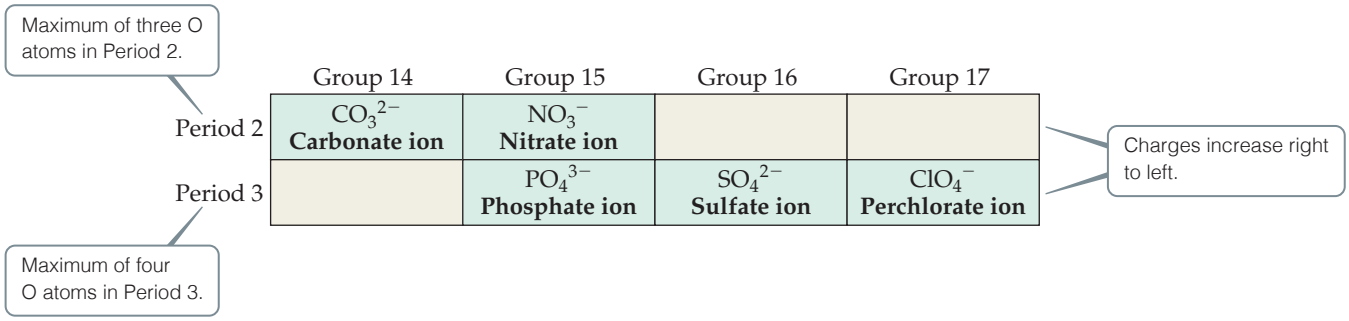
These rules are summarized in **Figure 2.21**.

Go Figure Name the anion obtained by removing one oxygen atom from the perbromate ion, BrO_4^-.



▲ **Figure 2.21 Procedure for naming anions.** Here the simple anion and polyatomic oxyanions derived from chlorine are used as an example.

Figure 2.22 can help you remember the charge and number of oxygen atoms in the various oxyanions. Notice that C and N, both Period 2 elements, have only three O atoms each, whereas the Period 3 elements P, S, and Cl have four O atoms each. Beginning at the lower right in Figure 2.22, note that ionic charge increases from right to left, from 1– for ClO_4^- to 3– for PO_4^{3-}. In the second period the charges also increase from right to left, from 1– for NO_3^- to 2– for CO_3^{2-}. Notice also that although each of the anions in Figure 2.22 ends in *-ate*, the ClO_4^- ion also has a *per-* prefix.



▲ **Figure 2.22 Common oxyanions.** The composition and charges of common oxyanions are related to their location in the periodic table.

Sample Exercise 2.11

Determining the Formula of an Oxyanion from Its Name

Based on the formula for the sulfate ion, predict the formula for (**a**) the selenate ion and (**b**) the selenite ion. (Sulfur and selenium are both in Group 16 and form analogous oxyanions.)

SOLUTION

(**a**) The sulfate ion is SO_4^{2-}. The analogous selenate ion is therefore SeO_4^{2-}.

(**b**) The ending *-ite* indicates an oxyanion with the same charge but one O atom fewer than the corresponding oxyanion that ends in *-ate*. Thus, the formula for the selenite ion is SeO_3^{2-}.

Practice Exercise

Which of the following oxyanions is incorrectly named? (**a**) ClO_2^-, chlorate (**b**) IO_4^-, periodate (**c**) SO_3^{2-}, sulfite (**d**) IO_3^-, iodate (**e**) NO_2^-, nitrite

c. *Anions derived by adding H^+ to an oxyanion are named by adding as a prefix the word* hydrogen *or* dihydrogen, *as appropriate*:

CO_3^{2-}	carbonate ion	PO_4^{3-}	phosphate ion
HCO_3^-	hydrogen carbonate ion	$H_2PO_4^-$	dihydrogen phosphate ion

Notice that each H^+ added reduces the negative charge of the parent anion by one. An older method for naming some of these ions uses the prefix *bi-*. Thus, the HCO_3^- ion is commonly called the bicarbonate ion, and HSO_4^- is sometimes called the bisulfate ion.

The names and formulas of the common anions are listed in Table 2.5 and on the back inside cover of the text. Those anions whose names end in *-ide* are listed on the left portion of Table 2.5, and those whose names end in *-ate* are listed on the right. The most common of these ions are shown in boldface. You should learn the names and formulas of these anions first. The formulas of the ions whose names end with *-ite* can be derived from those ending in *-ate* by removing an O atom. Notice the location of the monatomic ions in the periodic table. Those of Group 17 always have a 1– charge (F^-, Cl^-, Br^-, and I^-), and those of Group 16 have a 2– charge (O^{2-} and S^{2-}).

TABLE 2.5 Common Anions[a]

Charge	Formula	Name	Formula	Name
1–	H^-	hydride ion	**CH_3COO^-** (or $C_2H_3O_2^-$)	**acetate ion**
	F^-	**fluoride ion**	ClO_3^-	chlorate ion
	Cl^-	**chloride ion**	**ClO_4^-**	**perchlorate ion**
	Br^-	**bromide ion**	**NO_3^-**	**nitrate ion**
	I^-	**iodide ion**	MnO_4^-	permanganate ion
	CN^-	cyanide ion		
	OH^-	**hydroxide ion**		
2–	**O^{2-}**	**oxide ion**	**CO_3^{2-}**	**carbonate ion**
	O_2^{2-}	peroxide ion	CrO_4^{2-}	chromate ion
	S^{2-}	**sulfide ion**	$Cr_2O_7^{2-}$	dichromate ion
			SO_4^{2-}	**sulfate ion**
3–	N^{3-}	nitride ion	**PO_4^{3-}**	**phosphate ion**

[a]The ions we use most often are in boldface. Learn them first.

3. Ionic Compounds

Names of ionic compounds consist of the cation name followed by the anion name:

$CaCl_2$	calcium chloride
$Al(NO_3)_3$	aluminum nitrate
$Cu(ClO_4)_2$	copper(II) perchlorate (or cupric perchlorate)

In the chemical formulas for aluminum nitrate and copper(II) perchlorate, parentheses followed by the appropriate subscript are used because the compounds contain two or more polyatomic ions.

Sample Exercise 2.12

Determining the Names of Ionic Compounds from Their Formulas

Name the ionic compounds (**a**) K_2SO_4, (**b**) $Ba(OH)_2$, (**c**) $FeCl_3$.

SOLUTION

In naming ionic compounds, it is important to recognize polyatomic ions and to determine the charge of cations with variable charge.

(**a**) The cation is K^+, the potassium ion, and the anion is SO_4^{2-}, the sulfate ion, making the name potassium sulfate. (If you thought the compound contained S^{2-} and O^{2-} ions, you failed to recognize the polyatomic sulfate ion.)

(**b**) The cation is Ba^{2+}, the barium ion, and the anion is OH^-, the hydroxide ion: barium hydroxide.

(**c**) You must determine the charge of Fe in this compound because an iron atom can form more than one cation. Because the compound contains three chloride ions, Cl^-, the cation must be Fe^{3+}, the iron(III), or ferric, ion. Thus, the compound is iron(III) chloride or ferric chloride.

Practice Exercise

Which of the following ionic compounds is incorrectly named? (**a**) $Zn(NO_3)_2$, zinc nitrate (**b**) $TeCl_4$, tellurium(IV) chloride (**c**) Fe_2O_3, diiron oxide (**d**) BaO, barium oxide (**e**) $Mn_3(PO_4)_2$, manganese(II) phosphate

Names and Formulas of Acids

Acids are an important class of hydrogen-containing compounds, and they are named in a special way. For our present purposes, an *acid* is a substance whose molecules yield hydrogen ions (H^+) when dissolved in water. When we encounter the chemical formula for an acid at this stage of the course, it will be written with H as the first element, as in HCl and H_2SO_4.

An acid is composed of an anion connected to enough H^+ ions to neutralize, or balance, the anion's charge. Thus, the SO_4^{2-} ion requires two H^+ ions, forming H_2SO_4. The name of an acid is related to the name of its anion, as summarized in **Figure 2.23**.

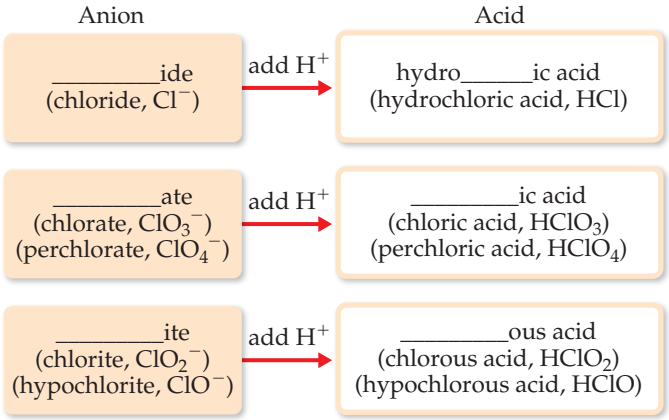
How to Name Acids

1. *Acids containing anions whose names end in* -ide *are named by changing the* -ide *ending to* -ic, *adding the prefix* hydro- *to this anion name, and then following with the word* acid:

Anion	Corresponding Acid
Cl^- (chloride)	HCl (hydrochloric acid)
S^{2-} (sulfide)	H_2S (hydrosulfuric acid)

2. *Acids containing anions whose names end in* -ate *or* -ite *are named by changing* -ate *to* -ic *and* -ite *to* -ous *and then adding the word* acid. Prefixes in the anion name are retained in the name of the acid:

Anion		Corresponding Acid	
ClO_4^-	(perchlorate)	$HClO_4$	(perchloric acid)
ClO_3^-	(chlorate)	$HClO_3$	(chloric acid)
ClO_2^-	(chlorite)	$HClO_2$	(chlorous acid)
ClO^-	(hypochlorite)	HClO	(hypochlorous acid)



▲ **Figure 2.23 Procedure for naming acids.** Here acids containing chlorine are used as an example. Prefixes used for oxyanions, such as, *per-* and *hypo-*, are retained in the acids derived from those anions.

Sample Exercise 2.13

Relating the Names and Formulas of Acids

Name the acids (**a**) HCN, (**b**) HNO_3, (**c**) H_2SO_4, (**d**) H_2SO_3.

SOLUTION

(**a**) The anion from which this acid is derived is CN^-, the cyanide ion. Because this ion has an *-ide* ending, the acid is given a *hydro-* prefix and an *-ic* ending: hydrocyanic acid. Only water solutions of HCN are referred to as hydrocyanic acid. The pure compound, which is a gas under normal conditions, is called hydrogen cyanide. Both hydrocyanic acid and hydrogen cyanide are *extremely* toxic.

(**b**) Because NO_3^- is the nitrate ion, HNO_3 is called nitric acid (the *-ate* ending of the anion is replaced with an *-ic* ending in naming the acid).

(**c**) Because SO_4^{2-} is the sulfate ion, H_2SO_4 is called sulfuric acid.

(**d**) Because SO_3^{2-} is the sulfite ion, H_2SO_3 is sulfurous acid (the *-ite* ending of the anion is replaced with an *-ous* ending).

Practice Exercise

Which of the following acids are incorrectly named? For those that are, provide a correct name or formula.
(**a**) hydrofluoric acid, HF (**b**) nitrous acid, HNO_3 (**c**) perbromic acid, $HBrO_4$ (**d**) iodic acid, HI (**e**) selenic acid, H_2SeO_4

TABLE 2.6 Prefixes Used in Naming Binary Compounds Formed between Nonmetals

Prefix	Meaning
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10

Names and Formulas of Binary Molecular Compounds

The procedures used for naming *binary* (two-element) molecular compounds are similar to those used for naming ionic compounds:

How to Name Binary Molecular Compounds

1. *The name of the element farther to the left in the periodic table (closest to the metals) is usually written first.* An exception occurs when the compound contains oxygen and chlorine, bromine, or iodine (any halogen except fluorine), in which case oxygen is written last.
2. *If both elements are in the same group, the one closer to the bottom of the table is named first.*
3. *The name of the second element is given an* -ide *ending.*
4. *Greek prefixes* (Table 2.6) indicate the number of atoms of each element. (Exception: The prefix *mono-* is never used with the first element.) When the prefix ends in *a* or *o* and the name of the second element begins with *a* vowel, the *a* or *o* of the prefix is often dropped.

The following examples illustrate these rules:

Cl_2O	dichlorine monoxide	NF_3	nitrogen trifluoride
N_2O_4	dinitrogen tetroxide	P_4S_{10}	tetraphosphorus decasulfide

Rule 4 is necessary because we cannot predict formulas for most molecular substances the way we can for ionic compounds. Molecular compounds that contain hydrogen and one other element are an important exception, however. These compounds can be treated as if they were neutral substances containing H^+ ions and anions. Thus, you can predict that the substance named hydrogen chloride has the formula HCl, containing one H^+ to balance the charge of one Cl^-. (The name *hydrogen chloride* is used only for the pure compound; water solutions of HCl are called hydrochloric acid. The distinction, which is important, will be explained in Section 4.1.) Similarly, the formula for hydrogen sulfide is H_2S because two H^+ ions are needed to balance the charge on S^{2-}.

Sample Exercise 2.14

Relating the Names and Formulas of Binary Molecular Compounds

Name the compounds (**a**) SO_2, (**b**) PCl_5, (**c**) Cl_2O_3.

SOLUTION

The compounds consist entirely of nonmetals, so they are molecular rather than ionic. Using the prefixes in Table 2.6 , we have (**a**) sulfur dioxide, (**b**) phosphorus pentachloride, (**c**) dichlorine trioxide.

Practice Exercise

Give the name for each of the following binary compounds of carbon: (**a**) CS_2, (**b**) CO, (**c**) C_3O_2, (**d**) CBr_4, (**e**) CF.

Self-Assessment Exercise

2.38 What is the name of $NaClO_2$?

(a) Sodium chlorine oxide

(b) Sodium chlorite

(c) Sodium chlorate

Exercises

2.39 Give the chemical formula for (**a**) chromate ion (**b**) bromide ion (**c**) nitrite ion (**d**) sulphite ion (**e**) permanganate ion.

2.40 Give the names and charges of the cation and anion in each of the following compounds: (**a**) CaO, (**b**) Na_2SO_4, (**c**) $KClO_4$, (**d**) $Fe(NO_3)_2$, (**e**) $Cr(OH)_3$.

2.41 Name the following ionic compounds: (**a**) Li_2O, (**b**) $FeCl_3$, (**c**) NaClO, (**d**) $CaSO_3$, (**e**) $Cu(OH)_2$, (**f**) $Fe(NO_3)_2$, (**g**) $Ca(CH_3COO)_2$, (**h**) $Cr_2(CO_3)_3$, (**i**) K_2CrO_4, (**j**) $(NH_4)_2SO_4$.

2.42 Write the chemical formulas for the following compounds: (**a**) aluminum hydroxide, (**b**) potassium sulfate, (**c**) copper(I) oxide, (**d**) zinc nitrate, (**e**) mercury(II) bromide, (**f**) iron(III) carbonate, (**g**) sodium hypobromite.

2.43 Give the name or chemical formula, as appropriate, for each of the following acids: (**a**) $HBrO_3$, (**b**) HBr, (**c**) H_3PO_4, (**d**) hypochlorous acid, (**e**) iodic acid, (**f**) sulfurous acid.

2.44 Give the name or chemical formula, as appropriate, for each of the following binary molecular substances: (**a**) SF_6, (**b**) IF_5, (**c**) XeO_3, (**d**) dinitrogen tetroxide, (**e**) hydrogen cyanide, (**f**) tetraphosphorus hexasulfide.

2.45 Write the chemical formula for each substance mentioned in the following word descriptions (use the front inside cover to find the symbols for the elements you do not know). (**a**) Zinc carbonate can be heated to form zinc oxide and carbon dioxide. (**b**) On treatment with hydrofluoric acid, silicon dioxide forms silicon tetrafluoride and water. (**c**) Sulfur dioxide reacts with water to form sulfurous acid. (**d**) The substance phosphorus trihydride, commonly called phosphine, is a toxic gas. (**e**) Perchloric acid reacts with cadmium to form cadmium(II) perchlorate. (**f**) Vanadium(III) bromide is a colored solid.

Answers to Self-Assessment Exercises

2.37 (b)

2.9 Some Simple Organic Compounds



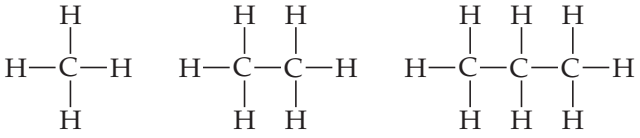
Organic compounds were believed to require living cells for their synthesis, either plant or animal in origin. Now there are many ways in which we may synthesize organic compound from inorganic materials. They represent over 99% of all known compounds and each one has carbon as a central element. By the end of this section, you should be able to

- Recognize and name simple alkanes and alcohols

The study of compounds of carbon is called **organic chemistry**, and as noted earlier, compounds that contain carbon and hydrogen, often in combination with oxygen, nitrogen, or other elements, are called *organic compounds*. Organic compounds are a very important part of chemistry, far outnumbering all other types of chemical substances. We will examine organic compounds in a systematic way later on, but you will encounter many examples of them throughout the text. Here we present a brief introduction to some of the simplest organic compounds and the ways in which they are named.

Alkanes

Compounds that contain only carbon and hydrogen are called **hydrocarbons**. In the simplest class of hydrocarbons, **alkanes**, each carbon is bonded to four other atoms. The three smallest alkanes are methane (CH_4), ethane (C_2H_6), and propane (C_3H_8). The structural formulas of these three alkanes are as follows:

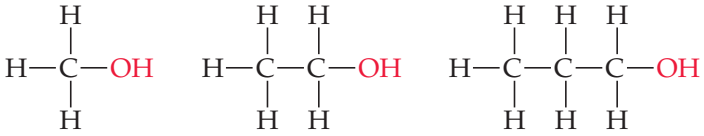


Although hydrocarbons are binary molecular compounds, they are not named like the binary inorganic compounds discussed in Section 2.8. Instead, each alkane has a

name that ends in *-ane*. The alkane with four carbons is called *butane*. For alkanes with five or more carbons, the names are derived from prefixes like those in Table 2.6. An alkane with eight carbon atoms, for example, is *octane* (C_8H_{18}), where the *octa-* prefix for eight is combined with the *-ane* ending for an alkane.

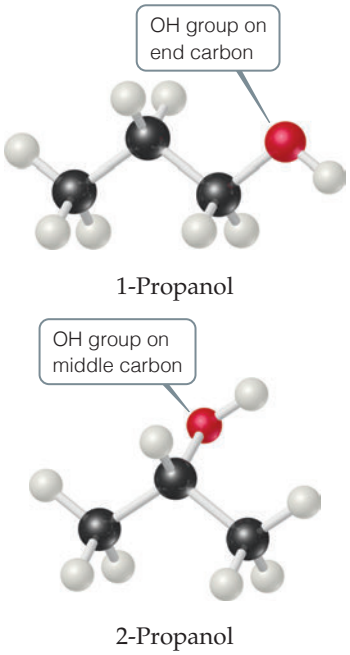
Some Derivatives of Alkanes

Other classes of organic compounds are obtained when one or more hydrogen atoms in an alkane are replaced with *functional groups*, which are specific groups of atoms. An **alcohol**, for example, is obtained by replacing an H atom of an alkane with an —OH group. The name of the alcohol is derived from that of the alkane by adding an *-ol* ending:



Alcohols have properties that are very different from those of the alkanes from which the alcohols are obtained. For example, methane, ethane, and propane are all colorless gases under normal conditions, whereas methanol, ethanol, and propanol are colorless liquids. We will discuss the reasons for these differences in Chapter 11.

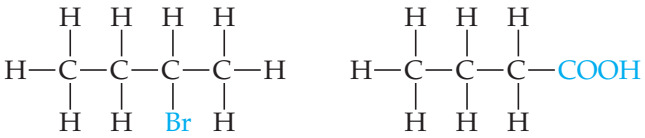
The prefix "1" in the name 1-propanol indicates that the replacement of H with OH has occurred at one of the "outer" carbon atoms rather than the "middle" carbon atom. A different compound, called 2-propanol is obtained when the OH functional group is attached to the middle carbon atom (**Figure 2.24**).

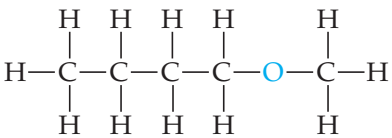


▲ **Figure 2.24** **The two forms (isomers) of propanol.**

Compounds with the same molecular formula but different arrangements of atoms are called **isomers**. For example, 1-propanol and 2-propanol are *structural isomers*, compounds that have the same molecular formula but different structural formulas. There are many different kinds of isomers, as we will discover later in this book.

As already noted, many different functional groups can replace one or more of the hydrogens on an alkane—for example, one or more of the halogens, or a special grouping of carbon and oxygen atoms, such as the carboxylic acid group, —COOH. Here are a few examples of functional groups you will be encountering in the chapters that lie ahead (the functional group is highlighted in blue):





Much of the richness of organic chemistry is possible because organic compounds can form long chains of carbon–carbon bonds. The series of alkanes that begins with methane, ethane, and propane and the series of alcohols that begins with methanol, ethanol, and propanol can both be extended for as long as we desire, in principle. The

properties of alkanes and alcohols change as the chains get longer. Octanes, which are alkanes with eight carbon atoms, are liquids under normal conditions. If the alkane series is extended to tens of thousands of carbon atoms, we obtain *polyethylene*, a solid substance that is used to make thousands of plastic products, such as plastic bags, food containers, and laboratory equipment.

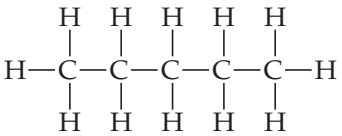
Sample Exercise 2.15

Writing Structural and Molecular Formulas for Hydrocarbons

Assuming the carbon atoms in *pentane* are in a linear chain, write (**a**) the structural formula and (**b**) the molecular formula for this alkane.

SOLUTION

(**a**) Alkanes contain only carbon and hydrogen, and each carbon is attached to four other atoms. The name *pentane* contains the prefix *penta-* for five (Table 2.6), and we are told that the carbons are in a linear chain. If we then add enough hydrogen atoms to make four bonds to each carbon, we obtain the structural formula



This form of pentane is often called *n*-pentane, where the *n-* stands for "normal" because all five carbon atoms are in one line in the structural formula.

(**b**) Once the structural formula is written, we determine the molecular formula by counting the atoms present. Thus, *n*-pentane has the molecular formula C_5H_{12}.

Practice Exercise

(**a**) What is the molecular formula of hexane, the alkane with six carbons? (**b**) What are the name and molecular formula of an alcohol derived from hexane?

STRATEGIES FOR SUCCESS How to Take a Test

At about this time in your study of chemistry, you are likely to face your first examination. The best way to prepare is to study, do homework diligently, and get help from the instructor on any material that is unclear or confusing. (See the advice for learning and studying chemistry presented in the preface of the book.) We present here some general guidelines for taking tests.

Depending on the nature of your course, the exam could consist of a variety of different types of questions.

1. **Multiple-choice questions** In large-enrollment courses, the most common kind of test question is the multiple-choice question. Many of the practice exercise problems in this book are written in this format to give you practice at this style of question. When faced with this type of problem, the first thing to realize is that the instructor has written the question so that at first glance all the answers appear to be correct. Thus, you should not jump to the conclusion that because one of the choices looks correct, it must be correct.

   If a multiple-choice question involves a calculation, do the calculation, check your work, and *only then* compare your answer with the choices. Keep in mind, though, that your instructor has anticipated the most common errors you might make in solving a given problem and has probably listed the incorrect answers resulting from those errors. Always double-check your reasoning and use dimensional analysis to arrive at the correct numeric answer and the correct units.

   In multiple-choice questions that do not involve calculations, if you are not sure of the correct choice, eliminate all the choices you know for sure to be incorrect. The reasoning you use in eliminating incorrect choices may offer insight into which of the remaining choices is correct.

2. **Calculations in which you must show your work** In questions of this kind, you may receive partial credit even if you do not arrive at the correct answer, depending on whether the instructor can follow your line of reasoning. It is important, therefore, to be neat and organized in your calculations. Pay particular attention to what information is given and to what your unknown is. Think about how you can get from the given information to your unknown.

   You may want to write a few words or a diagram on the test paper to indicate your approach. Then write out your calculations as neatly as you can. Show the units for every number you write down, and use dimensional analysis as much as you can, showing how units cancel.

3. **Questions requiring drawings** Questions of this kind will come later in the course, but it is useful to talk about them here. (You should review this box before each exam to remind yourself of good exam-taking practices.) Be sure to label your drawing as completely as possible.

Self-Assessment Exercise

2.46 Do isomers have the same molecular formula?

(a) Yes

(b) No

Exercises

2.47 (**a**) What is a hydrocarbon? (**b**) Pentane is the alkane with a chain of five carbon atoms. Write a structural formula for this compound and determine its molecular and empirical formulas.

2.48 (**a**) What is a functional group? (**b**) What functional group characterizes an alcohol? (**c**) Write a structural formula for 1-pentanol, the alcohol derived from pentane by making a substitution on one of the carbon atoms.

2.49 Chloropropane is derived from propane by substituting Cl for H on one of the carbon atoms. (**a**) Draw the structural formulas for the two isomers of chloropropane. (**b**) Suggest names for these two compounds.

Answers to Self-Assessment Exercises

2.45 (a)

Chapter Summary and Key Terms

THE ATOMIC THEORY OF MATTER; THE DISCOVERY OF ATOMIC STRUCTURE (SECTION 2.1 AND 2.2) **Atoms** are the basic building blocks of matter. They are the smallest units of an element that can combine with other elements. Atoms are composed of even smaller particles, called **subatomic particles**. Some of these subatomic particles are charged and follow the usual behavior of charged particles: Particles with the same charge repel one another, whereas particles with opposite charges are attracted to one another.

We considered some of the important experiments that led to the discovery and characterization of subatomic particles. Thomson's experiments on the behavior of **cathode rays** in magnetic and electric fields led to the discovery of the electron and allowed its charge-to-mass ratio to be measured. Millikan's oil-drop experiment determined the charge of the electron. Becquerel's discovery of **radioactivity**, the spontaneous emission of radiation by atoms, gave further evidence that the atom has a substructure. Rutherford's studies of how α particles scatter when passing through thin metal foils led to the **nuclear model** of the atom, showing that the atom has a dense, positively charged **nucleus**.

THE MODERN VIEW OF ATOMIC STRUCTURE (SECTION 2.3) Atoms have a nucleus that contains **protons** and **neutrons**; **electrons** move in the space around the nucleus. The magnitude of the charge of the electron, 1.602×10^{-19} C, is called the **electronic charge**. The charges of particles are usually represented as multiples of this charge—an electron has a 1− charge, and a proton has a 1+ charge. The masses of atoms are usually expressed in terms of **atomic mass units** ($1\text{ u} = 1.66054 \times 10^{-24}$ g).

Elements can be classified by **atomic number**, the number of protons in the nucleus of an atom. All atoms of a given element have the same atomic number. The **mass number** of an atom is the sum of the numbers of protons and neutrons. Atoms of the same element that differ in mass number are known as **isotopes**.

ATOMIC WEIGHTS (SECTION 2.4) The atomic mass scale is defined by assigning a mass of exactly 12 u to a ^{12}C atom. The **atomic weight** (average atomic mass) of an element can be calculated from the relative abundances and masses of that element's isotopes. The **mass spectrometer** provides the most direct and accurate means of experimentally measuring atomic (and molecular) weights.

THE PERIODIC TABLE (SECTION 2.5) The **periodic table** is an arrangement of the elements in order of increasing atomic number. Elements with similar properties are placed in vertical columns. The elements in a column are known as a **group**. The elements in a horizontal row are known as a **period**. The **metallic elements** (**metals**), which comprise the majority of the elements, dominate the left side and the middle of the table; the **nonmetallic elements** (**nonmetals**) are located on the upper right side. Many of the elements that lie along the line that separates metals from nonmetals are **metalloids**.

MOLECULES AND MOLECULAR COMPOUNDS (SECTION 2.6) Atoms can combine to form **molecules**. Compounds composed of molecules (**molecular compounds**) usually contain only nonmetallic elements. A molecule that contains two atoms is called a **diatomic molecule**. The composition of a substance is given by its **chemical formula**. A molecular substance can be represented by its **empirical formula**, which gives the relative numbers of atoms of each kind, but is usually represented by its **molecular formula**, which gives the actual numbers of each type of atom in a molecule. **Structural formulas** show the order in which the atoms in a molecule are connected. **Ball-and-stick models** and **space-filling models** convey additional information about the shapes of molecules.

IONS AND IONIC COMPOUNDS (SECTION 2.7) Atoms can either gain or lose electrons, forming charged particles called **ions**. Metals tend to lose electrons, becoming positively charged ions (**cations**). Nonmetals tend to gain electrons, forming negatively charged ions (**anions**). Because **ionic compounds** are electrically neutral, containing both cations and anions, they usually contain both metallic and nonmetallic elements. Atoms that are joined together, as in a molecule, but carry a net charge are called **polyatomic ions**. The chemical formulas used for ionic compounds are empirical formulas, which can be written readily if the charges of the ions are known. The total positive charge of the cations in an ionic compound must equal the total negative charge of the anions.

NAMING INORGANIC COMPOUNDS (SECTION 2.8) The set of rules for naming chemical compounds is called **chemical nomenclature**. We studied the systematic rules used for naming three classes of inorganic substances: ionic compounds, acids, and binary molecular compounds.

In naming an ionic compound, the cation is named first and then the anion. Cations formed from metal atoms have the same name as the metal. If the metal can form cations of differing charges, the charge is given using Roman numerals. Monatomic anions have names ending in *-ide*. Polyatomic anions containing oxygen and another element (**oxyanions**) have names ending in *-ate* or *-ite*. In naming binary molecular compounds, Greek prefixes are used to denote the number of each element in the molecular formula, and the element farthest to the left in the periodic table (closest to metallic elements) is generally written first.

SOME SIMPLE ORGANIC COMPOUNDS (SECTION 2.9) **Organic chemistry** is the study of compounds that contain carbon. The simplest class of organic molecules is the **hydrocarbons**, which contain only carbon and hydrogen. Hydrocarbons in which each carbon atom is attached to four other atoms are called **alkanes**. Alkanes have names that end in *-ane*, such as methane and ethane. Other organic compounds are formed when an H atom of a hydrocarbon is replaced with a functional group. An **alcohol**, for example, is a compound in which an H atom of a hydrocarbon is replaced by an OH functional group. Alcohols have names that end in *-ol*, such as methanol and ethanol. Compounds with the same molecular formula but different bonding arrangements of their constituent atoms are called **isomers**.

Learning Outcomes After studying this chapter, you should be able to:

- List the basic postulates of Dalton's atomic theory. (Section 2.1) *Related Exercises: 2.2, 2.3, 2.60, 2.61*
- Describe the key experiments that led to the discovery of electrons and to the nuclear model of the atom. (Section 2.2) *Related Exercises: 2.5, 2.6, 2.62, 2.63*
- Describe the structure of the atom in terms of protons, neutrons, and electrons and express the relative electrical charges and masses of these subatomic particles. (Section 2.3) *Related Exercises: 2.10, 2.65*
- Use chemical symbols together with atomic number and mass number to express the subatomic composition of isotopes. (Section 2.3) *Related Exercises: 2.11, 2.12, 2.14, 2.33*
- Calculate the atomic weight of an element from the masses of individual atoms and a knowledge of natural abundances. (Section 2.4) *Related Exercises: 2.18, 2.20, 2.71, 2.72*
- Describe how elements are organized in the periodic table by atomic number and by similarities in chemical behavior, giving rise to periods and groups. (Section 2.5) *Related Exercises: 2.23, 2.76*
- Identify the locations of metals and nonmetals in the periodic table. (Section 2.5) *Related Exercises: 2.22, 2.75*
- Distinguish between molecular substances and ionic substances in terms of their composition. (Section 2.6 and 2.7) *Related Exercises: 2.32, 2.36, 2.37, 2.87*
- Distinguish between empirical formulas and molecular formulas. (Section 2.6) *Related Exercises: 2.25, 2.26, 2.27, 2.77*
- Describe how molecular formulas and structural formulas are used to represent the compositions of molecules. (Section 2.6) *Related Exercises: 2.29, 2.81*
- Explain how ions are formed by the gain or loss of electrons and use the periodic table to predict the charges of common ions. (Section 2.7) *Related Exercises: 2.34, 2.82, 2.83*
- Write the empirical formulas of ionic compounds, given the charges of their component ions. (Section 2.7) *Related Exercises: 2.35, 2.36, 2.37, 2.85*
- Write the name of an ionic compound given its chemical formula or write the chemical formula given its name. (Section 2.8) *Related Exercises: 2.41, 2.42, 2.90, 2.91*
- Name or write chemical formulas for binary inorganic compounds and for acids. (Section 2.8) *Related Exercises: 2.43, 2.44, 2.92, 2.93*
- Identify organic compounds and name simple alkanes and alcohols. (Section 2.9) *Related Exercises: 2.47, 2.48, 2.49, 2.96*

Key Equations

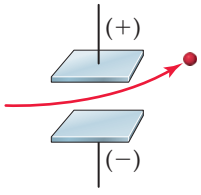
- $$\text{Atomic weight} = \sum_{\substack{\text{over} \\ \text{all isotopes}}} [(\text{isotope mass}) \times (\text{fractional isotope abundance})]$$ [2.1] Calculating atomic weight as a fractionally weighted average of isotopic masses.

Exercises

Visualizing Concepts

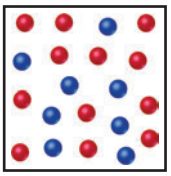
These exercises are intended to probe your understanding of key concepts rather than your ability to utilize formulas and perform calculations. Exercises with red numbers have answers in the back of the book.

2.50 A charged particle moves between two electrically charged plates, as shown here.

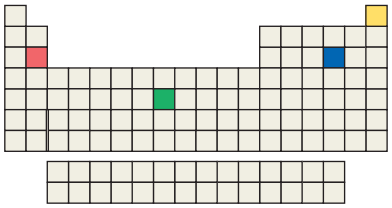


(**a**) What is the sign of the electrical charge on the particle? (**b**) As the charge on the plates is increased, would you expect the bending to increase, decrease, or stay the same? (**c**) As the mass of the particle is increased while the speed of the particles remains the same, would you expect the bending to increase, decrease, or stay the same? [Section 2.2]

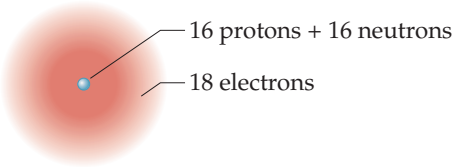
2.51 The following diagram is a representation of 20 atoms of a fictitious element, which we will call nevadium (Nv). The red spheres are ^{293}Nv, and the blue spheres are ^{295}Nv. (**a**) Assuming that this sample is a statistically representative sample of the element, calculate the percent abundance of each element. (**b**) If the mass of ^{293}Nv is 293.15 u and that of ^{295}Nv is 295.15 u, what is the atomic weight of Nv? [Section 2.4]



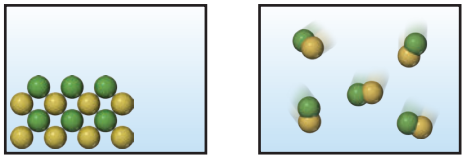
2.52 Four of the boxes in the following periodic table are colored. Which of these are metals and which are nonmetals? Which one is an alkaline earth metal? Which one is a noble gas? [Section 2.5]



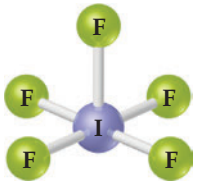
2.53 Does the following drawing represent a neutral atom or an ion? Write its complete chemical symbol, including mass number, atomic number, and net charge (if any). [Sections 2.3 and 2.7]



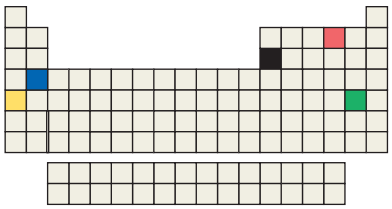
2.54 Which of the following diagrams most likely represents an ionic compound, and which represents a molecular one? Explain your choice. [Sections 2.6 and 2.7]



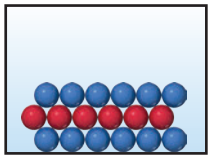
2.55 Write the chemical formula for the following compound. Is the compound ionic or molecular? Name the compound. [Sections 2.6 and 2.8]



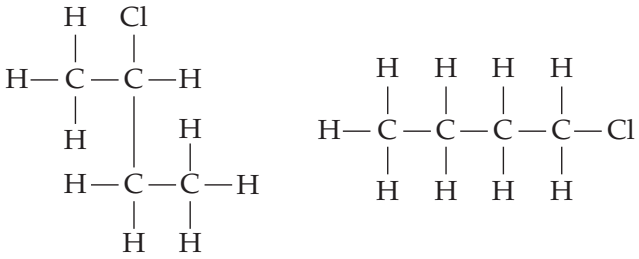
2.56 Five of the boxes in the following periodic table are colored. Predict the charge on the ion associated with each of these elements. [Section 2.7]



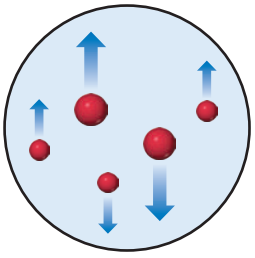
2.57 The following diagram represents an ionic compound in which the red spheres represent cations and the blue spheres represent anions. Which of the following formulas is consistent with the drawing? KBr, K_2SO_4, $Ca(NO_3)_2$, $Fe_2(SO_4)_3$. Name the compound. [Sections 2.7 and 2.8]



2.58 Are these two compounds isomers? Explain. [Section 2.9]



2.59 In the Millikan oil-drop experiment (see Figure 2.4), the tiny oil drops are observed through the viewing lens as rising, stationary, or falling, as shown here. (**a**) What causes their rate of fall to vary from their rate in the absence of an electric field? (**b**) Why do some drops move upward? [Section 2.2]



The following exercises are divided into sections that deal with specific topics in the chapter. The exercises are grouped in pairs, with the answers given in the back of the book to the odd-numbered exercises, as indicated by the red exercise numbers. Those exercises whose numbers appear in brackets are more challenging than the nonbracketed exercises.

The Atomic Theory of Matter and the Discovery of Atomic Structure (Sections 2.1 and 2.2)

2.60 Sodium reacts with oxygen in air to form two compounds: sodium oxide and sodium peroxide. In forming sodium oxide, 23.0 g of sodium combines with 8.0 g of hydrogen. In forming sodium peroxide, 23.0 g of sodium combines with 16.0 g of oxygen. (**a**) What are the mass ratios of oxygen in the two compounds? (**b**) What fundamental law does this experiment demonstrate?

2.61 In a series of experiments, a chemist prepared three different compounds that contain only iodine and fluorine and determined the mass of each element in each compound:

Compound	Mass of Iodine (g)	Mass of Fluorine (g)
1	4.75	3.56
2	7.64	3.43
3	9.41	9.86

(**a**) Calculate the mass of fluorine per gram of iodine in each compound. (**b**) How do the numbers in part (a) support the atomic theory?

2.62 Discovering which of the three subatomic particles proved to be the most difficult—the proton, neutron, or electron? Why?

2.63 Millikan determined the charge on the electron by studying the static charges on oil drops falling in an electric field (Figure 2.4). A student carried out this experiment using several oil drops for her measurements and calculated the charges on the drops. She obtained the following data:

Droplet	Calculated Charge (C)
A	1.60×10^{-19}
B	3.15×10^{-19}
C	4.81×10^{-19}
D	6.31×10^{-19}

(**a**) What is the significance of the fact that the droplets carried different charges? (**b**) What conclusion can the student draw from these data regarding the charge of the electron? (**c**) What value (and to how many significant figures) should she report for the electronic charge?

The Modern View of Atomic Structure; Atomic Weights (Sections 2.3 and 2.4)

2.64 The radius of an atom of copper (Cu) is about 140 pm. (**a**) Express this distance in millimeters (mm). (**b**) How many Cu atoms would have to be placed side by side to span a distance of 5.0 mm? (**c**) If you assume that the Cu atom is a sphere, what is the volume in cm^3 of a single atom?

2.65 Determine whether each of the following statements is true or false. If false, correct the statement to make it true: (**a**) The nucleus has most of the mass and comprises most of the volume of an atom. (**b**) Every atom of a given element has the same number of protons. (**c**) The number of electrons in an atom equals the number of neutrons in the atom. (**d**) The protons in the nucleus of the helium atom are held together by a force called the strong nuclear force.

2.66 Consider an atom of ^{58}Ni. (**a**) How many protons, neutrons, and electrons does this atom contain? (**b**) What is the symbol of the ion obtained by removing two electrons from ^{58}Ni? (**c**) What is the symbol for the isotope of ^{58}Ni that possesses 33 neutrons?

2.67 (**a**) Which two of the following are isotopes of the same element: $^{106}_{46}X$, $^{107}_{46}X$, $^{107}_{47}X$? (**b**) What is the identity of the element whose isotopes you have selected?

2.68 Each of the following isotopes is used in medicine. Indicate the number of protons and neutrons in each isotope: (**a**) samarium-153, (**b**) lutetium-177, (**c**) bismuth-213, (**d**) molybdenum-99, (**e**) lead-212, (**f**) caesium-131.

2.69 Fill in the gaps in the following table, assuming each column represents a neutral atom.

Symbol	^{89}Y				
Protons		78			89
Neutrons			123		
Electrons			81	50	
Mass no.		195		119	227

2.70 One way in which Earth's evolution as a planet can be understood is by measuring the amounts of certain isotopes in rocks. One quantity recently measured is the ratio of ^{129}Xe to ^{130}Xe in some minerals. In what way do these two isotopes differ from one another? In what respects are they the same?

2.71 (**a**) What is the mass in u of a carbon-12 atom? (**b**) Why is the atomic weight of carbon reported as 12.011 in the table of elements and the periodic table in the front inside cover of this text?

2.72 Bromine has two naturally occurring isotopes, bromine-79 (atomic mass = 78.9183 u; abundance = 50.69%) and bromine-81 (atomic mass = 80.9163 u; abundance = 49.31%). Calculate the atomic weight of bromine.

2.73 Consider the mass spectrometer shown in Figure 2.10. Determine whether each of the following statements is true or false. If false, correct the statement to make it true: (**a**) The paths of neutral (uncharged) atoms are not affected by the magnet. (**b**) The height of each peak in the mass spectrum is inversely proportional to the mass of that isotope. (**c**) For a given element, the number of peaks in the spectrum is equal to the number of naturally occurring isotopes of that element.

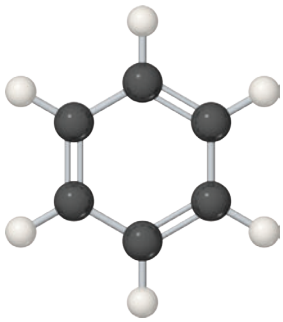
2.74 Mass spectrometry is more often applied to molecules than to atoms. We will see in Chapter 3 that the *molecular weight* of a molecule is the sum of the atomic weights of the atoms in the molecule. The mass spectrum of H_2 is taken under conditions that prevent decomposition into H atoms. The two naturally occurring isotopes of hydrogen are ^1H (atomic mass = 1.00783 u; abundance 99.9885%) and ^2H (atomic mass = 2.01410 u; abundance 0.0115%). (**a**) How many peaks will the mass spectrum have? (**b**) Give the relative atomic masses of each of these peaks. (**c**) Which peak will be the largest, and which the smallest?

The Periodic Table, Molecules, Molecular Compounds, Ions, and Ionic Compounds (Sections 2.5, 2.6, and 2.7)

2.75 Locate each of the following elements in the periodic table; give its name and atomic number, and indicate whether it is a metal, metalloid, or nonmetal: (**a**) Hg, (**b**) At, (**c**) Mo, (**d**) W, (**e**) Sn, (**f**) V, (**g**) K.

2.76 For each of the following elements, write its chemical symbol, determine the name of the group to which it belongs (Table 2.3), and indicate whether it is a metal, metalloid, or nonmetal: (**a**) polonium, (**b**) strontium, (**c**) neon, (**d**) rubidium, (**e**) bromine.

2.77 Ball-and-stick representations of benzene, a colorless liquid often used in organic chemistry reactions, and acetylene, a gas used as a fuel for high-temperature welding, are shown here. (**a**) Determine the molecular formula of each. (**b**) Determine the empirical formula of each.



benzene



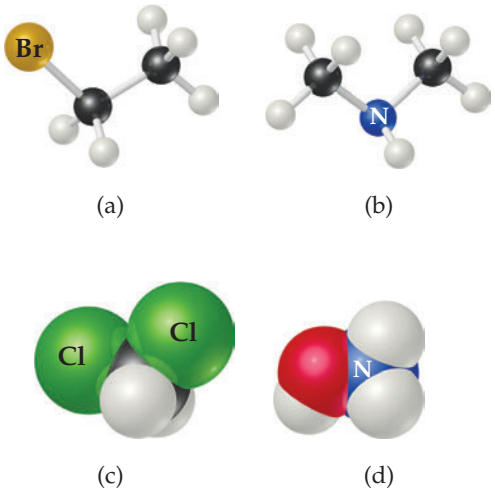
acetylene

2.78 Two substances have the same molecular and empirical formulas. Does this mean that they must be the same compound?

2.79 Determine the molecular and empirical formulas of the following: (**a**) the organic solvent *benzene*, which has six carbon atoms and six hydrogen atoms; (**b**) the compound *silicon tetrachloride*, which has a silicon atom and four chlorine atoms and is used in the manufacture of computer chips; (**c**) the reactive substance *diborane*, which has two boron atoms and six hydrogen atoms; (**d**) the sugar called *glucose,* which has six carbon atoms, twelve hydrogen atoms, and six oxygen atoms.

2.80 How many of the indicated atoms are represented by each chemical formula: (**a**) carbon atoms in $C_4H_9COOCH_3$, (**b**) oxygen atoms in $Ca(ClO_3)_2$, (**c**) hydrogen atoms in $(NH_4)_2HPO_4$?

2.81 Write the molecular and structural formulas for the compounds represented by the following models:



(a) (b) (c) (d)

2.82 Fill in the gaps in the following table:

Symbol	$^{133}Cs^+$			
Protons		35	15	
Neutrons		46	16	30
Electrons			18	20
Net charge		1−		5+

2.83 Using the periodic table, predict the charge of the most stable ion of the following elements: (**a**) Li, (**b**) Ba, (**c**) Po, (**d**) I, (**e**) Sb.

2.84 The most common charge associated with selenium is 2−. Indicate the chemical formulas you would expect for compounds formed between selenium and (**a**) barium, (**b**) lithium, (**c**) aluminum.

2.85 Predict the chemical formulas of the compounds formed by the following pairs of ions: (**a**) Cr^{3+} and CN^-, (**b**) Mn^{2+} and ClO_4^-, (**c**) Na^+ and $Cr_2O_7^{2-}$, (**d**) Cd^{2+} and CO_3^{2-}, (**e**) Ti^{4+} and O^{2-}.

2.86 Complete the table by filling in the formula for the ionic compound formed by each pair of cations and anions, as shown for the first pair.

Ion	Na^+	Ca^{2+}	Fe^{2+}	Al^{3+}
O^{2-}	Na_2O			
NO_3^-				
SO_4^{2-}				
AsO_4^{3-}				

2.87 Predict whether each of the following compounds is molecular or ionic: (**a**) BI_3 (**b**) $N(CH_3)_3$ (**c**) $Zr(NO_3)_2$ (**d**) N_2H_4 (**e**) $OsCO_3$ (**f**) H_2SO_4 (**g**) HgS (**h**) IOH.

Naming Inorganic Compounds; Some Simple Organic Compounds (Sections 2.8 and 2.9)

2.88 Selenium, an element required nutritionally in trace quantities, forms compounds analogous to sulfur. Name the following ions: (**a**) SeO_4^{2-}, (**b**) Se^{2-}, (**c**) HSe^-, (**d**) $HSeO_3^-$.

2.89 Give the names and charges of the cation and anion in each of the following compounds: (**a**) CuS, (**b**) Ag_2SO_4, (**c**) $Al(ClO_3)_3$, (**d**) $Co(OH)_2$, (**e**) $PbCO_3$.

2.90 Name the following ionic compounds: (**a**) KCN, (**b**) $NaBrO_2$, (**c**) $Sr(OH)_2$, (**d**) CoTe, (**e**) $Fe_2(CO_3)_3$, (**f**) $Cr(NO_3)_3$, (**g**) $(NH_4)_2SO_3$, (**h**) NaH_2PO_4, (**i**) $KMnO_4$, (**j**) $Ag_2Cr_2O_7$.

2.91 Give the chemical formula for each of the following ionic compounds: (**a**) sodium phosphate, (**b**) zinc nitrate, (**c**) barium bromate, (**d**) iron(II) perchlorate, (**e**) cobalt(II) hydrogen carbonate, (**f**) chromium(III) acetate, (**g**) potassium dichromate.

2.92 Provide the name or chemical formula, as appropriate, for each of the following acids: (**a**) hydroiodic acid, (**b**) chloric acid, (**c**) nitrous acid, (**d**) H_2CO_3, (**e**) $HClO_4$, (**f**) CH_3COOH.

2.93 The oxides of nitrogen are very important components in urban air pollution. Name each of the following compounds: (**a**) N_2O, (**b**) NO, (**c**) NO_2, (**d**) N_2O_5, (**e**) N_2O_4.

2.94 Assume that you encounter the following sentences in your reading. What is the chemical formula for each substance mentioned? (**a**) Sodium hydrogen carbonate is used as a deodorant. (**b**) Calcium hypochlorite is used in some bleaching solutions. (**c**) Hydrogen cyanide is a very poisonous gas. (**d**) Magnesium hydroxide is used as a cathartic. (**e**) Tin(II) fluoride has been used as a fluoride additive in toothpastes. (**f**) When cadmium sulfide is treated with sulfuric acid, fumes of hydrogen sulfide are given off.

2.95 (**a**) What is meant by the term *isomer*? (**b**) Among the four alkanes, ethane, propane, butane, and pentane, which is capable of existing in isomeric forms?

2.96 Consider the following organic substances: ethylethanoate, ethylmethylether, hexanol, and propanone. (**a**) Which of these molecules contains three carbons? (**b**) Which of these molecules contain a C = O group?

2.97 Draw the structural formulas for four structural isomers of C_4H_9Br.

Additional Exercises

These exercises are not divided by category, although they are roughly in the order of the topics in the chapter.

2.98 Suppose a scientist repeats the Millikan oil-drop experiment but reports the charges on the drops using an unusual (and imaginary) unit called the *warmomb* (wa). The scientist obtains the following data for four of the drops:

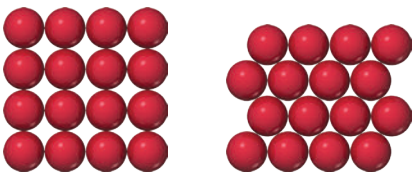
Droplet	Calculated Charge (wa)
A	3.84×10^{-8}
B	4.80×10^{-8}
C	2.88×10^{-8}
D	8.64×10^{-8}

(**a**) If all the droplets were the same size, which would fall most slowly through the apparatus? (**b**) From these data, what is the best choice for the charge of the electron in warmombs? (**c**) Based on your answer to part (b), how many electrons are there on each of the droplets? (**d**) What is the conversion factor between warmombs and coulombs?

2.99 The natural abundance of ^{3}He is 0.000137%. (**a**) How many protons, neutrons, and electrons are in an atom of ^{3}He? (**b**) Based on the sum of the masses of their subatomic particles, which is expected to be more massive, an atom of ^{3}He or an atom of ^{3}H (which is also called *tritium*)? (**c**) Based on your answer to part (b), what would need to be the precision of a mass spectrometer that is able to differentiate between peaks that are due to $^3He^+$ and $^3H^+$?

2.100 A cube of gold that is 1.00 cm on a side has a mass of 19.3 g. A single gold atom has a mass of 197.0 u. (**a**) How many gold atoms are in the cube? (**b**) From the information given, estimate the diameter in Å of a single gold atom. (**c**) What assumptions did you make in arriving at your answer for part (**b**)?

2.101 The diameter of a rubidium atom is 495 pm We will consider two different ways of placing the atoms on a surface. In arrangement A, all the atoms are lined up with one another to form a square grid. Arrangement B is called a *close-packed* arrangement because the atoms sit in the "depressions" formed by the previous row of atoms:



A B

(**a**) Using arrangement A, how many Rb atoms could be placed on a square surface that is 1.0 cm on a side? (**b**) How many Rb atoms could be placed on a square surface that is 1.0 cm on a side, using arrangement B? (**c**) By what factor has the number of atoms on the surface increased in going to arrangement B from arrangement A? If extended to three dimensions, which arrangement would lead to a greater density for Rb metal?

2.102 (**a**) Assuming the dimensions of the nucleus and atom shown in Figure 2.9, what fraction of the *volume* of the atom is taken up by the nucleus? (**b**) Using the mass of the proton from Table 2.1 and assuming its diameter is 1.0×10^{-15} m, calculate the density of a proton in g/cm^3.

2.103 Identify the element represented by each of the following symbols and give the number of protons and neutrons in each: (**a**) $^{11}_{5}X$ (**b**) $^{75}_{33}X$ (**c**) $^{86}_{36}X$ (**d**) $^{67}_{30}X$.

2.104 The nucleus of ^{6}Li is a powerful absorber of neutrons. It exists in the naturally occurring metal to the extent of 7.5%. In the era of nuclear deterrence, large quantities of lithium were processed to remove ^{6}Li for use in hydrogen bomb production. The lithium metal remaining after removal of ^{6}Li was sold on the market. (**a**) What are the compositions of the nuclei of ^{6}Li and ^{7}Li? (**b**) The atomic masses of ^{6}Li and ^{7}Li are 6.015122 and 7.016004 u, respectively. A sample of lithium depleted in the lighter isotope was found on analysis to contain 1.442% ^{6}Li. What is the average atomic weight of this sample of the metal?

2.105 The element argon has three naturally occurring isotopes, with 18, 20, and 22 neutrons in the nucleus, respectively. (**a**) Write the full chemical symbols for these three isotopes. (**b**) Describe the similarities and differences between the three kinds of atoms of argon.

2.106 The element chromium (Cr) consists of four naturally occurring isotopes with atomic masses 49.9460, 51.9405, 52.9407, and 53.9389 u. The relative abundances of these four isotopes are 4.3, 83.8, 9.5, and 2.4%, respectively. From these data, calculate the atomic weight of chromium.

2.107 Copper (Cu) consists of two naturally occurring isotopes with masses of 62.9296 and 64.9278 u. (**a**) How many protons and neutrons are in the nucleus of each isotope? Write the complete atomic symbol for each, showing the atomic number and mass number. (**b**) The average atomic mass of Cu is 63.55 u. Calculate the abundance of each isotope.

2.108 Using a suitable reference such as the *CRC Handbook of Chemistry and Physics* or http://www.webelements.com, look up the following information for nickel: (**a**) the number of known isotopes, (**b**) the atomic masses (in u), (**c**) the natural abundances of the five most abundant isotopes.

2.109 There are two different isotopes of bromine atoms. Under normal conditions, elemental bromine consists of Br_2 molecules, and the mass of a Br_2 molecule is the sum of the masses of the two atoms in the molecule. The mass spectrum of Br_2 consists of three peaks:

Mass (u)	Relative Size
157.836	0.2569
159.834	0.4999
161.832	0.2431

(**a**) What is the origin of each peak (of what isotopes does each consist)? (**b**) What is the mass of each isotope? (**c**) Determine the average molecular mass of a Br_2 molecule. (**d**) Determine the average atomic mass of a bromine atom. (**e**) Calculate the abundances of the two isotopes.

2.110 It is common in mass spectrometry to assume that the mass of a cation is the same as that of its parent atom. (**a**) Using data in Table 2.1, determine the number of significant figures that must be reported before the difference in masses of ^{1}H and $^1H^+$ is significant. (**b**) What percentage of the mass of an ^{1}H atom does the electron represent?

2.111 From the following list of elements—Mg, Li, Tl, Pb, Se, Cl, Xe, Si, C—pick the one that best fits each description. Use each element only once: (**a**) an alkali metal, (**b**) an alkaline earth metal, (**c**) a noble gas, (**d**) a halogen, (**e**) a metalloidin Group 14, (**f**) a nonmetal listed in Group 14, (**g**) a metal that forms a 3+ ion, (**h**) a nonmetal that forms a 2− ion, (**i**) an element that is used as radiation shielding.

2.112 The first atoms of seaborgium (Sg) were identified in 1974. The longest-lived isotope of Sg has a mass number of 266. (**a**) How many protons, electrons, and neutrons are in an ^{266}Sg atom? (**b**) Atoms of Sg are very unstable, and it is therefore difficult to study this element's properties. Based on the position of Sg in the periodic table, what element should it most closely resemble in its chemical properties?

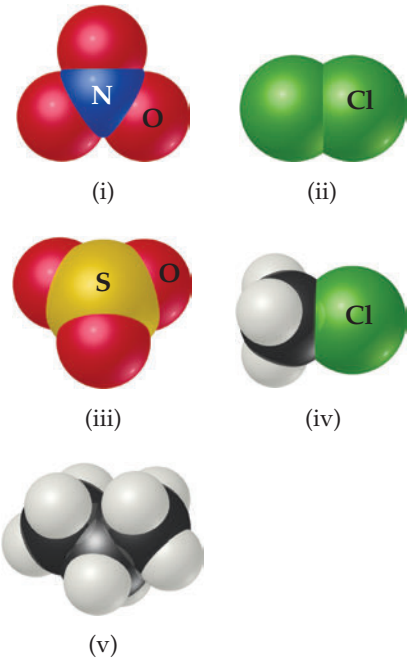
2.113 The explosion of an atomic bomb releases many radioactive isotopes, including strontium-90. Considering the location of strontium in the periodic table, suggest a reason for the fact that this isotope is particularly dangerous for human health.

2.114 A U.S. 1-cent coin (a penny) has a diameter of 19 mm and a thickness of 1.5 mm. Assume the coin is made of pure copper, whose density and approximate market price are 8.9 g/cm^3 and \$2.40 per pound, respectively. Calculate the value of the copper in the coin, assuming its thickness is uniform.

2.115 The U.S. Mint produces a dollar coin called the American Silver Eagle that is made of nearly pure silver. This coin has a diameter of 41 mm and a thickness of 2.5 mm. The density and approximate market price of silver are 10.5 g/cm^3 and

$0.51 per gram, respectively. Calculate the value of the silver in the coin, assuming its thickness is uniform.

2.116 From the molecular structures shown here, identify the one that corresponds to each of the following species: (**a**) chlorine gas; (**b**) propane; (**c**) nitrate ion; (**d**) sulfur trioxide; (**e**) methyl chloride, CH_3Cl.



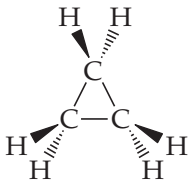
(i) (ii) (iii) (iv) (v)

2.117 Name each of the following chlorides. Assuming that the compounds are ionic, what charge is associated with the metallic element in each case? (**a**) AgCl, (**b**) $TiCl_4$, (**c**) $IrC1_3$, (**d**) LiCl.

2.118 Fill in the blanks in the following table:

Cation	Anion	Formula	Name
			Sodium carbonate
Ni^{2+}	CH_3COO-		
		$Cu(ClO_4)_2$	
Ca^{2+}	F^-		
		$NaMnO_4$	
			Zinc sulfide
		Mg_3N_2	

2.119 Cyclopropane is an interesting hydrocarbon. Instead of having three carbons in a row, the three carbons form a ring, as shown in this perspective drawing (see Figure 2.16 for a prior example of this kind of drawing):



Cyclopropane was at one time used as an anesthetic, but its use was discontinued, in part because it is highly flammable. (**a**) What is the empirical formula of cyclopropane? How does it differ from that of propane? (**b**) The three carbon atoms are necessarily in a plane. What do the different wedges mean? (**c**) What change would you make to the structure shown to illustrate chlorocyclopropane? Are there isomers of chlorocyclopropane?

2.120 Elements in the same group of the periodic table often form oxyanions with the same general formula. The anions are also named in a similar fashion. Based on these observations, suggest a chemical formula or name, as appropriate, for each of the following ions: (**a**) BrO_4^-, (**b**) SeO_3^{2-}, (**c**) arsenate ion, (**d**) hydrogen tellurate ion.

2.121 Carbonic acid occurs in carbonated beverages. When allowed to react with lithium hydroxide, it produces lithium carbonate. Lithium carbonate is used to treat depression and bipolar disorder. Write chemical formulas for carbonic acid, lithium hydroxide, and lithium carbonate.

2.122 Give the chemical names of each of the following familiar compounds: (**a**) NaCl (table salt), (**b**) $NaHCO_3$ (baking soda), (**c**) NaOCl (in many bleaches), (**d**) NaOH (caustic soda), (**e**) $(NH_4)_2CO_3$ (smelling salts), (**f**) $CaSO_4$ (plaster of Paris).

2.123 Many familiar substances have common, unsystematic names. For each of the following, give the correct systematic name: (**a**) saltpeter, KNO_3; (**b**) soda ash, Na_2CO_3; (**c**) lime, CaO; (**d**) muriatic acid, HCl; (**e**) Epsom salts, $MgSO_4$; (**f**) milk of magnesia, $Mg(OH)_2$.

2.124 Because many ions and compounds have very similar names, there is great potential for confusing them. Write the correct chemical formulas to distinguish between (**a**) sodium carbonate and sodium bicarbonate, (**b**) potassium peroxide and potassium oxide, (**c**) calcium sulfide and calcium sulfate, (**d**) manganese (II) oxide and manganese (III) oxide, (**e**) hydride ion and hydroxide ion, (**f**) magnesium nitride and magnesium nitrite, (**g**) silver nitrate and silver nitrite, (**h**) cuprous oxide and cupric oxide.

2.125 In what part of the atom does the strong nuclear force operate?

WHAT'S AHEAD

3.1 ▶ The Conservation of Mass, Chemical Equations, and Stoichiometry

3.2 ▶ Simple Patterns of Chemical Reactivity: Combination, Decomposition, and Combustion

3.3 ▶ Formula Weights and Elemental Compositions of Substances

3.4 ▶ Avogadro's Number and the Mole; Molar Mass

3.5 ▶ Formula Weights and Elemental Compositions of Substances

3.6 ▶ Reaction Stoichiometry

3.7 ▶ Limiting Reactants

3

CHEMICAL REACTIONS AND STOICHIOMETRY

3.1 The Conservation of Mass, Chemical Equations, and Stoichiometry



Much of the energy that we use in our daily lives, including transportation, comes from chemical reactions. In the internal combustion engine, fuel and air react to produce energy, along with gaseous byproducts (mostly carbon dioxide and water) that exit the exhaust pipes of vehicles, an issue that is central to discussions surrounding climate change. Suppose we wanted to know how many molecules of CO_2 are produced by burning a certain amount of fuel. The tools of chemistry we will learn in this section enable us

to accurately determine how many molecules of hydrocarbon and oxygen are consumed and how many molecules of byproducts are generated.

When you finish this section, you should be able to:

- Explain the law of conservation of mass in terms of reactants and products in a chemical equation
- Balance chemical equations by writing out the chemical formulas (and appropriate coefficients) of the reactants and products in chemical reactions

Stoichiometry (pronounced stoy-key-OM-uh-tree, roughly meaning "element measure" in Greek) is the area of study that examines the quantities of substances consumed and produced in chemical reactions. Chemists and chemical engineers use stoichiometry every day in running the reactions of the worldwide chemical industry.

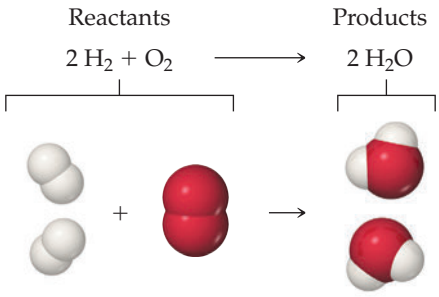
Stoichiometry is built on an understanding of atomic weights (Section 2.4), chemical formulas, and the **law of conservation of mass** (Section 2.1). This important principle tells us that: *Atoms are neither created nor destroyed during a chemical reaction*. The changes that occur during any reaction merely rearrange the atoms. The same collection of atoms is present both before and after the reaction.

We represent chemical reactions by **chemical equations**. When the gas hydrogen (H_2) burns, for example, it reacts with oxygen (O_2) in the air to form water, H_2O. We write the chemical equation for this reaction as

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O \qquad [3.1]$$

We read the + sign as "reacts with" and the arrow as "produces." The chemical formulas on the left side of the arrow represent the starting substances, called **reactants**. The chemical formulas on the right side of the arrow represent substances produced in the reaction, called **products**. The numbers in front of the formulas, called coefficients, indicate the relative numbers of molecules of each kind involved in the reaction. (As in algebraic equations, *the coefficient 1 is usually not written*).

Because atoms are neither created nor destroyed in any chemical reaction, a balanced chemical equation must have an equal number of atoms of each element on each side of the arrow. On the right side of Equation 3.1, for example, there are two molecules of H_2O, each composed of two atoms of hydrogen and one atom of oxygen (**Figure 3.1**). Thus, $2\,H_2O$ (read "two molecules of water") contains $2 \times 2 = 4$ H atoms and $2 \times 1 = 2$ O atoms. Notice *that the number of atoms is obtained by multiplying each subscript in a chemical formula by the coefficient for the formula*. Because there are four H atoms and two O atoms on each side of the equation, the equation is balanced.



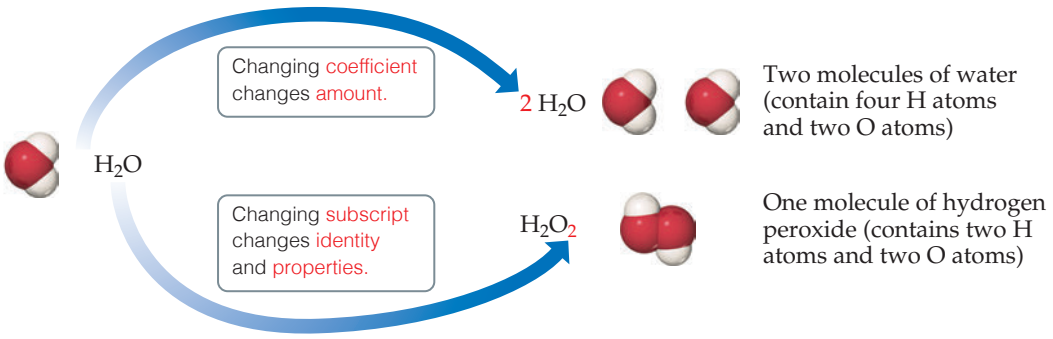
▲ **Figure 3.1** **A balanced chemical equation.**

How to Balance Chemical Equations

Chemists write chemical equations to identify the reactants and products in a reaction. To determine the amount of product that can be made, or the amount of a reactant that is required, the equation needs to be *balanced* using stoichiometry.

To construct a **balanced chemical equation**, we start by writing the formulas for the reactants on the left-hand side of the arrow and the products on the right-hand side. We balance the equation by determining the coefficients that provide equal numbers of each type of atom on both sides of the equation. For most purposes, a balanced equation should contain the smallest possible whole-number coefficients.

In balancing an equation, you need to understand the difference between coefficients and subscripts. As **Figure 3.2** illustrates, changing a subscript in a formula—from H_2O to H_2O_2, for example—changes the identity of the substance. The substance H_2O_2, hydrogen peroxide, is quite different from the substance H_2O, water. *Never change subscripts when balancing an equation*. In contrast, placing a coefficient in front of a formula changes only the amount of the substance and not its identity. Thus, $2\,H_2O$ means two molecules of water, $3\,H_2O$ means three molecules of water, and so forth.



▶ **Figure 3.2** **The difference between changing subscripts and changing coefficients in chemical equations.**

A Step-by-Step Example of Balancing a Chemical Equation

To illustrate the process of balancing an equation, consider the reaction that occurs when methane (CH_4), the principal component of natural gas, burns in air to produce carbon dioxide gas (CO_2) and water vapor (H_2O) (**Figure 3.3**). Both products contain oxygen atoms that come from O_2 in the air. Thus, O_2 is a reactant, and the unbalanced equation is:

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O \quad \text{(unbalanced)} \qquad [3.2]$$

It is usually best to first balance those elements that occur in the fewest chemical formulas in the equation. In our example, C appears in only one reactant, CH_4, and one product, CO_2. The same is true for H (CH_4 and H_2O). Notice, however, that O appears in one reactant (O_2) and two products (CO_2 and H_2O). So, let's begin with C. Because one molecule of CH_4 contains the same number of C atoms as one molecule of CO_2, the coefficients for these substances must be the same in the balanced equation. Therefore, we start by choosing the coefficient 1 (unwritten) for both CH_4 and CO_2.

Next we focus on H. On the left side of the equation we have CH_4, which has four H atoms, whereas on the right side of the equation we have H_2O, containing two H atoms. To balance the H atoms in the equation we place the coefficient 2 in front of H_2O. Now there are four H atoms on each side of the equation:

$$CH_4 + O_2 \longrightarrow CO_2 + 2\,H_2O \quad \text{(unbalanced)} \qquad [3.3]$$

While the equation is now balanced with respect to hydrogen and carbon, it is not yet balanced for oxygen: there are 2 O atoms on the left-hand side, and a total of 4 O atoms on the right-hand side. Adding the coefficient 2 in front of O_2 balances the equation by giving four O atoms on each side:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \quad \text{(balanced)} \qquad [3.4]$$

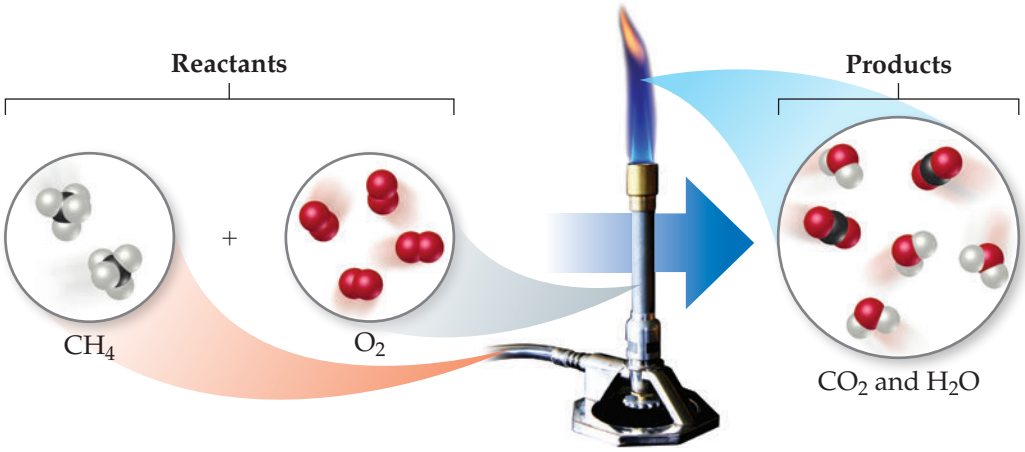
We can provide even more information in a chemical equation: the physical state of the reactants, products, and more details about what conditions are required for the reaction to proceed. We use the symbols (*g*), (*l*), (*s*), and (*aq*) for substances that are gases, liquids, solids, and dissolved in aqueous (water) solution, respectively. Thus, Equation 3.4 is fully written as:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad [3.5]$$

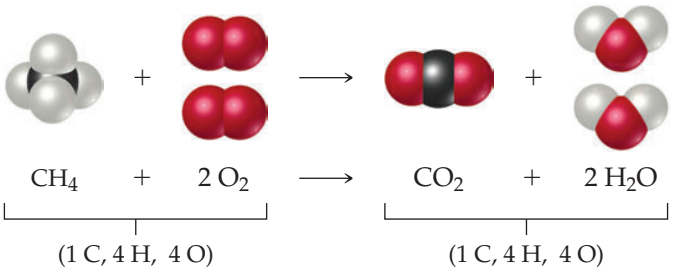
Symbols that represent the conditions under which the reaction proceeds can appear above or below the reaction arrow. One example that we will encounter later in this chapter involves the symbol Δ (Greek uppercase delta); a delta above the reaction arrow indicates the addition of heat.

For Equation 3.5, Figures 3.3 and 3.4 provide molecular views of the reaction as it would happen in a Bunsen burner and the balanced reaction, respectively.

Go Figure In the molecular level views shown in the figure, how many C, H, and O atoms are present as reactants? Are the same number of each type of atom present as products?



▲ **Figure 3.3** Methane reacts with oxygen in a Bunsen burner.

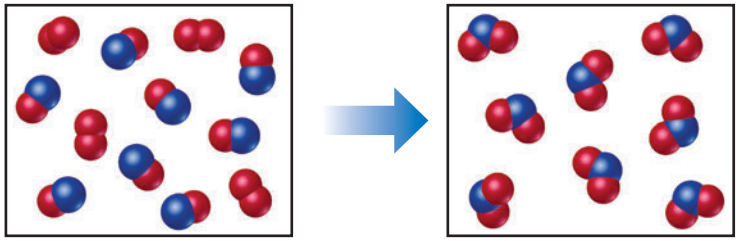


◀ **Figure 3.4** Balanced chemical equation for the combustion of CH_4.

Sample Exercise 3.1

Interpreting and Balancing Chemical Equations

The following diagram represents a chemical reaction in which the red spheres are oxygen atoms and the blue spheres are nitrogen atoms. (**a**) Write the chemical formulas for the reactants and products. (**b**) Write a balanced equation for the reaction. (**c**) Is the diagram consistent with the law of conservation of mass?



SOLUTION

(**a**) The left box, which represents reactants, contains two kinds of molecules, those composed of two oxygen atoms (O_2) and those composed of one nitrogen atom and one oxygen atom (NO). The right box, which represents products, contains only one kind of molecule, which is composed of one nitrogen atom and two oxygen atoms (NO_2).

(**b**) The unbalanced chemical equation is

$$O_2 + NO \longrightarrow NO_2 \quad \text{(unbalanced)}$$

An inventory of atoms on each side of the equation shows that there are one N and three O on the left side of the arrow and one N and two O on the right. To balance O, we must increase the number of O atoms on the right while keeping the coefficients for NO and NO_2 equal. Sometimes a trial-and-error approach is required; we need to go back and forth several times from one side of an equation to the other, changing coefficients first on one side of the equation and then the other until it is balanced. In our present case, let's start by increasing the number of O atoms on the right side of the equation by placing the coefficient 2 in front of NO_2:

$$O_2 + NO \longrightarrow 2\,NO_2 \quad \text{(unbalanced)}$$

Now the equation gives two N atoms and four O atoms on the right, so we go back to the left side. Placing the coefficient 2 in front of NO balances both N and O:

$$O_2 + 2\,NO \longrightarrow 2\,NO_2 \quad \text{(balanced)}$$
$$(2\ N, 4\ O) \qquad (2\ N, 4\ O)$$

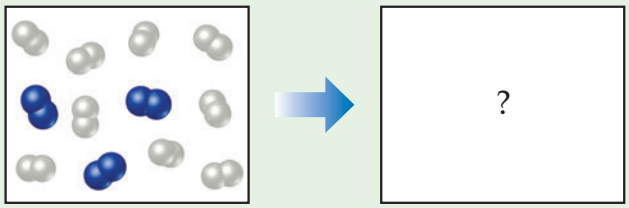
Continued

(**c**) The reactants box contains four O_2 and eight NO. Thus, the molecular ratio is one O_2 for each two NO, as required by the balanced equation. The products box contains eight NO_2, which means the number of NO_2 product molecules equals the number of NO reactant molecules, as the balanced equation requires.

There are eight N atoms in the eight NO molecules in the reactants box. There are also $4 \times 2 = 8$ O atoms in the O_2 molecules and 8 O atoms in the NO molecules, giving a total of 16 O atoms. In the products box, we find eight NO_2 molecules, which contain eight N atoms and $8 \times 2 = 16$ O atoms. Because there are equal numbers of N and O atoms in the two boxes, the drawing is consistent with the law of conservation of mass.

Practice Exercise

In the following diagram, the white spheres represent hydrogen atoms and the blue spheres represent nitrogen atoms.



The two reactants combine to form a single product, ammonia, NH_3, which is not shown. Write a balanced chemical equation for the reaction. Based on the equation and the contents of the left (reactants) box, how many NH_3 molecules should be shown in the right (products) box?
(**a**) 2 (**b**) 3 (**c**) 4 (**d**) 6 (**e**) 9

Sample Exercise 3.2

Balancing Chemical Equations

Balance the equation

$$Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

SOLUTION

Begin by counting each kind of atom on the two sides of the arrow. There are one Na, one O, and two H on the left side, and one Na, one O, and three H on the right. The Na and O atoms are balanced, but the number of H atoms is not. To increase the number of H atoms on the left, let's try placing the coefficient 2 in front of H_2O:

$$Na(s) + 2\,H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Although beginning this way does not balance H, it does increase the number of reactant H atoms, which we need to do. (Also, adding the coefficient 2 on H_2O unbalances O, but we will take care of that after we balance H.) Now that we have 2 H_2O on the left, we balance H by putting the coefficient 2 in front of NaOH:

$$Na(s) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g)$$

Balancing H in this way brings O into balance, but now Na is unbalanced, with one Na on the left and two on the right. To rebalance Na, we put the coefficient 2 in front of the reactant:

$$2\,Na(s) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g)$$

We now have two Na atoms, four H atoms, and two O atoms on each side. The equation is balanced.

Comment Notice that we moved back and forth, placing a coefficient in front of H_2O, then NaOH, and finally Na. In balancing equations, we often find ourselves following this pattern of moving back and forth from one side of the arrow to the other, placing coefficients first in front of a formula on one side and then in front of a formula on the other side until the equation is balanced. You can always tell if you have balanced your equation correctly by checking that the number of atoms of each element is the same on the two sides of the arrow, and that you've chosen the smallest set of coefficients that balances the equation.

Practice Exercise

Balance these equations by providing the missing coefficients:

(**a**) $__\,Fe(s) + __\,O_2(g) \longrightarrow __\,Fe_2O_3(s)$

(**b**) $__\,Al(s) + __\,HCl(aq) \longrightarrow __\,AlCl_3(aq) + __\,H_2(g)$

(**c**) $__\,CaCO_3(s) + __\,HCl(aq) \longrightarrow __\,CaCl_2(aq) + __\,CO_2(g) + __\,H_2O(l)$

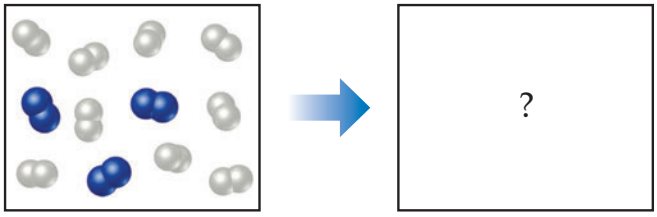
Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.1 How many atoms of oxygen are represented by the notation $3\,Mg(OH)_2$?

(a) 1 **(b)** 2 **(c)** 3 **(d)** 5 **(e)** 6

3.2 In the following diagram, the white spheres represent hydrogen atoms and the blue spheres represent nitrogen atoms.



The two reactants combine to form a single product, ammonia, NH_3, which is not shown. Write a balanced chemical equation for the reaction. Based on the equation and the contents of the left (reactants) box, how many NH_3 molecules should be shown in the right (products) box?

(a) 2 **(b)** 3 **(c)** 4 **(d)** 6 **(e)** 9

3.3 The unbalanced equation for the reaction between methane and bromine is

$$__CH_4(g) + __Br_2(l) \longrightarrow __CBr_4(s) + __HBr(g)$$

Once this equation is balanced with the smallest possible integers, what is the value of the coefficient in front of bromine, Br_2?

(a) 1 **(b)** 2 **(c)** 3 **(d)** 4 **(e)** 6

Exercises

3.4 Write "true" or "false" for each statement. (**a**) We balance chemical equations as we do because energy must be conserved. (**b**) If the reaction $2\ O_3(g) \rightarrow 3\ O_2(g)$ goes to completion and all O_3 is converted to O_2, then the mass of O_3 at the beginning of the reaction must be the same as the mass of O_2 at the end of the reaction. (**c**) You can balance the "water-splitting" reaction $H_2O(l) \rightarrow H_2(g) + O_2(g)$ by writing it this way: $H_2O_2(l) \rightarrow H_2(g) + O_2(g)$.

3.5 Balance the following equations:

(a) $SiCl_4(l) + H_2O(l) \longrightarrow Si(OH)_4(s) + HCl(aq)$

(b) $CO_2(g) + H_2O \longrightarrow C_6H_{12}O_6(s) + O_2(g)$

(c) $Al(OH)_3(s) + H_2SO_4(l) \longrightarrow Al_2(SO_4)_3(s) + H_2O(l)$

(d) $H_3PO_4(aq) \longrightarrow H_4P_2O_7(aq) + H_2O(l)$

3.6 Balance the following equations:

(a) $CaS(s) + H_2O(l) \longrightarrow Ca(HS)_2(aq) + Ca(OH)_2(aq)$

(b) $NH_3(g) + O_2(g) \longrightarrow NO(g) + H_2O(g)$

(c) $FeCl_3(s) + Na_2CO_3(aq) \longrightarrow Fe_2(CO_3)_3(s) + NaCl(aq)$

(d) $FeS_2(s) + O_2(g) \longrightarrow Fe_2O_3(s) + SO_2(g)$

3.7 Write balanced chemical equations corresponding to each of the following descriptions: (**a**) Potassium cyanide reacts with an aqueous solution of sulfuric acid to form hydrogen cyanide gas. (**b**) When an aqueous solution of ammonium nitrite (NH_4NO_2) reacts with an aqueous solution of potassium hydroxide, ammonia gas, water and metal nitrate is formed. (**c**) When hydrogen gas is passed over solid hot iron(III) oxide, the resulting reaction produces iron and gaseous water. (**d**) When liquid ethanoic acid (CH_3COOH) is combusted, carbon dioxide and water are formed.

Answers to Self-Assessment Exercises

3.1 (e) 3.2 (d) 3.3 (d)

3.2 Simple Patterns of Chemical Reactivity: Combination, Decomposition, and Combustion



One of the great triumphs of chemistry over the last hundred years is the development of fertilizers that enable us to feed the world. Ammonia, NH_3, is one of the principle chemicals farmers use to increase crop yield. The industrial process that are used to convert the elements nitrogen and hydrogen into ammonia is one of the most important chemical reactions in the world.

In this section, we will learn about broad classes of chemical reactions. When you finish this section, you should be able to:

- Recognize chemical reactions that are combination, decomposition, or combustion reactions
- Predict the products of these reactions
- Balance chemical equations for these reactions

Combination and Decomposition Reactions

In **combination reactions**, two or more substances react to form one product, according to

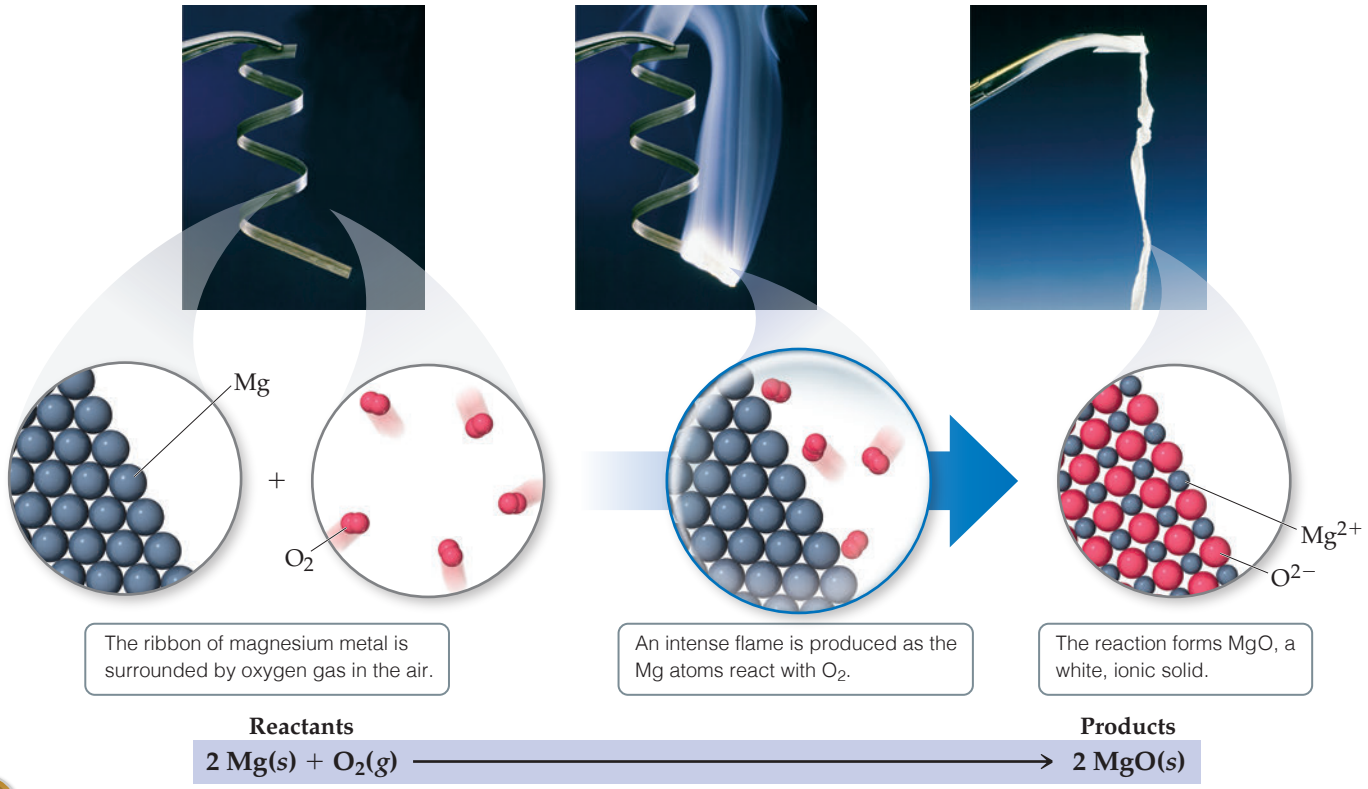
$$A + B \longrightarrow C \qquad [3.6]$$

For example, magnesium metal burns brilliantly in air to produce magnesium oxide. This reaction is used to produce the bright white flame generated by flares and some fireworks (Figure 3.5):

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s) \qquad [3.7]$$

A combination reaction between a metal and a nonmetal, as in Equation 3.7, produces an ionic solid. Recall that the formula of an ionic compound can be determined from the charges of its ions (Section 2.7). When magnesium reacts with oxygen, the magnesium loses electrons and forms the magnesium ion, Mg^{2+}.The oxygen gains electrons and forms the oxide ion, O^{2-}. Thus, the reaction product is MgO.

You should be able to recognize when a reaction is a combination reaction, and to predict the products when the reactants are a metal and a nonmetal.



▲ **Figure 3.5** **Combustion of magnesium metal in air, a combination reaction.**

Other examples of combination reactions include the formation of small gaseous molecules such as CO_2 and NH_3 from their elements; and the reaction of calcium oxide with water to produce calcium hydroxide:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad [3.8]$$

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \quad [3.9]$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) \quad [3.10]$$

In a **decomposition reaction**, a single substance undergoes a reaction to produce two or more products:

$$C \longrightarrow A + B \quad [3.11]$$

An example of a decomposition reaction is when a metal carbonate decomposes to a metal oxide and carbon dioxide upon heating:

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \quad [3.12]$$

Industrially, the decomposition of calcium carbonate at high temperatures is quite important. Limestone and seashells, natural sources of calcium carbonate, are heated to prepare calcium oxide, known as "quicklime" or "lime." Tens of millions of tons of CaO are used each year in making glass, in metallurgy to isolate metals from ores, in cement, and in steel manufacturing to remove impurities.

Another important example of a decomposition reaction is the decomposition of sodium azide, NaN_3, to form sodium metal and nitrogen gas:

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g) \quad [3.13]$$

This reaction is what you find in automobile airbags (Figure 3.6). Approximately 100 g of NaN_3, upon physical impact, will explosively produce about 50 L of nitrogen gas.



▲ **Figure 3.6** **Decomposition of sodium azide, $NaN_3(s)$, produces $N_2(g)$ that inflates air bags in automobiles.**

Combustion Reactions

Combustion reactions are rapid reactions that produce a flame. Most combustion reactions involve O_2 from air as a reactant. The combustion of hydrocarbons (compounds that contain only carbon and hydrogen) in air, illustrated in Equation 3.5, is a major energy-producing process in our world.

Hydrocarbons combusted in air react with O_2 to form CO_2 and H_2O. The number of molecules of O_2 required, as well as the number of product molecules formed, depend on the composition of the hydrocarbon, which acts as the fuel in the reaction. For example, the combustion of propane (C_3H_8, Figure 3.7), a gas used for cooking and home heating, is described by the chemical equation

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g) \quad [3.14]$$

Go Figure

Does this reaction produce or consume thermal energy (heat)?



▲ **Figure 3.7** **Propane burning in air.** Liquid propane in the tank, C_3H_8, vaporizes and mixes with air as it escapes through the nozzle. The combustion reaction of C_3H_8 and O_2 produces a blue flame.

TABLE 3.1 Combination and Decomposition Reactions

Combination Reactions	
$A + B \longrightarrow C$	Two or more reactants combine to form a single product. Many elements react with one another in this fashion to form compounds.
$C(s) + O_2(g) \longrightarrow CO_2(g)$	
$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$	
$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$	
Decomposition Reactions	
$C \longrightarrow A + B$	A single reactant breaks apart to form two or more substances. Many compounds react this way when heated.
$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$	
$PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$	
$Cu(OH)_2(s) \longrightarrow CuO(s) + H_2O(g)$	

The state of the water in this reaction is listed as gas here, since the propane flame burns at a high temperature; but depending on conditions, the water molecules that are produced could be in the gas or liquid phase.

Millions of compounds are made only of carbon, hydrogen, and oxygen. Notable classes of such molecules are sugars and alcohols. Combustion of these oxygen-containing derivatives of hydrocarbons in air also produces CO_2, H_2O and energy. Many of the substances that function as energy sources in metabolism, such as the sugar glucose ($C_6H_{12}O_6$), react with O_2 to ultimately form CO_2 and H_2O. In our bodies, however, the reactions take place in a series of intermediate steps that occur at body temperature. These reactions that involve intermediate steps are called *oxidation reactions* rather than combustion reactions.

Sample Exercise 3.3

Writing Balanced Equations for Combination and Decomposition Reactions

Write a balanced equation for (**a**) the combination reaction between lithium metal and fluorine gas and (**b**) the decomposition reaction that occurs when solid barium carbonate is heated (two products form, a solid and a gas).

SOLUTION

(**a**) With the exception of mercury, all metals are solids at room temperature. Fluorine occurs as a diatomic molecule. Thus, the reactants are Li(s) and $F_2(g)$. The product will be composed of a metal and a nonmetal, so we expect it to be an ionic solid. Lithium ions have a 1+ charge, Li^+, whereas fluoride ions have a 1− charge, F^-. Thus, the chemical formula for the product is LiF. The balanced chemical equation is

$$2\,Li(s) + F_2(g) \longrightarrow 2\,LiF(s)$$

(**b**) The chemical formula for barium carbonate is $BaCO_3$. As mentioned, many metal carbonates decompose to metal oxides and carbon dioxide when heated. In Equation 3.7, for example, $CaCO_3$ decomposes to form CaO and CO_2. Thus, we expect $BaCO_3$ to decompose to BaO and CO_2. Barium and calcium are both in Group 2 in the periodic table, which further suggests they react in the same way:

$$BaCO_3(s) \longrightarrow BaO(s) + CO_2(g)$$

Practice Exercise

Which of the following reactions is the balanced equation that represents the decomposition reaction that occurs when silver(I) oxide is heated?

(**a**) $AgO(s) \longrightarrow Ag(s) + O(g)$ (**b**) $2\,AgO(s) \longrightarrow 2\,Ag(s) + O_2(g)$
(**c**) $Ag_2O(s) \longrightarrow 2\,Ag(s) + O(g)$ (**d**) $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$
(**e**) $Ag_2O(s) \longrightarrow 2\,Ag(s) + O_2(g)$

Sample Exercise 3.4

Writing Balanced Equations for Combustion Reactions

Write the balanced equation for the reaction that occurs when methanol, $CH_3OH(l)$, is burned in air.

SOLUTION

When any compound containing C, H, and O is combusted, it reacts with the $O_2(g)$ in air to produce $CO_2(g)$ and $H_2O(g)$. Thus, the unbalanced equation is

$$CH_3OH(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$

The C atoms are balanced, one on each side of the arrow. Because CH_3OH has four H atoms, we place the coefficient 2 in front of H_2O to balance the H atoms:

$$CH_3OH(l) + O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Adding this coefficient balances H but gives four O atoms in the products. Because there are only three O atoms in the reactants, we are not finished. We can place the coefficient $\frac{3}{2}$ in front of O_2 to give four O atoms in the reactants ($\frac{3}{2} \times 2 = 3$ O atoms in $\frac{3}{2}\,O_2$):

$$CH_3OH(l) + \tfrac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Although this equation is balanced, it is not in its most conventional form because it contains a fractional coefficient. However, multiplying through by 2 removes the fraction and keeps the equation balanced:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$$

Practice Exercise

Write the balanced equation for the reaction that occurs when ethylene glycol, $C_2H_4(OH)_2$, burns in air.

(**a**) $C_2H_4(OH)_2(l) + 5\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$
(**b**) $2\,C_2H_4(OH)_2(l) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(g)$
(**c**) $C_2H_4(OH)_2(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$
(**d**) $C_2H_4(OH)_2(l) + 5\,O(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$
(**e**) $4\,C_2H_4(OH)_2(l) + 10\,O_2(g) \longrightarrow 8\,CO_2(g) + 12\,H_2O(g)$

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.8 When Na and S undergo a combination reaction, what is the chemical formula of the product?

(a) NaS **(c)** NaS_2 **(e)** Na_3S_2

(b) Na_2S **(d)** Na_2S_3

3.9 Which of the following reactions is the balanced equation for the decomposition of silver(I) oxide?

(a) $AgO(s) \longrightarrow Ag(s) + O(g)$

(b) $2\,AgO(s) \longrightarrow 2\,Ag(s) + O_2(g)$

(c) $Ag_2O(s) \longrightarrow 2\,Ag(s) + O(g)$

(d) $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$

(e) $Ag_2O(s) \longrightarrow 2\,Ag(s) + O_2(g)$

3.10 Write the balanced equation for the reaction that occurs when ethylene glycol, $C_2H_4(OH)_2$, burns in air.

(a) $C_2H_4(OH)_2(l) + 5\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$

(b) $2\,C_2H_4(OH)_2(l) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(g)$

(c) $C_2H_4(OH)_2(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$

(d) $C_2H_4(OH)_2(l) + 5\,O(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g)$

(e) $4\,C_2H_4(OH)_2(l) + 10\,O_2(g) \longrightarrow 8\,CO_2(g) + 12\,H_2O(g)$

Exercises

3.11 (**a**) When the metallic element lithium combines with the nonmetallic element chlorine, $Cl_2(g)$, what is the chemical formula of the product? (**b**) Is the product a solid, liquid, or gas at room temperature? (**c**) In the balanced chemical equation for this reaction, what is the coefficient in front of the product if the coefficient in front of $Cl_2(g)$ is 1?

3.12 Write a balanced chemical equation for the reaction that occurs when (**a**) $Mg(s)$ reacts with $Cl_2(g)$; (**b**) barium carbonate decomposes into barium oxide and carbon dioxide gas when heated; (**c**) the hydrocarbon styrene, $C_8H_8(l)$, is combusted in air; (**d**) dimethylether, $CH_3OCH_3(g)$, is combusted in air.

3.13 Balance the following equations and indicate whether they are combination, decomposition, or combustion reactions:

(a) $C_7H_{16}(s) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$

(b) $Li_3N(s) + BN(s) \longrightarrow Li_3BN_2(s)$

(c) $Zn(OH)_2(s) \longrightarrow ZnO(s) + H_2O(l)$

(d) $Ag_2O(s) \longrightarrow Ag(s) + O_2(g)$

Answers to Self-Assessment Exercises

3.8 (b) **3.9** (d) **3.10** (b)

3.3 Formula Weights and Elemental Compositions of Substances



Sulfuric acid, $H_2SO_4(l)$, is a common laboratory chemical that is used by the metric ton in many reactions in the chemical industry. We can see from the molecular model on the left that one molecule of H_2SO_4 contains one sulfur atom (yellow), four oxygen atoms (red), and two hydrogen atoms (white). But in the lab, we dispense milliliters of liquid H_2SO_4, or more commonly, milliliters of its aqueous solution, $H_2SO_4(aq)$. How can we connect the chemical equations that we write, which represent individual molecules, to the reactions we do in the lab, where quantities are measured in grams or milliliters? That is the topic we explore in this section.

When you finish this section, you should be able to:

- Calculate the formula weight of a substance from its empirical formula or it's molecular weight from its molecular formula
- Calculate the elemental composition of a substance from the mass percentages of the elements that make up the substance

Formula and Molecular Weights

The **formula weight** (FW) of a substance is the sum of the atomic weights (AW) of the atoms in the chemical formula of the substance. Using the atomic weights from the periodic table, we find, for example, that the formula weight of sulfuric acid, H_2SO_4, is 98.1 u (atomic mass units):

$$\begin{aligned}\text{FW of } H_2SO_4 &= 2(\text{AW of H}) + (\text{AW of S}) + 4(\text{AW of O}) \\ &= 2(1.0\text{ amu}) + (32.1\text{ amu}) + 4(16.0\text{ amu}) \\ &= 98.1\text{ amu}\end{aligned}$$

For convenience, we have rounded off the atomic weight to one decimal place, a practice we will follow in most calculations in this book.

If the chemical formula is the chemical symbol of an element, such as Na, the formula weight equals the atomic weight of the element (for Na, this would be 23.1 amu). If the chemical formula is that of a molecule, like H_2SO_4, the formula weight can also be called the **molecular weight** (MW).

Not all substances, though, are molecules. For instance, ionic substances such as calcium chloride exist as three-dimensional arrays of ions (see Figure 2.18). In these cases, the empirical formula is used as the formula unit, and the formula weight is the sum of the atomic weights of the atoms in the empirical formula. For example, the formula unit of $CaCl_2$ consists of one Ca^{2+} ion and two Cl^- ions. Thus, the formula weight of $CaCl_2$ is

$$\text{FW of } CaCl_2 = (\text{AW Ca}) + 2\,(\text{AW Cl}) = 40.1\text{ amu} + 2(35.5\text{ amu}) = 111.1\text{ amu}$$

Elemental Compositions of Substances

Let's say you are a forensic chemist, working in a crime lab. Your colleagues find a mysterious white powder at a crime scene. Is it salt, sugar, methamphetamine, cocaine or something else?

One way to determine the identity of a substance is to measure its **elemental composition** and compare it to the calculated elemental compositions of possible candidate substances. We do these calculations based on the masses of each element in the compound:

$$\%\text{ mass composition of element} = \frac{\left(\begin{matrix}\text{number of atoms}\\ \text{of element}\end{matrix}\right)\left(\begin{matrix}\text{AW}\\ \text{of element}\end{matrix}\right)}{\text{FW of substance}} \times 100\% \qquad [3.15]$$

The sum of all the mass percentages of each element in the compound must add up to 100%.

As an example, let's calculate the mass percentage of sulfur in sulfuric acid. Based on atoms we can see that for each H_2SO_4 molecule, one atom out of seven is sulfur. But that does not mean that 1/7 of the mass of the compound is sulfur, since the atoms weigh different amounts:

$$\%\,\text{S in } H_2SO_4 = \frac{(1)(32.1\text{ amu})}{98.1\text{ amu}} \times 100\% = 32.7\%$$

So we find that almost a third of the mass of a given quantity of pure H_2SO_4 is due to sulfur.

Sample Exercise 3.5

Calculating Formula Weights

Calculate the formula weight of (**a**) sucrose, $C_{12}H_{22}O_{11}$ (table sugar); and (**b**) calcium nitrate, $Ca(NO_3)_2$.

SOLUTION

(**a**) By adding the atomic weights of the atoms in sucrose, we find the formula weight to be 342.0 amu:

$$\begin{aligned} 12\text{ C atoms} &= 12(12.0\text{ amu}) = 144.0\text{ amu} \\ 22\text{ H atoms} &= 22(1.0\text{ amu}) = 22.0\text{ amu} \\ 11\text{ O atoms} &= 11(16.0\text{ amu}) = 176.0\text{ amu} \\ &\qquad\qquad\qquad\quad 342.0\text{ amu} \end{aligned}$$

(**b**) If a chemical formula has parentheses, the subscript outside the parentheses is a multiplier for all atoms inside. Thus, for $Ca(NO_3)_2$ we have

$$\begin{aligned} 1\text{ Ca atom} &= 1(40.1\text{ amu}) = 40.1\text{ amu} \\ 2\text{ N atoms} &= 2(14.0\text{ amu}) = 28.0\text{ amu} \\ 6\text{ O atoms} &= 6(16.0\text{ amu}) = 96.0\text{ amu} \\ &\qquad\qquad\quad 164.1\text{ amu} \end{aligned}$$

Practice Exercise

Calculate the formula weight of (**a**) $Al(OH)_3$, (**b**) CH_3OH, and (**c**) TaON.

STRATEGIES FOR SUCCESS Problem Solving

Practice is the key to success in solving problems. As you practice, you can improve your skills by following these steps:

1. **Analyze the problem.** Read the problem carefully. What does it say? Draw a picture or diagram that will help you to visualize the problem. Write down both the data you are given and the quantity you need to obtain (the unknown).
2. **Develop a plan for solving the problem.** Consider a possible path between the given information and the unknown. What principles or equations relate the known data to the unknown? Recognize that some data may not be given explicitly in the problem; you may be expected to know certain quantities or look them up in tables (such as atomic weights). Recognize also that your plan may involve either a single step or a series of steps with intermediate answers.
3. **Solve the problem.** Use the known information and suitable equations or relationships to solve for the unknown. Dimensional analysis (Section 1.7) is a useful tool for solving a great number of problems. Be careful with significant figures, signs, and units.
4. **Check the solution.** Read the problem again to make sure you have found all the solutions asked for in the problem. Does your answer make sense? That is, is the answer outrageously large or small or is it in the ballpark? Finally, are the units and significant figures correct?

Sample Exercise 3.6

Calculating Percentage Composition

Calculate the percentage of carbon, hydrogen, and oxygen (by mass) in $C_{12}H_{22}O_{11}$.

SOLUTION

We'll use the steps outlined in the Strategies For Success: Problem Solving feature to answer the question.

Analyze We are given a chemical formula and asked to calculate the percentage by mass of each element.

Plan We use Equation 3.10, obtaining our atomic weights from a periodic table. We know the denominator in Equation 3.10, the formula weight of $C_{12}H_{22}O_{11}$, from Sample Exercise 3.5. We must use that value in three calculations, one for each element.

Solve

$$\%C = \frac{(12)(12.0\text{ u})}{342.0\text{ u}} \times 100\% = 42.1\%$$

$$\%H = \frac{(22)(1.0\text{ u})}{342.0\text{ u}} \times 100\% = 6.4\%$$

$$\%O = \frac{(11)(16.0\text{ u})}{342.0\text{ u}} \times 100\% = 51.5\%$$

Check Our calculated percentages must add up to 100%, which they do. We could have used more significant figures for our atomic weights, giving more significant figures for our percentage composition, but we have adhered to our suggested guideline of rounding atomic weights to one digit beyond the decimal point.

Practice Exercise

What is the percentage of nitrogen, by mass, in calcium nitrate? (**a**) 8.54% (**b**) 17.1% (**c**) 13.7% (**d**) 24.4% (**e**) 82.9%

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.14 Which of the following is the correct formula weight for calcium phosphate?

(a) 310.2 amu **(b)** 135.1 amu
(c) 182.2 amu **(d)** 278.2 amu
(e) 175.1 amu

3.15 What is the percentage of nitrogen, by mass, in calcium nitrate?

(a) 8.54% **(b)** 17.1%
(c) 13.7% **(d)** 24.4%
(e) 82.9%

3.16 A mysterious white powder found at a crime scene is analyzed and contains 66.8 ± 0.5% carbon by mass. One of the investigators hypothesizes that the substance is cocaine ($C_{17}H_{21}NO_4$). What percent carbon, by mass, is in cocaine?

(a) 39.5% **(b)** 64.3%
(c) 67.3% **(d)** 70.6%
(e) 72.5%

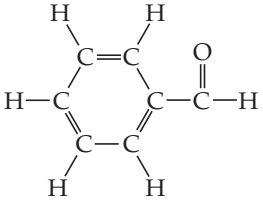
Exercises

3.17 Determine the formula weights of each of the following compounds: (**a**) lead (IV) chloride; (**b**) copper(II) oxide; (**c**) iodic acid, HIO_3; (**d**) sodium perchlorate, $NaClO_4$; (**e**) indium nitride, (**f**) phosphorus pentoxide, P_4O_{10}; (**g**) boron trichloride.

3.18 Calculate the percentage by mass of oxygen in the following compounds: (**a**) vanillin, $C_8H_8O_3$; (**b**) isopropyl alcohol, C_3H_8O; (**c**) acetaminophen, $C_8H_9NO_2$; (**d**) cyclopropanone, C_3H_4O; (**e**) dioxin, $C_{12}H_4Cl_4O_2$; (**f**) penicillin, $C_{16}H_{18}N_2O_4S$.

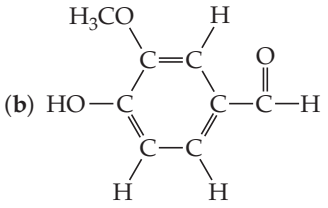
3.19 Based on the following structural formulas, calculate the percentage of carbon by mass present in each compound:

(a)



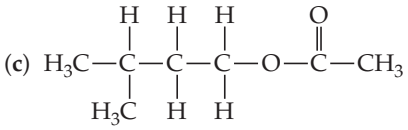
Benzaldehyde
(almond fragrance)

(b)



Vanillin
(vanilla flavor)

(c)



Isopentyl acetate
(banana flavor)

Answers to Self-Assessment Exercises (a) 3.14 (b) 3.15 (c) 3.16

3.4 Avogadro's Number and the Mole; Molar Mass



Even the smallest samples in the laboratory contain enormous numbers of atoms, ions or molecules.For example, a teaspoon (about 5 mL) of water contains 2×10^{23} water molecules, a number so large it defies comprehension. Chemists, therefore, have devised a way to conveniently count such enormous numbers.

When you finish this section, you should be able to:

- Explain the *mole* and the origin of *Avogadro's number*
- Calculate the *molar mass* for a compound and relate this to its formula weight
- Convert between grams, molecules, and moles of a substance

The Mole and Avogadro's Number

In everyday life, we use counting units such as dozen (12 objects), score (20 objects), gross (144 objects) or ream (500 objects).In chemistry, the counting unit for numbers of atoms, ions, or molecules in a laboratory-size sample is the *mole*, abbreviated mol.One **mole** is the amount of matter that contains as many objects as the number of atoms in exactly 12 g of isotopically pure ^{12}C. From experiments, scientists have determined this number to be 6.0221415×10^{23}, which we usually round to 6.02×10^{23}. Scientists call this value **Avogadro's number**, N_A, in honor of the Italian scientist Amedeo Avogadro (1776–1856), and it is often cited with units of reciprocal moles, $\mathbf{6.02 \times 10^{23}\ mol^{-1}}$.* The unit (read as either "inverse mole" or "per mole") reminds us that there are 6.02×10^{23} objects per one mole.A mole of atoms, a mole of molecules, or a mole of anything else all contain Avogadro's number of objects:

$$1\ \text{mol}\ ^{12}\text{C atoms} = 6.02 \times 10^{23}\ ^{12}\text{C atoms}$$
$$1\ \text{mol}\ H_2O\ \text{molecules} = 6.02 \times 10^{23}\ H_2O\ \text{molecules}$$
$$1\ \text{mol}\ NO_3^-\ \text{ions} = 6.02 \times 10^{23}\ NO_3^-\ \text{ions}$$

Avogadro's number is so large that it is difficult to imagine.Spreading 6.02×10^{23} marbles over the Earth's surface would produce a layer about 3 miles thick.Avogadro's number of pennies placed side by side in a straight line would encircle the Earth 300 trillion(3×10^{14}) times.

Molar Mass

A dozen is the same number, 12, whether we have a dozen eggs or a dozen elephants. Clearly, however, a dozen eggs does not have the same mass as a dozen elephants. Similarly, a mole is always the same number (6.02×10^{23}), but 1 mol samples of different substances have *different masses*.

Compare, for example, 1 mol of ^{12}C and 1 mol of ^{24}Mg. A single ^{12}C atom has a mass of 12 amu, whereas a single ^{24}Mg atom is twice as massive, 24 amu (to two significant figures).Because a mole of anything always contains the same number of particles, a mole of ^{24}Mg must be twice as massive as a mole of ^{12}C. Because 1 mol of ^{12}C has a mass of 12 g (by definition), 1 mol of ^{24}Mg must have a mass of 24 g.This example illustrates a general rule relating the mass of an atom the mass of Avogadro's number (1 mol) of these atoms: *The atomic weight of an element in atomic mass units is numerically equal to the mass in grams of 1 mol of that element.*

For example, Cl has an atomic weight of 35.5 amu; therefore, 1 mol of Cl atoms has a mass of 35.5 g.

Au has an atomic weight of 197 amu; therefore, 1 mol of Au atoms has a mass of 197 g.

The same relationship holds for the formula weight or molecular weight of a substance and the mass of 1 mol of that substance:

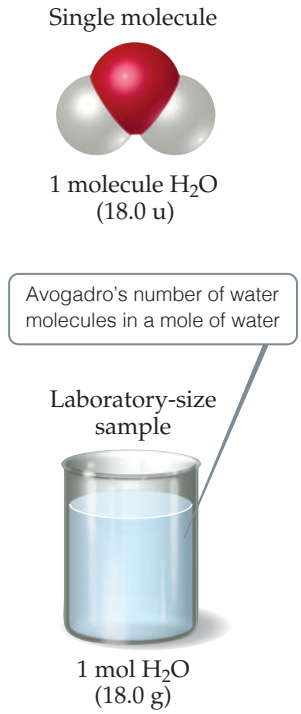
H_2O has a molecular weight of 18.0 amu; therefore, 1 mol of H_2O has a mass of 18.0 g

NaCl has a formula weight of 58.5 amu; therefore 1 mol of NaCl has a mass of 58.5 g.

The mass in grams of one mole of a substance is called the **molar mass** of the substance.The units of molar mass are g/mol, or g mol^{-1}.*The molar mass in grams per mole of any substance is numerically equal to its formula weight in atomic mass units*.For NaCl, for

Go Figure

What number do you get if you divide the mass of 1 mol of water by the mass of 1 molecule of water?

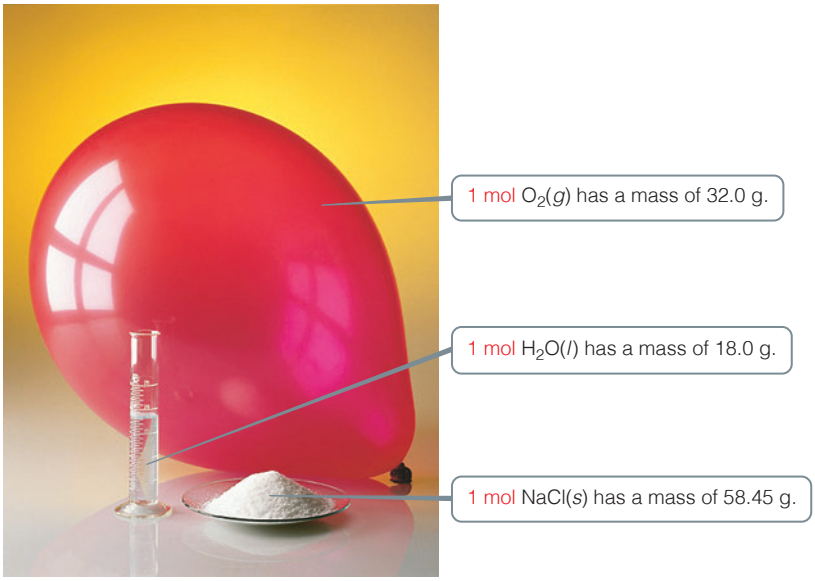


▲ **Figure 3.8 Comparing the mass of 1 molecule and 1 mol of H_2O.** Both masses have the same number but different units (atomic mass units and grams). Expressing both masses in grams indicates their huge difference: 1 molecule of H_2O has a mass of 2.99×10^{-23} g, whereas 1 mol H_2O has a mass of 18.0 g.

TABLE 3.2 Mole Relationships

Name of Substance	Formula	Formula Weight (amu)	Molar Mass (g/mol)	Number and Kind of Particles in One Mole
Atomic nitrogen	N	14.0	14.0	6.02×10^{23} N atoms
Molecular nitrogen or "dinitrogen"	N_2	28.0	28.0	6.02×10^{23} N_2 molecules $2(6.02 \times 10^{23})$ N atoms
Silver	Ag	107.9	107.9	6.02×10^{23} Ag atoms
Silver ions	Ag^+	107.9[a]	107.9	6.02×10^{23} Ag^+ ions
Barium chloride	$BaCl_2$	208.2	208.2	6.02×10^{23} $BaCl_2$ formula units 6.02×10^{23} Ba^{2+} ions $2(6.02 \times 10^{23})$ Cl^- ions

[a]Recall that the mass of an electron is more than 1800 times smaller than the masses of the proton and the neutron; thus, ions and atoms have essentially the same mass.



▲ **Figure 3.9 One mole each of a solid (NaCl), a liquid (H_2O), and a gas (O_2).** In each case, the mass in grams of 1 mol—that is, the molar mass—is numerically equal to the formula weight in atomic mass units. Each of these samples contains 6.02×10^{23} formula units.

instance, the formula weight is 58.5 amu and therefore its molar mass is 58.5 g/mol.Mole relationships for several substances are shown in Table 3.1, and **Figures 3.8** and **3.9** illustrate 1 mol quantities of common substances.

The entries in **Table 3.2** for N and N_2 point out the importance of stating the chemical form of a substance when using the mole concept. For instance, suppose you read that 1 mol of nitrogen is used to make ammonia.You might interpret this statement to mean that 1 mol of nitrogen atoms was used (14.0 g). Unless otherwise stated, however, what is meant is 1 mol of nitrogen molecules, N_2 (28.0 g), was used, because N_2 is the naturally occurring form of the element. To avoid ambiguity, it is important to explicitly state the chemical form being discussed.Using the chemical formula—N or N_2, for instance—avoids any confusion.

Converting Between Masses, Moles, and Atoms/Molecules/Ions

Now we are ready to learn how to relate chemical equations to the amounts of chemicals used and produced in reactions.We will use the mole concept with dimensional analysis (Section 1.7) to help us (**Figure 3.10**).

Go Figure What units would you put under "molar mass" and "Avogadro's number" on this diagram?



▲ **Figure 3.10 Procedure for interconverting mass and number of formula units.** The number of moles of the substance is central to the calculation. Thus, the mole concept can be thought of as the bridge between the mass of a sample in grams and the number of formula units contained in the sample.

For example, let's calculate how many copper atoms are in an old copper penny. Such a penny has a mass of about 3 grams, and let's assume for simplicity that the penny is pure copper:

$$\text{Number of Cu atoms} = (3\text{ g Cu})\left(\frac{1\text{ mol Cu}}{63.5\text{ g Cu}}\right)\left(\frac{6.02 \times 10^{23}\text{ Cu atoms}}{1\text{ mol Cu}}\right)$$
$$= 3 \times 10^{22}\text{ Cu atoms}$$

We have rounded the answer to one significant figure because we only used one significant figure for the mass of the penny. Notice how dimensional analysis provides a straightforward route from grams to number of atoms.The molar mass and Avogadro's number are used as conversion factors to convert grams to moles and then moles to atoms.Also notice that our answer is a very large number: this makes sense, since there are enormous numbers of atoms in a macroscopic sample we can pick up with our hands.Any time that you calculate the number of atoms, ions, or molecules in a laboratory-scale sample, you should expect the number to be very large.However, if you were to calculate number of moles in a laboratory sample, the number may not be that large, and in fact might be less than 1.That is true for the moles of copper in our old penny:

$$\text{Moles of Cu} = (3\text{ g Cu})\left(\frac{1\text{ mol Cu}}{63.5\text{ g Cu}}\right)$$
$$= 5 \times 10^{-2}\text{ mol Cu}$$

CHEMISTRY AND LIFE Glucose Monitoring

Our body converts most of the food we eat into glucose. After digestion, glucose is delivered to cells via the blood. Cells need glucose to live, and the hormone insulin must be present in order for glucose to enter the cells. Normally, the body adjusts the concentration of insulin automatically, in concert with the glucose concentration after eating, so that normal blood glucose levels are 70–120 mg/dL. However, in a diabetic person, either little or no insulin is produced (Type 1 diabetes) or insulin is produced but the cells cannot take it up properly (Type 2 diabetes). In either case the blood glucose levels are higher than they are in a normal person. A person who has not eaten for 8 hours or more is diagnosed as diabetic if his or her glucose level is 126 mg/dL or higher.

Glucose meters work by the introduction of blood from a person, usually by a prick of the finger, onto a small strip of paper that contains chemicals that react with glucose. Insertion of the strip into a small battery-operated reader gives the glucose concentration (**Figure 3.11**). The mechanism of the readout varies from one monitor to another—it may be a measurement of a small electrical current or a measurement of light produced in a chemical reaction. Depending on the reading on any given day, a diabetic person may need to receive an injection of insulin or simply limit his or her intake of sugar-rich foods for a while.



▲ **Figure 3.11 Glucose meter.**

Sample Exercise 3.7

Estimating Numbers of Atoms

Without using a calculator, arrange these samples in order of increasing numbers of carbon atoms: 12 g ^{12}C, 1 mol C_2H_2, 9×10^{23} molecules of CO_2.

SOLUTION

Analyze We are given amounts of three substances expressed in grams, moles, and number of molecules and asked to arrange the samples in order of increasing numbers of C atoms.

Plan To determine the number of C atoms in each sample, we must convert 12 g ^{12}C, 1 mol C_2H_2, and 9×10^{23} molecules CO_2 to numbers of C atoms. To make these conversions, we use the definition of mole and Avogadro's number.

Solve One mole is defined as the amount of matter that contains as many units of the matter as there are C atoms in exactly 12 g of ^{12}C. Thus, 12 g of ^{12}C contains 1 mol of C atoms $= 6.02 \times 10^{23}$ C atoms.

One mol of C_2H_2 contains 6.02×10^{23} C_2H_2 molecules. Because there are two C atoms in each molecule, this sample contains 12.04×10^{23} C atoms.

Because each CO_2 molecule contains one C atom, the CO_2 sample contains 9×10^{23} C atoms.

Hence, the order is 12 g ^{12}C (6×10^{23} C atoms) $<$ 9×10^{23} CO_2 molecules (9×10^{23} C atoms) $<$ 1 mol C_2H_2 (12×10^{23} C atoms).

Check We can check our results by comparing numbers of moles of C atoms in the samples because the number of moles is proportional to the number of atoms. Thus, 12 g of ^{12}C is 1 mol C, 1 mol of C_2H_2 contains 2 mol C, and 9×10^{23} molecules of CO_2 contain 1.5 mol C, giving the same order as stated previously.

Practice Exercise

Which of the following samples contains the fewest sodium atoms?
(**a**) 1 mol sodium oxide (**b**) 45 g sodium fluoride
(**c**) 50 g sodium chloride (**d**) 1 mol sodium nitrate

Sample Exercise 3.8

Converting Grams to Moles

Calculate the number of moles of glucose ($C_6H_{12}O_6$) in a 5.380 g sample.

SOLUTION

Analyze We are given the number of grams of a substance and its chemical formula and asked to calculate the number of moles.

Plan The molar mass of a substance provides the factor for converting grams to moles. The molar mass of $C_6H_{12}O_6$ is 180.0 g/mol (Sample Exercise 3.9).

Solve Using 1 mol $C_6H_{12}O_6$ = 180.0 g $C_6H_{12}O_6$ to write the appropriate conversion factor, we have

$$\text{Moles } C_6H_{12}O_6 = (5.380 \text{ g } \cancel{C_6H_{12}O_6})\left(\frac{1 \text{ mol } C_6H_{12}O_6}{180.0 \text{ g } \cancel{C_6H_{12}O_6}}\right)$$
$$= 0.02989 \text{ mol } C_6H_{12}O_6$$

Check Because 5.380 g is less than the molar mass, an answer less than 1 mol is reasonable. The unit mol is appropriate. The original data had four significant figures, so our answer has four significant figures.

Practice Exercise

How many moles of water are in 1.00 L of water, whose density is 1.00 g/mL?

Sample Exercise 3.9

Converting Moles to Grams

Calculate the mass, in grams, of 0.433 mol of calcium nitrate.

SOLUTION

Analyze We are given the number of moles and the name of a substance and asked to calculate the number of grams in the substance.

Plan To convert moles to grams, we need the molar mass, which we can calculate using the chemical formula and atomic weights.

Solve Because the calcium ion is Ca^{2+} and the nitrate ion is NO_3^-, the chemical formula for calcium nitrate is $Ca(NO_3)_2$. Adding the atomic weights of the elements in the compound gives a formula weight of 164.1 u. Using 1 mol $Ca(NO_3)_2$ = 164.1 g $Ca(NO_3)_2$ to write the appropriate conversion factor, we have

$$\text{Grams } Ca(NO_3)_2 = (0.433 \text{ } \cancel{\text{mol } Ca(NO_3)_2})\left(\frac{164.1 \text{ g } Ca(NO_3)_2}{1 \text{ } \cancel{\text{mol } Ca(NO_3)_2}}\right)$$
$$= 71.1 \text{ g } Ca(NO_3)_2$$

Check The number of moles is less than 1, so the number of grams must be less than the molar mass, 164.1 g. Using rounded numbers to estimate, we have $0.5 \times 150 = 75$ g, which means the magnitude of our answer is reasonable. Both the units (g) and the number of significant figures (3) are correct.

Practice Exercise
What is the mass, in grams, of (**a**) 6.33 mol of $NaHCO_3$ and (**b**) 3.0×10^{-5} mol of sulfuric acid?

Sample Exercise 3.10

Calculating Numbers of Molecules and Atoms from Mass

(**a**) How many glucose molecules are in 5.23 g of $C_6H_{12}O_6$?
(**b**) How many oxygen atoms are in this sample?

SOLUTION

Analyze We are given the number of grams and the chemical formula of a substance and asked to calculate (**a**) the number of molecules and (**b**) the number of O atoms in the substance.

Plan (**a**) The strategy for determining the number of molecules in a given quantity of a substance is summarized in Figure 3.12. We must convert 5.23 g to moles of $C_6H_{12}O_6$ and then convert moles to molecules of $C_6H_{12}O_6$. The first conversion uses the molar mass of $C_6H_{12}O_6$, 180.0 g/mol, and the second conversion uses Avogadro's number.

(**b**) To determine the number of O atoms, we use the fact that there are six O atoms in each $C_6H_{12}O_6$ molecule. Thus, multiplying the number of molecules we calculated in (a) by the factor (6 atoms O/1 molecule $C_6H_{12}O_6$) gives the number of O atoms.

Solve

(**a**) Convert grams $C_6H_{12}O_6$ to molecules $C_6H_{12}O_6$.

$$\text{Molecules } C_6H_{12}O_6 = (5.23 \text{ g } \cancel{C_6H_{12}O_6})\left(\frac{1 \text{ mol } \cancel{C_6H_{12}O_6}}{180.0 \text{ g } \cancel{C_6H_{12}O_6}}\right)\left(\frac{6.02 \times 10^{23} \text{ molecules } C_6H_{12}O_6}{1 \text{ mol } \cancel{C_6H_{12}O_6}}\right)$$

$$= 1.75 \times 10^{22} \text{ molecules } C_6H_{12}O_6$$

(**b**) Convert molecules $C_6H_{12}O_6$ to atoms O.

$$\text{Atoms O} = (1.75 \times 10^{22} \cancel{\text{ molecules } C_6H_{12}O_6})\left(\frac{6 \text{ atoms O}}{\text{molecule } \cancel{C_6H_{12}O_6}}\right)$$

$$= 1.05 \times 10^{23} \text{ atoms O}$$

Check
(**a**) Because the mass we began with is less than a mole, there should be fewer than 6.02×10^{23} molecules in the sample, which means the magnitude of our answer is reasonable. A ballpark estimate of the answer comes reasonably close to the answer we derived in this exercise: $5/200 = 2.5 \times 10^{-2}$ mol; $(2.5 \times 10^{-2})(6 \times 10^{23}) = 15 \times 10^{21} = 1.5 \times 10^{22}$ molecules. The units (molecules) and the number of significant figures (three) are appropriate.

(**b**) The answer is six times as large as the answer to part (a), exactly what it should be. The number of significant figures (three) and the units (atoms O) are correct.

Practice Exercise
How many chlorine atoms are in 12.2 g of CCl_4?
(**a**) 4.77×10^{22}
(**b**) 7.34×10^{24}
(**c**) 1.91×10^{23}
(**d**) 2.07×10^{23}

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.20 Which of the following samples contains the fewest sodium atoms?
(a) 1.0 mol sodium oxide
(b) 45 g sodium fluoride
(c) 50 g sodium chloride
(d) 1.0 mol sodium nitrate

3.21 A sample of an ionic compound containing iron and chlorine is analyzed and found to have a molar mass of 126.8 g/mol. What is the charge of the iron in this compound?
(a) 1+ **(b)** 2+ **(c)** 3+ **(d)** 4+

3.22 How many chlorine atoms are in 12.2 g of CCl_4?
(a) 4.77×10^{22}
(b) 7.34×10^{24}
(c) 1.91×10^{23}
(d) 2.07×10^{23}

Exercises

3.23 (**a**) Write "true" or "false" for each statement. (**a**) A mole of ducks contain a mole of feathers. (**b**) A mole of ammonia gas has a mass of 17.0 g. (**c**) The mass of 1 ammonia molecule is 17.0 g. (**d**) A mole of $MgSO_4(s)$ contains 4 moles of oxygen atoms.

3.24 Without doing any detailed calculations (but using a periodic table to give atomic weights), rank the following samples in order of increasing numbers of atoms: 0.5 mol BCl_3 molecules, 197 g gold, 6.0×10^{23} CCl_4 molecules.

3.25 Calculate the following quantities:

(**a**) mass, in grams, of 0.105 mol sucrose ($C_{12}H_{22}O_{11}$)

(**b**) moles of $Zn(NO_3)_2$ in 143.50 g of this substance

(**c**) number of molecules in 1.0×10^{-6} mol CH_3CH_2OH

(**d**) number of N atoms in 0.410 mol NH_3

3.26 (**a**) What is the mass, in grams, of 2.50×10^{-3} mol of ammonium phosphate?

(**b**) How many moles of chloride ions are in 0.2550 g of aluminum chloride?

(**c**) What is the mass, in grams, of 7.70×10^{20} molecules of caffeine, $C_8H_{10}N_4O_2$?

(**d**) What is the molar mass of cholesterol if 0.00105 mol has a mass of 0.406 g?

3.27 The molecular formula of saccharin, an artificial sweetener, is $C_7H_5NO_3S$. (**a**) What is the molar mass of saccharin? (**b**) How many moles of sachharin are in 2.00 mg of this substance? (**c**) How many molecules are in 2.00 mg of this substance? (**d**) How many C atoms are present in 2.00 mg of saccharin?

3.28 A sample of glucose, $C_6H_{12}O_6$, contains 1.250×10^{21} carbon atoms. (**a**) How many atoms of hydrogen does it contain? (**b**) How many molecules of glucose does it contain? (**c**) How many moles of glucose does it contain? (**d**) What is the mass of this sample in grams?

3.29 The allowable concentration level of vinyl chloride, C_2H_3Cl, in the atmosphere in a chemical plant is 2.0×10^{-6} g/L. How many moles of vinyl chloride in each liter does this represent? How many molecules per liter?

Answers to Self-Assessment Exercises

3.20 (c) 3.21 (b) 3.22 (c)

3.5 Formula Weights and Elemental Compositions of Substances



The empirical formula for a substance tells us the relative number of atoms of each element in the substance. (Section 2.6) The empirical formula H_2O shows that water contains two H atoms for each O atom. This ratio also applies on the molar level: 1 mol of

H_2O contains 2 mol of H atoms and 1 mol of O atoms. Conversely, *the ratio of the numbers of moles of all elements in a compound gives the subscripts in the compound's empirical formula*. Thus, the mole concept provides a way of calculating empirical formulas from experimental data.

When you finish this section, you should be able to:

- Calculate the empirical formula of a compound from the mass percentages of the elements that make up the compound.
- Calculate the molecular formula of a compound from its molar mass and empirical formula.

Mercury and chlorine combine to form a compound that is measured to be 74.0% mercury and 26.0% chlorine by mass. Thus, if we had a 100.0 g sample of the compound, it would contain 74.0 g of mercury and 26.0 g of chlorine. (Samples of any size can be used in problems of this type, but we will generally use 100.0 g to simplify the calculation of mass from percentage.) Using atomic weights to get molar masses, we calculate the number of moles of each element in the sample:

$$(74.0\ \text{g}\ \cancel{\text{Hg}})\left(\frac{1\ \text{mol Hg}}{200.6\ \text{g}\ \cancel{\text{Hg}}}\right) = 0.369\ \text{mol Hg}$$

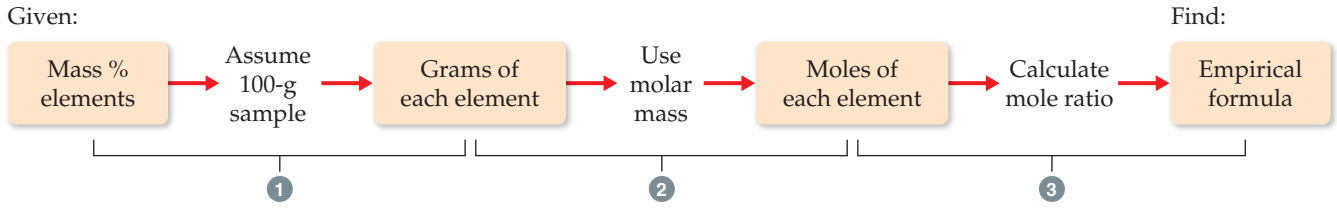
$$(26.0\ \text{g}\ \cancel{\text{Cl}})\left(\frac{1\ \text{mol Cl}}{35.5\ \text{g}\ \cancel{\text{Cl}}}\right) = 0.732\ \text{mol Cl}$$

We then divide the larger number of moles by the smaller number to obtain the Cl:Hg mole ratio:

$$\frac{\text{moles of Cl}}{\text{moles of Hg}} = \frac{0.732\ \text{mol Cl}}{0.369\ \text{mol Hg}} = \frac{1.98\ \text{mol Cl}}{1\ \text{mol Hg}}$$

Because of experimental errors, calculated values for a mole ratio may not be whole numbers, as in the calculation here. The number 1.98 is very close to 2, however, and so we can confidently conclude that the empirical formula for the compound is $HgCl_2$. The empirical formula is correct because its subscripts are the smallest integers that express the *ratio* of atoms present in the compound.

The general procedure for determining empirical formulas is outlined in Figure 3.12



▲ **Figure 3.12** **Procedure for calculating an empirical formula from percentage composition.**

Sample Exercise 3.11

Calculating an Empirical Formula

Ascorbic acid (vitamin C) contains 40.92% C, 4.58% H, and 54.50% O by mass. What is the empirical formula of ascorbic acid?

SOLUTION

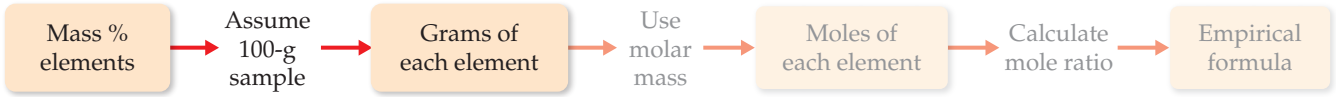
Analyze We are to determine the empirical formula of a compound from the mass percentages of its elements.

Plan The strategy for determining the empirical formula involves the three steps given in Figure 3.13.

Continued

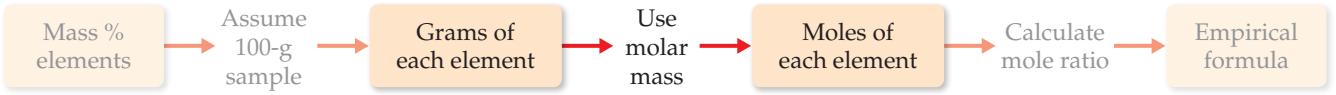
Solve

(**1**) For simplicity we assume we have exactly 100 g of material, although any other mass could also be used.



In 100.00 g of ascorbic acid we have 40.92 g C, 4.58 g H, and 54.50 g O.

(**2**) Next we calculate the number of moles of each element. We use atomic masses with four significant figures to match the precision of our experimental masses.



$$\text{Moles C} = (40.92\ \text{g}\cancel{\text{C}})\left(\frac{1\ \text{mol C}}{12.01\ \text{g}\cancel{\text{C}}}\right) = 3.407\ \text{mol C}$$

$$\text{Moles H} = (4.58\ \text{g}\cancel{\text{H}})\left(\frac{1\ \text{mol C}}{1.008\ \text{g}\cancel{\text{H}}}\right) = 4.54\ \text{mol H}$$

$$\text{Moles O} = (54.50\ \text{g}\cancel{\text{O}})\left(\frac{1\ \text{mol O}}{16.00\ \text{g}\cancel{\text{O}}}\right) = 3.406\ \text{mol O}$$

(**3**) We determine the simplest whole-number ratio of moles by dividing each number of moles by the smallest number of moles.



$$\text{C}: \frac{3.407}{3.406} = 1.000 \quad \text{H}: \frac{4.54}{3.406} = 1.33 \quad \text{O}: \frac{3.406}{3.406} = 1.000$$

The ratio for H is too far from 1 to attribute the difference to experimental error; in fact, it is quite close to $1\frac{1}{3}$. This suggests we should multiply the ratios by 3 to obtain whole numbers:

$$\text{C} : \text{H} : \text{O} = (3 \times 1 : 3 \times 1.33 : 3 \times 1) = (3 : 4 : 3)$$

Thus, the empirical formula is $C_3H_4O_3$.

Check It is reassuring that the subscripts are moderate-size whole numbers. Also, calculating the percentage composition of $C_3H_4O_3$ gives values very close to the original percentages.

Practice Exercise

A 2.144-g sample of phosgene, a compound used as a chemical warfare agent during World War I, contains 0.260 g of carbon, 0.347 g of oxygen, and 1.537 g of chlorine. What is the empirical formula of this substance?
(**a**) CO_2Cl_6 (**b**) $COCl_2$ (**c**) $C_{0.022}O_{0.022}Cl_{0.044}$ (**d**) C_2OCl_2

Molecular Formulas from Empirical Formulas

For molecular substances, the empirical formula and the molecular formula are often different. For example, benzene has a molecular formula of C_6H_6, but it's empirical formula CH is the same as that of the gas acetylene, whose molecular formula is C_2H_2. Knowledge of the empirical formula is not sufficient to differentiate these two very different compounds. Fortunately, we can obtain the molecular formula for any compound from its empirical formula if we know either the molecular weight of the compound, which can be measured by a variety of methods, including mass spectrometry (link to Section 2.4). *The subscripts in the molecular formula of a substance are always whole-number multiples of the subscripts in its empirical formula.* (Section 2.6) This multiple can be found by dividing the molecular weight by the empirical formula weight:

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}}$$

For example, the empirical formula of ascorbic acid (vitamin C) is $C_3H_4O_3$.. This means the empirical formula weight is 3(12.0 amu) + 4(1.0 amu) + 3(16.0 amu) = 88.0 amu. The experimentally determined molecular weight is 176 amu. Thus, we find the whole-number multiple that converts the empirical formula to the molecular formula by dividing

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{176\ \text{amu}}{88.0\ \text{amu}} = 2$$

Consequently, we multiply the subscripts in the empirical formula by this multiple, giving the molecular formula: $C_6H_8O_6$.

Sample Exercise 3.12

Determining a Molecular Formula

Mesitylene, a hydrocarbon found in crude oil, has an empirical formula of C_3H_4 and an experimentally determined molecular weight of 121 amu. What is its molecular formula?

SOLUTION

Analyze We are given an empirical formula and a molecular weight of a compound and asked to determine its molecular formula.

Plan The subscripts in a compound's molecular formula are whole-number multiples of the subscripts in its empirical formula. We find the appropriate multiple by using Equation 3.11.

Solve The formula weight of the empirical formula C_3H_4 is

$$3(12.0\ \text{amu}) + 4(1.0\ \text{amu}) = 40.0\ \text{amu}$$

Next, we use this value in Equation 3.11:

$$\text{Whole-number multiple} = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{121}{40.0} = 3.03$$

Only whole-number ratios make physical sense because molecules contain whole atoms. The 3.03 in this case could result from a small experimental error in the molecular weight. We therefore multiply each subscript in the empirical formula by 3 to give the molecular formula: C_9H_{12}.

Check We can have confidence in the result because dividing molecular weight by empirical formula weight yields nearly a whole number.

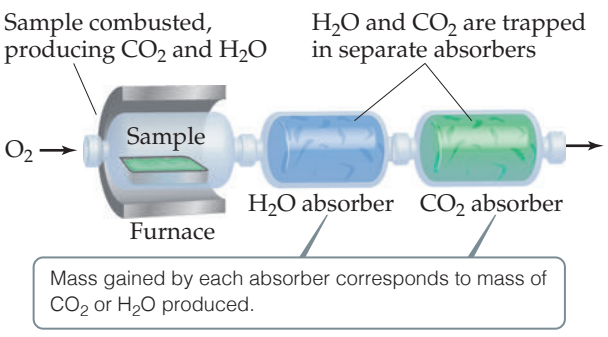
Practice Exercise

Cyclohexane, a commonly used organic solvent, is 85.6% C and 14.4% H by mass with a molar mass of 84.2 g/mol. What is its molecular formula?
(**a**) C_6H (**b**) CH_2 (**c**) C_5H_{24} (**d**) C_6H_{12} (**e**) C_4H_8

Combustion Analysis

One technique for determining empirical formulas in the laboratory is *combustion analysis*, commonly used for compounds containing principally carbon and hydrogen.

When a compound containing carbon and hydrogen is completely combusted in an apparatus such as that shown in Figure 3.13, the carbon is converted to CO_2 and the hydrogen is converted to H_2O. (Section 3.2). From the masses of CO_2 and H_2O we can calculate the number of moles of C and H in the original sample and thereby the empirical formula. If a third element is present in the compound, its mass can be determined by subtracting the measured masses of C and H from the original sample mass.



◀ **Figure 3.13** Apparatus for combustion analysis.

Sample Exercise 3.13

Determining an Empirical Formula by Combustion Analysis

2-propanol, sold as rubbing alcohol, is composed of C, H, and O. Combustion of 0.255 g of 2-propanol produces 0.561 g of CO_2 and 0.306 g of H_2O. Determine the empirical formula of 2-propanol.

SOLUTION

Analyze We are told that 2-propanol contains C, H, and O atoms and are given the quantities of CO_2 and H_2O produced when a given quantity of the alcohol is combusted. We must determine the empirical formula for 2-propanol, a task that requires us to calculate the number of moles of C, H, and O in the sample.

Plan We can use the mole concept to calculate grams of C in the CO_2 and grams of H in the H_2O—the masses of C and H in the alcohol before combustion. The mass of O in the compound equals the mass of the original sample minus the sum of the C and H masses. Once we have the C, H, and O masses, we can proceed as in Sample Exercise 3.13.

Solve Because all of the carbon in the sample is converted to CO_2, we can use dimensional analysis and the following steps to calculate the mass C in the sample.

Mass CO_2 produced → Molar mass CO_2 44.0 g/mol → Moles CO_2 produced → 1 C atom per CO_2 molecule → Moles of C original sample → Molar mass C 12.0 g/mol → Mass C in original sample

Using the values given in this example, the mass of C is

$$\text{Grams C} = (0.561\ \text{g}\cancel{\text{CO}_2})\left(\frac{1\ \text{mol}\cancel{\text{CO}_2}}{44.0\ \text{g}\cancel{\text{CO}_2}}\right)\left(\frac{1\ \text{mol C}}{1\ \text{mol}\cancel{\text{CO}_2}}\right)\left(\frac{12.0\ \text{g C}}{1\ \text{mol C}}\right)$$

$$= 0.153\ \text{g C}$$

Because all of the hydrogen in the sample is converted to H_2O, we can use dimensional analysis and the following steps to calculate the mass H in the sample. We use three significant figures for the atomic mass of H to match the significant figures in the mass of H_2O produced.

Mass H_2O produced → Molar mass H_2O 18.0 g/mol → Moles H_2O produced → 2 H atoms per H_2O molecule → Moles H in original sample → Molar mass H 1.01 g/mol → Mass H in original sample

Using the values given in this example, we find that the mass of H is

$$\text{Grams H} = (0.306\ \text{g}\cancel{\text{H}_2\text{O}})\left(\frac{1\ \text{mol}\cancel{\text{H}_2\text{O}}}{18.0\ \text{g}\cancel{\text{H}_2\text{O}}}\right)\left(\frac{2\ \text{mol H}}{1\ \text{mol}\cancel{\text{H}_2\text{O}}}\right)\left(\frac{1.01\ \text{g H}}{1\ \text{mol H}}\right) = 0.0343\ \text{g H}$$

The mass of the sample, 0.255 g, is the sum of the masses of C, H, and O. Thus, the O mass is

$$\text{Mass of O} = \text{mass of sample} - (\text{mass of C} + \text{mass of H}) = 0.255\ \text{g} - (0.153\ \text{g} + 0.0343\ \text{g}) = 0.068\ \text{g O}$$

The number of moles of C, H, and O in the sample is therefore

$$\text{Moles C} = (0.153\ \text{g}\cancel{\text{C}})\left(\frac{1\ \text{mol C}}{12.0\ \text{g}\cancel{\text{C}}}\right) = 0.0128\ \text{mol C}$$

$$\text{Moles H} = (0.0343\ \text{g}\cancel{\text{H}})\left(\frac{1\ \text{mol H}}{1.01\ \text{g}\cancel{\text{H}}}\right) = 0.0340\ \text{mol H}$$

$$\text{Moles O} = (0.068\ \text{g}\cancel{\text{O}})\left(\frac{1\ \text{mol O}}{16.0\ \text{g}\cancel{\text{O}}}\right) = 0.0043\ \text{mol O}$$

To find the empirical formula, we must compare the relative number of moles of each element in the sample, as illustrated in Sample Exercise 3.13.

$$\text{C}:\frac{0.0128}{0.0043} = 3.0 \quad \text{H}:\frac{0.0340}{0.0043} = 7.9 \quad \text{O}:\frac{0.0043}{0.0043} = 1.0$$

The first two numbers are very close to the whole numbers 3 and 8, giving the empirical formula C_3H_8O.

▶ Practice Exercise

The compound dioxane, which is used as a solvent in various industrial processes, is composed of C, H, and O atoms. Combustion of a 2.203-g sample of this compound produces 4.401 g CO_2 and 1.802 g H_2O. A separate experiment shows that it has a molar mass of 88.1 g/mol. Which of the following is the correct molecular formula for dioxane?
(**a**) C_2H_4O (**b**) $C_4H_4O_2$ (**c**) CH_2 (**d**) $C_4H_8O_2$

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.30 A 2.144-g sample of phosgene, a compound used as a chemical warfare agent during World War I, contains 0.260 g of carbon, 0.347 g of oxygen, and 1.537 g of chlorine. What is the empirical formula of this substance?

(a) CO_2

(b) $COCl_2$

(c) $C_{0.022}O_{0.022}Cl_{0.044}$

(d) C_2OCl_2

3.31 Cyclohexane, a commonly used organic solvent, is 85.6% carbon and 14.4% hydrogen by mass, with a molar mass of 84.2 g/mol. What is its molecular formula?

(**a**) C_6H

(b) CH_2

(c) C_5H_{24}

(d) C_6H_{12}

(e) C_4H_8

3.32 The compound dioxane, which is used as a solvent in various industrial processes, is composed of C, H, and O atoms. Combustion of a 2.203-g sample of this compound produces 4.401 g CO_2 and 1.802 g H_2O. A separate experiment shows that it has a molar mass of 88.1 g/mol. Which of the following is the correct molecular formula for dioxane?

(a) C_2H_4O

(b) $C_4H_4O_2$

(c) CH_2

(d) $C_4H_8O_2$

Exercises

3.33 Give the empirical formula of each of the following compounds if a sample contains (**a**) 0.052 mol C, 0.103 mol H, and 0.017 mol O; (**b**) 2.10 g nickel and 0.58 g oxygen; (**c**) 26.56% K, 35.41% Cr, and 38.03% O by mass.

3.34 Determine the empirical formulas of the compounds with the following compositions by mass:

(**a**) 74.0% C, 8.7% H, and 17.3% N

(**b**) 57.5% Na, 40.0% O, and 2.5% H

(**c**) 41.1% N, 11.8% H, and the remainder S

3.35 A compound whose empirical formula is XF_3 consists of 65% F by mass. What is the atomic mass of X?

3.36 What is the molecular formula of each of the following compounds?

(**a**) empirical formula CH, molar mass = 78.0 g/mol

(**b**) empirical formula OH, molar mass = 34.0 g/mol

3.37 Determine the empirical and molecular formulas of each of the following substances:

(**a**) Styrene, a compound used to make Styrofoam® cups and insulation, contains 92.3% C and 7.7% H by mass and has a molar mass of 104 g/mol.

(**b**) Caffeine, a stimulant found in coffee, contains 49.5% C, 5.15% H, 28.9% N, and 16.5% O by mass and has a molar mass of 195 g/mol.

(**c**) Monosodium glutamate (MSG), a flavor enhancer in certain foods, contains 35.51% C, 4.77% H, 37.85% O, 8.29% N, and 13.60% Na, and has a molar mass of 169 g/mol.

3.38 (**a**) Combustion analysis of toluene, a common organic solvent, gives 5.86 mg of CO_2 and 1.37 mg of H_2O. If the compound contains only carbon and hydrogen, what is its empirical formula? (**b**) Menthol, the substance we can smell in mentholated cough drops, is composed of C, H, and O. A 0.1005-g sample of menthol is combusted, producing 0.2829 g of CO_2 and 0.1159 g of H_2O. What is the empirical formula for menthol? If menthol has a molar mass of 156 g/mol, what is its molecular formula?

3.39 Valproic acid, used to treat seizures and bipolar disorder, is composed of C, H, and O. A 0.165-g sample is combusted to produce 0.166 g of water and 0.403 g of carbon dioxide. What is the empirical formula for valproic acid? If the molar mass is 144 g/mol, what is the molecular formula?

3.40 Washing soda, a compound used to prepare hard water for washing laundry, is a hydrate, which means that a certain number of water molecules are included in the solid structure. Its formula can be written as $Na_2CO_3 \cdot xH_2O$, where x is the number of moles of H_2O per mole of Na_2CO_3. When a 2.558-g sample of washing soda is heated at 125 °C, all the water of hydration is lost, leaving 0.948 g of Na_2CO_3. What is the value of x?

Answers to Self-Assessment Exercises

3.30 (b) 3.31 (d) 3.32 (d)

3.6 Reaction Stoichiometry



When a chemical reaction is carried out, it's vital to understand how much of each product will be produced and how much of each reactant will be consumed. To carry out chemical reactions without this knowledge can lead to unintended consequences. Maybe an expensive reactant will be wasted because much more of it was added than was needed. A reaction might generate more gas than the reaction container can hold, leading to an explosion. In some reactions, particularly those involving solids, it can be difficult to separate the desired product from excess reactants. In this section, you will learn how to calculate the quantities of reactants consumed and products produced, given a balanced chemical equation representing the reaction.

When you finish this section, you should be able to:

- Determine the number of grams (or moles) of a product formed in a chemical reaction given the number of grams (or moles) of the reactants, and vice versa

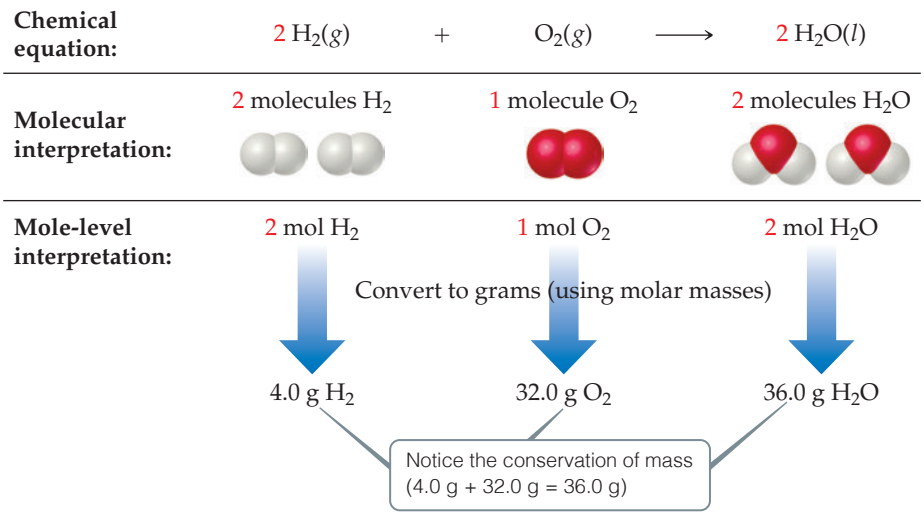
The coefficients in a chemical equation represent the relative numbers of molecules in a reaction. The mole concept allows us to convert this information to the masses of the substances in the reaction. For instance, the coefficients in the balanced equation:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \qquad [3.16]$$

indicate that two molecules of H_2 react with one molecule of O_2 to form two molecules of H_2O. It follows that the relative numbers of moles are identical to the relative numbers of molecules:

$2\,H_2(g)$	+	$O_2(g)$	$\longrightarrow$	$2\,H_2O(l)$
2 molecules		1 molecule		2 molecules
$2(6.02 \times 10^{23}$ molecules)		$1(6.02 \times 10^{23}$ molecules)		$2(6.02 \times 10^{23}$ molecules)
2 mol		1 mol		2 mol

We can generalize this observation to all balanced chemical equations: *The coefficients in a balanced chemical equation indicate both the relative numbers of molecules (or formula units) in the reaction and the relative numbers of moles*. **Figure 3.14** shows how this result corresponds to the law of conservation of mass.



◀ **Figure 3.14** **Interpreting a balanced chemical equation quantitatively.**

The quantities 2 mol H_2, 1 mol O_2, and 2 mol H_2O given by the coefficients in Equation 3.16 are called stoichiometrically equivalent quantities. The relationship between these quantities can be represented as

$$2\ \text{mol}\ H_2 \simeq 1\ \text{mol}\ O_2 \simeq 2\ \text{mol}\ H_2O$$

where the $\simeq$ symbol means "is stoichiometrically equivalent to." Stoichiometric relations such as these can be used to convert between quantities of reactants and products in a chemical reaction. For example, the number of moles of H_2O produced from 1.57 mol of O_2 is

$$\text{Moles}\ H_2O = (1.57\ \cancel{\text{mol}\ O_2})\left(\frac{2\ \text{mol}\ H_2O}{1\ \cancel{\text{mol}\ O_2}}\right) = 3.14\ \text{mol}\ H_2O$$

As an additional example, consider the combustion of butane (C_4H_{10}), the fuel in disposable lighters:

$$2\,C_4H_{10}(l) + 13\,O_2(g) \longrightarrow 8\,CO_2(g) + 10\,H_2O(g) \qquad [3.17]$$

Let's calculate the mass of CO_2 produced when 1.00 g of C_4H_{10} is burned. The coefficients in Equation 3.17 tell us how the amount of C_4H_{10} consumed is related to the amount of CO_2 produced: 2 mol $C_4H_{10} \simeq 8$ mol CO_2. To use this stoichiometric relationship, we must convert grams of C_4H_{10} to moles using the molar mass of C_4H_{10}, 58.0 g/mol:

$$\text{Moles}\ C_4H_{10} = (1.00\ \cancel{\text{g}\ C_4H_{10}})\left(\frac{1\ \text{mol}\ C_4H_{10}}{58.0\ \cancel{\text{g}\ C_4H_{10}}}\right)$$
$$= 1.72 \times 10^{-2}\ \text{mol}\ C_4H_{10}$$

We then use the stoichiometric factor from the balanced equation to calculate moles of CO_2:

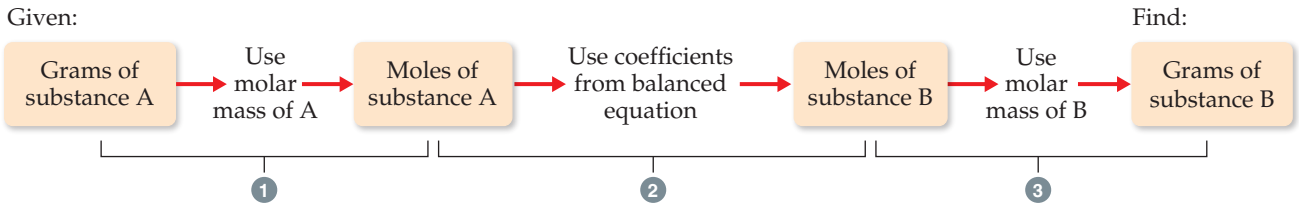
$$\text{Moles}\ CO_2 = (1.72 \times 10^{-2}\ \cancel{\text{mol}\ C_4H_{10}})\left(\frac{8\ \text{mol}\ CO_2}{2\ \cancel{\text{mol}\ C_4H_{10}}}\right)$$
$$= 6.88 \times 10^{-2}\ \text{mol}\ CO_2$$

Finally, we use the molar mass of CO_2, 44.0 g/mol, to calculate the CO_2 mass in grams:

$$\text{Grams}\ CO_2 = (6.88 \times 10^{-2}\ \cancel{\text{mol}\ CO_2})\left(\frac{44.0\ \text{g}\ CO_2}{1\ \cancel{\text{mol}\ CO_2}}\right)$$
$$= 3.03\ \text{g}\ CO_2$$

This conversion sequence involves three steps, as illustrated in **Figure 3.15**. These three conversions can be combined in a single equation:

$$\text{Grams}\ CO_2 = (1.00\ \cancel{\text{g}\ C_4H_{10}})\left(\frac{1\ \cancel{\text{mol}\ C_4H_{10}}}{58.0\ \cancel{\text{g}\ C_4H_{10}}}\right)\left(\frac{8\ \cancel{\text{mol}\ CO_2}}{2\ \cancel{\text{mol}\ C_4H_{10}}}\right)\left(\frac{44.0\ \text{g}\ CO_2}{1\ \cancel{\text{mol}\ CO_2}}\right)$$
$$= 3.03\ \text{g}\ CO_2$$



▲ **Figure 3.15 Procedure for calculating amounts of reactants consumed or products formed in a reaction.** The number of grams of a reactant consumed or product formed can be calculated in three steps, starting with the number of grams of any reactant or product.

To calculate the amount of O_2 consumed in the reaction of Equation 3.17, we again rely on the coefficients in the balanced equation for our stoichiometric factor, $2\ mol\ C_4H_{10} \simeq 13\ mol\ O_2$:

$$\text{Grams } O_2 = (1.00\ g\ C_4H_{10})\left(\frac{1\ mol\ C_4H_{10}}{58.0\ g\ C_4H_{10}}\right)\left(\frac{13\ mol\ O_2}{2\ mol\ C_4H_{10}}\right)\left(\frac{32.0\ g\ O_2}{1\ mol\ O_2}\right)$$
$$= 3.59\ g\ O_2$$

Many chemical reactions either consume or produce heat (Figure 3.7). This heat is also a stoichiometric quantity. For instance, if a reaction of a given number of reactant moles produces 100 J of energy in the form of heat, performing the reaction with twice the number of reactant moles will produce 200 J of heat. We will explore these ideas further in Chapter 5.

Sample Exercise 3.14

Calculating Amounts of Reactants and Products

Determine how many grams of water are produced in the oxidation of 1.00 g of glucose, $C_6H_{12}O_6$:

$$C_6H_{12}O_6(s) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

SOLUTION

Analyze We are given the mass of a reactant and must determine the mass of a product in the given reaction.

Plan We follow the general strategy outlined in Figure 3.16:

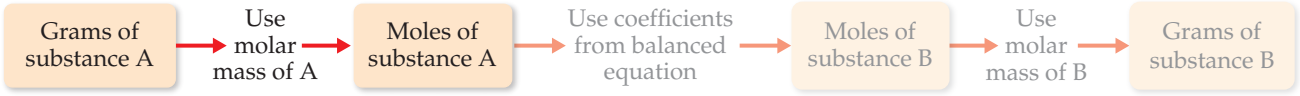
(**1**) Convert grams of $C_6H_{12}O_6$ to moles using the molar mass of $C_6H_{12}O_6$.

(**2**) Convert moles of $C_6H_{12}O_6$ to moles of H_2O using the stoichiometric relationship $1\ mol\ C_6H_{12}O_6 \simeq 6\ mol\ H_2O$.

(**3**) Convert moles of H_2O to grams using the molar mass of H_2O.

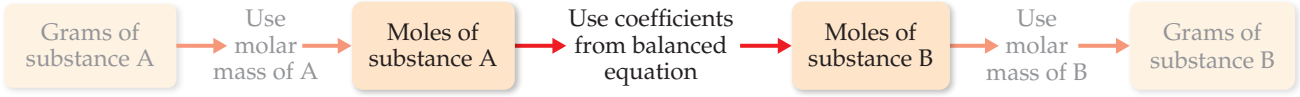
Solve

(**1**) First we convert grams of $C_6H_{12}O_6$ to moles using the molar mass of $C_6H_{12}O_6$.



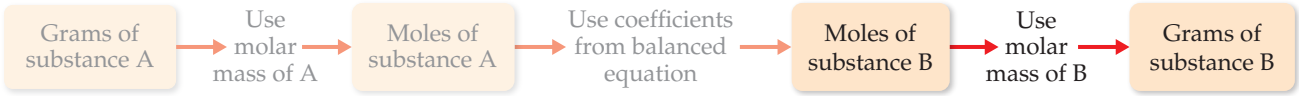
$$\text{Moles } C_6H_{12}O_6 = (1.00\ g\ C_6H_{12}O_6)\left(\frac{1\ mol\ C_6H_{12}O_6}{180.0\ g\ C_6H_{12}O_6}\right)$$

(**2**) Next we convert moles of $C_6H_{12}O_6$ to moles of H_2O using the stoichiometric relationship $1\ mol\ C_6H_{12}O_6 \simeq 6\ mol\ H_2O$.



$$\text{Moles } H_2O = (1.00\ g\ C_6H_{12}O_6)\left(\frac{1\ mol\ C_6H_{12}O_6}{180.0\ g\ C_6H_{12}O_6}\right)\left(\frac{6\ mol\ H_2O}{1\ mol\ C_6H_{12}O_6}\right)$$

(**3**) Finally, we convert moles of H_2O to grams using the molar mass of H_2O.



$$\text{Grams } H_2O = (1.00\text{ g } \cancel{C_6H_{12}O_6})\left(\frac{1\text{ mol } \cancel{C_6H_{12}O_6}}{180.0\text{ g } \cancel{C_6H_{12}O_6}}\right)\left(\frac{6\text{ mol } \cancel{H_2O}}{1\text{ mol } \cancel{C_6H_{12}O_6}}\right)\left(\frac{18.0\text{ g } H_2O}{1\text{ mol } \cancel{H_2O}}\right)$$
$$= 0.600\text{ g } H_2O$$

Check We can check how reasonable our result is by doing a ballpark estimate of the mass of H_2O. Because the molar mass of glucose is 180 g/mol, 1 g of glucose equals 1/180 mol. Because 1 mol of glucose yields 6 mol H_2O, we would have $6/180 = 1/30$ mol H_2O. The molar mass of water is 18 g/mol, so we have $1/30 \times 18 = 6/10 = 0.6$ g of H_2O, which agrees with the full calculation. The units, grams H_2O, are correct. The initial data had three significant figures, so three significant figures for the answer is correct.

Practice Exercise

Sodium hydroxide reacts with carbon dioxide to form sodium carbonate and water:

$$2\,NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

How many grams of Na_2CO_3 can be prepared from 2.40 g of NaOH? (**a**) 3.18 g (**b**) 6.36 g (**c**) 1.20 g (**d**) 0.0300 g

Sample Exercise 3.15

Calculating Amounts of Reactants and Products

Solid lithium hydroxide is used in space vehicles to remove the carbon dioxide gas exhaled by astronauts. The hydroxide reacts with the carbon dioxide to form solid lithium carbonate and liquid water. How many grams of carbon dioxide can be absorbed by 1.00 g of lithium hydroxide?

SOLUTION

Analyze We are given a verbal description of a reaction and asked to calculate the number of grams of one reactant that reacts with 1.00 g of another.

Plan The verbal description of the reaction can be used to write a balanced equation:

$$2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(l)$$

We are given the mass in grams of LiOH and asked to calculate the mass in grams of CO_2. We can accomplish this with the three conversion steps in Figure 3.15. The conversion of Step 1 requires the molar mass of LiOH (6.94 + 16.00 + 1.01 = 23.95 g/mol). The conversion of Step 2 is based on a stoichiometric relationship from the balanced chemical equation: 2 mol LiOH $\simeq$ 1 mol CO_2. For the Step 3 conversion, we use the molar mass of CO_2: 12.01 + 2(16.00) = 44.01 g/mol.

Solve

$$(1.00\text{ g } \cancel{LiOH})\left(\frac{1\text{ mol } \cancel{LiOH}}{23.95\text{ g } \cancel{LiOH}}\right)\left(\frac{1\text{ mol } \cancel{CO_2}}{2\text{ mol } \cancel{LiOH}}\right)\left(\frac{44.01\text{ g } CO_2}{1\text{ mol } \cancel{CO_2}}\right)$$
$$= 0.919\text{ g } CO_2$$

Check Notice that 23.95 g LiOH/mol $\approx$ 24 g LiOH/mol, 24 g LiOH/mol $\times$ 2 mol LiOH = 48 g LiOH, and (44 g CO_2/mol)/(48 g LiOH) is slightly less than 1. Thus, the magnitude of our answer, 0.919 g CO_2, is reasonable based on the amount of starting LiOH. The number of significant figures and units are also appropriate.

Practice Exercise

Propane, C_3H_8 (Figure 3.7), is a common fuel used for cooking and home heating. What mass of O_2 is consumed in the combustion of 1.00 g of propane?
(**a**) 5.00 g (**b**) 0.726 g (**c**) 2.18 g (**d**) 3.63 g

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.41 In this section, we learned that when 1.00 g of butane (C_4H_{10}) reacts with 3.59 g of oxygen (O_2) it produces 3.03 g of carbon dioxide (CO_2). True or False: Is it possible using only addition and/or subtraction, to calculate the number of grams H_2O produced.

3.42 Sodium hydroxide reacts with carbon dioxide to form sodium carbonate and water:

$$2\,NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

How many grams of Na_2CO_3 can be prepared from 2.40 g of NaOH?
(a) 3.18 g
(b) 6.36 g
(c) 1.20 g
(d) 0.0300 g

3.43 Propane, C_3H_8, is a common fuel used for cooking and home heating. What mass of O_2 is consumed in the combustion of 1.00 g of propane?
(a) 5.00 g
(b) 0.726 g
(c) 2.18 g
(d) 3.63 g

3.44 Calcium hydride reacts with water to form calcium hydroxide and hydrogen gas. How many grams of calcium hydride are needed to form 4.50 g of hydrogen?
(a) 1.11 g
(b) 2.25 g
(c) 46.9 g
(d) 93.8 g

Exercises

3.45 Hydrofluoric acid, HF(*aq*), cannot be stored in glass bottles because compounds called silicates in the glass are attacked by the HF(*aq*). Sodium silicate (Na_2SiO_3), for example, reacts as follows:

$$Na_2SiO_3(s) + 8\,HF(aq) \longrightarrow H_2SiF_6(aq) + 2\,NaF(aq) + 3\,H_2O(l)$$

(a) How many moles of HF are needed to react with 0.300 mol of Na_2SiO_3?

(b) How many grams of NaF form when 0.500 mol of HF reacts with excess Na_2SiO_3?

(c) How many grams of Na_2SiO_3 can react with 0.800 g of HF?

3.46 Several brands of antacids use $Al(OH)_3$ to react with stomach acid, which contains primarily HCl:

$$Al(OH)_3(s) + HCl(aq) \longrightarrow AlCl_3(aq) + H_2O(l)$$

(a) Balance this equation.

(b) Calculate the number of grams of HCl that can react with 0.500 g of $Al(OH)_3$.

(c) Calculate the number of grams of $AlCl_3$ and the number of grams of H_2O formed when 0.500 g of $Al(OH)_3$ reacts.

(d) Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.47 Aluminum sulfide reacts with water to form aluminum hydroxide and hydrogen sulfide. (**a**) Write the balanced chemical equation for this reaction. (**b**) How many grams of aluminum hydroxide are obtained from 14.2 g of aluminum sulfide?

3.48 Automotive air bags inflate when sodium azide, NaN_3, rapidly decomposes to its component elements:

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$$

(a) How many moles of N_2 are produced by the decomposition of 1.50 mol of NaN_3?

(b) How many grams of NaN_3 are required to form 10.0 g of nitrogen gas?

(c) How many grams of NaN_3 are required to produce 10.0 ft^3 of nitrogen gas, about the size of an automotive air bag, if the gas has a density of 1.25 g/L?

3.49 A piece of aluminum foil 1.00 cm^2 and 0.550-mm thick is allowed to react with bromine to form aluminum bromide.



(**a**) How many moles of aluminum were used? (The density of aluminum is 2.699 g/cm^3.) (**b**) How many grams of aluminum bromide form, assuming the aluminum reacts completely?

3.50 The complete combustion of octane, C_8H_{18}, produces 5470 kJ of heat. Calculate how many grams of octane is required to produce 20,000 kJ of heat.

Answers to Self-Assessment Exercises

3.41 True **3.42** (a) **3.43** (d) **3.44** (c)

3.7 Limiting Reactants



Often, the reactants used in a chemical reaction are not present in precise stoichiometric amounts. For example, a natural gas-fired power plant generates electricity by producing hot gases that drive turbines, predominantly through the following combustion reaction:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad [3.18]$$

Power plants typically operate with an excess of $O_2(g)$ to achieve the maximum energy from the hydrocarbon fuel and minimize production of harmful byproducts, like carbon monoxide, that result from incomplete combustion. Consequently, the amount of CH_4 introduced determines how much CO_2 and H_2O water are produced, as well as the amount of energy released. In this section, we will learn how to do quantitative calculations for reactions where the reactants are not present in stoichiometrically equivalent quantities.

When you have completed this section, you should be able to:

- Identify limiting reactants and calculate amounts, in grams or moles, of reactants consumed and products formed in chemical reactions.
- Calculate the percent yield of a chemical reaction from the actual yield and the quantities of each reactant.

Suppose you wish to make several sandwiches using one slice of cheese and two slices of bread for each. Using Bd = bread, Ch = cheese, and Bd_2Ch = sandwich, we can represent the recipe for making a sandwich like a chemical equation:

$$2\,Bd + Ch \longrightarrow Bd_2Ch \qquad [3.19]$$

If you have ten slices of bread and seven slices of cheese, you can make only five sandwiches and will have two slices of cheese left over. The amount of bread available limits the number of sandwiches.

An analogous situation occurs in chemical reactions when one reactant is used up before the others. The reaction stops as soon as any reactant is totally consumed, leaving the excess reactants as leftovers. Suppose, for example, we have a mixture of 10 mol H_2 and 7 mol O_2, which react to form water:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad [3.20]$$

Because 2 mol H_2 ≏ 1 mol O_2, the number of moles of O_2 needed to react with all the H_2 is

$$\text{Moles } O_2 = (10\ \cancel{\text{mol } H_2})\left(\frac{1\ \text{mol } O_2}{2\ \cancel{\text{mol } H_2}}\right) = 5\ \text{mol } O_2$$

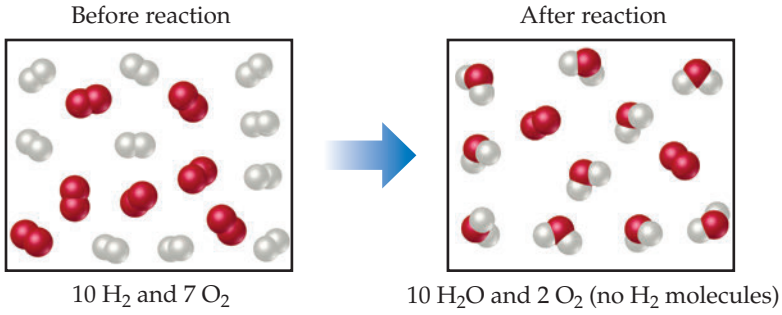
Because 7 mol O_2 is available at the start of the reaction, 7 mol O_2 − 5 mol O_2 = 2 mol O_2 is still present when all the H_2 is consumed.

The reactant that is completely consumed in a reaction is called the **limiting reactant** because it determines, or limits, the amount of product formed. The other reactants are sometimes called *excess reactants*. In our example, shown in Figure 3.16, H_2 is the limiting reactant, which means that once all the H_2 has been consumed, the reaction stops. At that point some of the excess reactant O_2 is left over.

There are no restrictions on the starting amounts of reactants in any reaction. Indeed, many reactions are carried out using an excess of one reactant. The quantities of reactants consumed and products formed, however, are restricted by the quantity of the limiting reactant. For example, when a combustion reaction takes place in the open air, oxygen is plentiful and is therefore the excess reactant. If you run out of fuel while driving, the car stops because the fuel is the limiting reactant in the combustion reaction that moves the car. Before we leave the example illustrated in **Figure 3.16**, let's summarize the data:

	$2\,H_2(g)$	+	$O_2(g)$	⟶	$2\,H_2O(g)$
Before reaction:	10 mol		7 mol		0 mol
Change (reaction):	−10 mol		−5 mol		+10 mol
After reaction:	0 mol		2 mol		10 mol

Go Figure If the amount of H_2 is doubled, how many moles of H_2O would have formed?



▲ **Figure 3.16 Limiting reactant.** Because H_2 is completely consumed, it is the limiting reactant. Because some O_2 is left over after the reaction is complete, it is the excess reactant. The amount of H_2O formed depends on the amount of limiting reactant, H_2.

The second line in the table (Change) summarizes the amounts of reactants consumed (where this consumption is indicated by the minus signs) and the amount of the product formed (indicated by the plus sign). These quantities are restricted by the quantity of the limiting reactant and depend on the coefficients in the balanced equation. The mole ratio H_2:O_2:H_2O = 10:5:10 is a multiple of the ratio of the coefficients in the balanced equation, 2:1:2. The after quantities are found by adding the before and change quantities for each column. The amount of the limiting reactant (H_2) must be zero at the end of the reaction. What remains is 2 mol O_2 (excess reactant) and 10 mol H_2O (product).

Sample Exercise 3.16

Calculating the Amount of Product Formed from a Limiting Reactant

The most important commercial process for converting N_2 from the air into nitrogen-containing compounds is based on the reaction of N_2 and H_2 to form ammonia (NH_3):

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

How many moles of NH_3 can be formed from 3.0 mol of N_2 and 6.0 mol of H_2?

SOLUTION

Analyze We are asked to calculate the number of moles of product, NH_3, given the quantities of each reactant, N_2 and H_2, available in a reaction. This is a limiting reactant problem.

Plan If we assume one reactant is completely consumed, we can calculate how much of the second reactant is needed. By comparing the calculated quantity of the second reactant with the amount available, we can determine which reactant is limiting. We then proceed with the calculation, using the quantity of the limiting reactant.

Solve

The number of moles of H_2 needed for complete consumption of 3.0 mol of N_2 is

$$\text{Moles } H_2 = (3.0 \cancel{\text{ mol } N_2})\left(\frac{3 \text{ mol } H_2}{1 \cancel{\text{ mol } N_2}}\right) = 9.0 \text{ mol } H_2$$

Because only 6.0 mol H_2 is available, we will run out of H_2 before the N_2 is gone, which tells us that H_2 is the limiting reactant. Therefore, we use the quantity of H_2 to calculate the quantity of NH_3 produced:

$$\text{Moles } NH_3 = (6.0 \cancel{\text{ mol } H_2})\left(\frac{2 \text{ mol } NH_3}{3 \cancel{\text{ mol } H_2}}\right) = 4.0 \text{ mol } NH_3$$

Notice that we can calculate not only the number of moles of NH_3 formed but also the number of moles of each reactant remaining after the reaction. Notice also that although the initial (before) number of moles of H_2 is greater than the final (after) number of moles of N_2, H_2 is nevertheless the limiting reactant because of its larger coefficient in the balanced equation.

Check Examine the change row of the summary table to see that the mole ratio of reactants consumed and product formed, 2:6:4, is a multiple of the coefficients in the balanced equation, 1:3:2. We confirm that H_2 is the limiting reactant because it is completely consumed in the reaction, leaving 0 mol at the end. Because 6.0 mol H_2 has two significant figures, our answer has two significant figures.

Comment It is useful to summarize the reaction data in a table:

	$N_2(g)$	+	$3\,H_2(g)$	$\longrightarrow$	$2\,NH_3(g)$
Before reaction:	3.0 mol		6.0 mol		0 mol
Change (reaction):	−2.0 mol		−6.0 mol		+4.0 mol
After reaction:	1.0 mol		0 mol		4.0 mol

Practice Exercise

When 24 mol of methanol and 15 mol of oxygen combine in the combustion reaction $2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$, what is the excess reactant and how many moles of it remains at the end of the reaction?
(**a**) 9 mol $CH_3OH(l)$ (**b**) 10 mol $CO_2(g)$ (**c**) 10 mol $CH_3OH(l)$
(**d**) 14 mol $CH_3OH(l)$ (**e**) 1 mol $O_2(g)$

Sample Exercise 3.17

Calculating the Amount of Product Formed from a Limiting Reactant

The reaction

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$

is used to produce electricity in a hydrogen fuel cell. Suppose a fuel cell contains 150 g of $H_2(g)$ and 1500 g of $O_2(g)$ (each measured to two significant figures). How many grams of water can form?

SOLUTION

Analyze We are asked to calculate the amount of a product, given the amounts of two reactants, so this is a limiting reactant problem.

Plan To identify the limiting reactant, we can calculate the number of moles of each reactant and compare their ratio with the ratio of coefficients in the balanced equation. We then use the quantity of the limiting reactant to calculate the mass of water that forms.

Solve From the balanced equation, we have the stoichiometric relations

$$2\text{ mol } H_2 \simeq 1\text{ mol } O_2 \simeq 2\text{ mol } H_2O$$

Using the molar mass of each substance, we calculate the number of moles of each reactant:

$$\text{Moles } H_2 = (150\text{ g } \cancel{H_2})\left(\frac{1\text{ mol } H_2}{2.02\text{ g } \cancel{H_2}}\right) = 74\text{ mol } H_2$$

$$\text{Moles } O_2 = (1500\text{ g } \cancel{O_2})\left(\frac{1\text{ mol } O_2}{32.0\text{ g } \cancel{O_2}}\right) = 47\text{ mol } O_2$$

The coefficients in the balanced equation indicate that the reaction requires 2 mol of H_2 for every 1 mol of O_2. Therefore, for all the O_2 to completely react, we would need $2 \times 47 = 94$ mol of H_2. Since there are only 74 mol of H_2, all of the O_2 cannot react, so it is the excess reactant, and H_2 must be the limiting reactant. (Notice that the limiting reactant is not necessarily the one present in the lowest amount.)

We use the given quantity of H_2 (the limiting reactant) to calculate the quantity of water formed. We could begin this calculation with the given H_2 mass, 150 g, but we can save a step by starting with the moles of H_2, 74 mol, we just calculated:

$$\text{Grams } H_2O = (74\text{ mol } \cancel{H_2})\left(\frac{2\text{ mol } \cancel{H_2O}}{2\text{ mol } \cancel{H_2}}\right)\left(\frac{18.0\text{ g } H_2O}{1\text{ mol } \cancel{H_2O}}\right)$$

$$= 1.3 \times 10^2\text{ g } H_2O$$

Check The magnitude of the answer seems reasonable based on the amounts of the reactants. The units are correct, and the number of significant figures (two) corresponds to those in the values given in the problem statement.

Comment The quantity of the limiting reactant, H_2, can also be used to determine the quantity of O_2 used:

$$\text{Grams } O_2 = (74\text{ mol } \cancel{H_2})\left(\frac{1\text{ mol } \cancel{O_2}}{2\text{ mol } \cancel{H_2}}\right)\left(\frac{32.0\text{ g } O_2}{1\text{ mol } \cancel{O_2}}\right)$$

$$= 1.2 \times 10^3\text{ g } O_2$$

The mass of O_2 remaining at the end of the reaction equals the starting amount minus the amount consumed:

$$1500\text{ g} - 1200\text{ g} = 300\text{ g}.$$

Practice Exercise

Molten gallium reacts with arsenic to form the semiconductor, gallium arsenide, GaAs, used in light-emitting diodes and solar cells:

$$Ga(l) + As(s) \longrightarrow GaAs(s)$$

If 4.00 g of gallium is reacted with 5.50 g of arsenic, how many grams of the excess reactant are left at the end of the reaction?
(**a**) 1.20 g As (**b**) 1.50 g As (**c**) 4.30 g As (**d**) 8.30 g Ga

Theoretical and Percent Yields

The quantity of product calculated to form when all the limiting reactant is consumed is called the **theoretical yield**. The amount of product actually obtained, called the *actual yield*, is almost always less than (and can never be greater than) the theoretical yield. There are many reasons for this difference. Some of the reactants may not react, for example, or they may react in a way different from that desired (side reactions). In addition, it is not always possible to recover all of the product from the reaction mixture. The **percent yield** of a reaction is the actual yield divided by the theoretical yield, multiplied by 100 to convert to percent:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Sample Exercise 3.18

Calculating Theoretical Yield and Percent Yield

Adipic acid, $H_2C_6H_8O_4$, used to produce nylon, is made commercially by a reaction between cyclohexane (C_6H_{12}) and O_2:

$$2\,C_6H_{12}(l) + 5\,O_2(g) \longrightarrow 2\,H_2C_6H_8O_4(l) + 2\,H_2O(g)$$

(**a**) Assume that you carry out this reaction with 25.0 g of cyclohexane and that cyclohexane is the limiting reactant. What is the theoretical yield of adipic acid? (**b**) If you obtain 33.5 g of adipic acid, what is the percent yield for the reaction?

SOLUTION

Analyze We are given a chemical equation and the quantity of the limiting reactant (25.0 g of C_6H_{12}). We are asked to calculate the theoretical yield of a product $H_2C_6H_8O_4$ and the percent yield if only 33.5 g of product is obtained.

Plan

(**a**) The theoretical yield, which is the calculated quantity of adipic acid formed, can be calculated using the sequence of conversions shown in Figure 3.15.

(**b**) The percent yield is calculated by using Equation 3.14 to compare the given actual yield (33.5 g) with the theoretical yield.

Solve

(**a**) The theoretical yield is:

$$\text{Grams } H_2C_6H_8O_4 = (25.0\ \text{g } \cancel{C_6H_{12}})\left(\frac{1\ \text{mol } \cancel{C_6H_{12}}}{84.0\ \text{g } \cancel{C_6H_{12}}}\right)\left(\frac{2\ \text{mol } \cancel{H_2C_6H_8O_4}}{2\ \text{mol } \cancel{C_6H_{12}}}\right)\left(\frac{146.0\ \text{g } H_2C_6H_8O_4}{1\ \text{mol } \cancel{H_2C_6H_8O_4}}\right)$$
$$= 43.5\ \text{g } H_2C_6H_8O_4$$

(**b**) The percent yield is:

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{33.5\ \text{g}}{43.5\ \text{g}} \times 100\% = 77.0\%$$

Check We can check our answer in (**a**) by doing a ballpark calculation. From the balanced equation we know that each mole of cyclohexane gives 1 mol adipic acid. We have $25/84 \approx 25/75 = 0.3$ mol hexane, so we expect 0.3 mol adipic acid, which equals about $0.3 \times 150 = 45$ g, about the same magnitude as the 43.5 g obtained in the more detailed calculation given previously. In addition, our answer has the appropriate units and number of significant figures. In (**b**) the answer is less than 100%, as it must be from the definition of percent yield.

Practice Exercise

If 3.00 g of titanium metal is reacted with 6.00 g of chlorine gas, Cl_2, to form 7.7 g of titanium(IV) chloride in a combination reaction, what is the percent yield of the product?
(**a**) 65% (**b**) 96% (**c**) 48% (**d**) 86%

STRATEGIES FOR SUCCESS Design an Experiment

One of the most important skills you can learn in school is how to think like a scientist. Questions such as: "What experiment might test this hypothesis?", "How do I interpret these data?", and "Do these data support the hypothesis?" are asked every day by chemists and other scientists as they go about their work.

We want you to become a good critical thinker as well as an active, logical, and curious learner. For this purpose, starting in this chapter, we include at the end of each chapter a special exercise called "Design an Experiment." Here is an example:

Is milk a pure liquid or a mixture of chemical components in water? Design an experiment to distinguish between these two possibilities.

You might already know the answer—milk is indeed a mixture of components in water—but the goal is to think of how to demonstrate this in practice. Upon thinking about it, you will likely realize that the key idea for this experiment is separation: You can prove that milk is a mixture of chemical components if you can figure out how to separate these components.

Testing a hypothesis is a creative endeavor. While some experiments may be more efficient than others, there is often more than one good way to test a hypothesis. Our question about milk, for example, might be explored by an experiment in which you boil a known quantity of milk until it is dry. Does a solid residue form in the bottom of the pan? If so, you could weigh it and calculate the percentage of solids in milk, which would offer good evidence that milk is a mixture. If there is no residue after boiling, then you still cannot distinguish between the two possibilities.

What other experiments might you do to demonstrate that milk is a mixture? You could put a sample of milk in a centrifuge, which you might have used in a biology lab, spin your sample, and observe if any solids collect at the bottom of the centrifuge tube; large molecules can be separated in this way from a mixture. Measurement of the mass of the solid at the bottom of the tube is a way to obtain a value for the % solids in milk and also tells you that milk is indeed a mixture.

Keep an open mind: Lacking a centrifuge, how else might you separate solids in the milk? You could consider using a filter with really tiny holes in it or perhaps even a fine strainer. You could propose that if milk were poured through this filter, some (large) solid components should stay on the top of the filter, while water (and really small molecules or ions) would pass through the filter. That result would be evidence that milk is a mixture. Does such a filter exist? Yes! But for our purposes, the existence of such a filter is not the point: The point is, can you use your imagination and your knowledge of chemistry to design a reasonable experiment? Don't worry too much about the exact apparatus you need for the Design an Experiment exercises. The goal is to imagine what you would need to do, or what kind of data you would need to collect, in order to answer the question. If your instructor allows it, you can collaborate with others in your class to develop ideas. Scientists discuss their ideas with other scientists all the time. We find that discussing ideas, and refining them, makes us better scientists and helps us collectively answer important questions.

The design and interpretation of scientific experiments is at the heart of the scientific method. Think of the Design an Experiment exercises as puzzles that can be solved in various ways, and enjoy your explorations!

Self-Assessment Exercises

Here are a few problems designed to test your understanding of the material.

3.51 When 24 mol of methanol and 15 mol of oxygen combine in the combustion reaction $2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$, what is the excess reactant and how many moles of it remains at the end of the reaction?

(a) 9 mol $CH_3OH(l)$

(b) 10 mol $CO_2(g)$

(c) 10 mol $CH_3OH(l)$

(d) 14 mol $CH_3OH(l)$

(e) 1 mol $O_2(g)$

3.52 Molten gallium reacts with arsenic to form the semiconductor, gallium arsenide, GaAs, used in light-emitting diodes and solar cells:

$$Ga(l) + As(s) \longrightarrow GaAs(s)$$

If 4.00 g of gallium reacted with 5.50 g of arsenic, how many grams of the excess reactant are left at the end of the reaction?

(a) 1.20 g As

(b) 1.50 g As

(c) 4.30 g As

(d) 8.30 g Ga

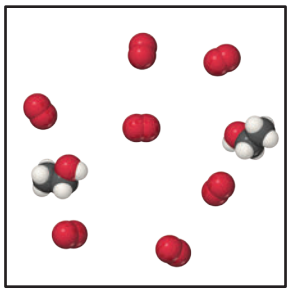
3.53 If 3.00 g of titanium metal is reacted with 6.00 g of chlorine gas, Cl_2, to form 7.7 g of titanium(IV) chloride in a combination reaction, what is the percent yield of the product?

(a) 65%
(b) 96%
(c) 48%
(d) 86%

Exercises

3.54 (**a**) Define the terms *limiting reactant* and *excess reactant*. (**b**) Why are the amounts of products formed in a reaction determined only by the amount of the limiting reactant? (**c**) Why should you base your choice of which compound is the limiting reactant on its number of initial moles, not on its initial mass in grams?

3.55 Consider the mixture of ethanol, C_2H_5OH, and O_2 shown in the accompanying diagram. (**a**) Write a balanced equation for the combustion reaction that occurs between ethanol and oxygen. (**b**) Which reactant is the limiting reactant? (**c**) How many molecules of CO_2, H_2O, C_2H_5OH, and O_2 will be present if the reaction goes to completion?



3.56 Sodium hydroxide reacts with carbon dioxide as follows:

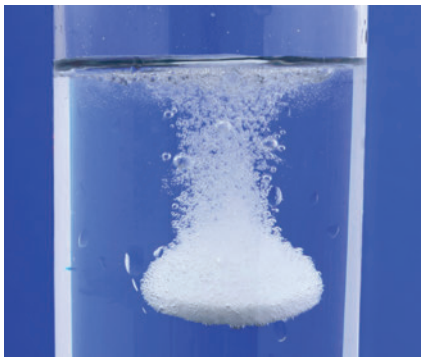
$$2\,NaOH(s) + CO_2(g) \longrightarrow Na_2CO_3(s) + H_2O(l)$$

Which is the limiting reactant when 1.85 mol NaOH and 1.00 mol CO_2 are allowed to react? How many moles of Na_2CO_3 can be produced? How many moles of the excess reactant remain after the completion of the reaction?

3.57 The fizz produced when an Alka-Seltzer tablet is dissolved in water is due to the reaction between sodium bicarbonate ($NaHCO_3$) and citric acid ($H_3C_6H_5O_7$):

$$3\,NaHCO_3(aq) + H_3C_6H_5O_7(aq) \longrightarrow 3\,CO_2(g) + 3H_2O(l) + Na_3C_6H_5O_7(aq)$$

In a certain experiment 1.00 g of sodium bicarbonate and 1.00 g of citric acid are allowed to react. (**a**) Which is the limiting reactant? (**b**) How many grams of carbon dioxide form? (**c**) How many grams of the excess reactant remain after the limiting reactant is completely consumed?



3.58 Solutions of sodium carbonate and silver nitrate react to form solid silver carbonate and a solution of sodium nitrate. A solution containing 3.50 g of sodium carbonate is mixed with one containing 5.00 g of silver nitrate. How many grams of sodium carbonate, silver nitrate, silver carbonate, and sodium nitrate are present after the reaction is complete?

3.59 When benzene (C_6H_6) reacts with bromine (Br_2), bromobenzene (C_6H_5Br) is obtained:

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

(**a**) When 30.0 g of benzene reacts with 65.0 g of bromine, what is the theoretical yield of bromobenzene? (**b**) If the actual yield of bromobenzene is 42.3 g, what is the percentage yield?

3.60 Hydrogen sulfide is an impurity in natural gas that must be removed. One common removal method is called the Claus process, which relies on the reaction:

$$8\,H_2S(g) + 4\,O_2(g) \longrightarrow S_8(l) + 8\,H_2O(g)$$

Under optimal conditions the Claus process gives 98% yield of S_8 from H_2S. If you started with 30.0 g of H_2S and 50.0 g of O_2, how many grams of S_8 would be produced, assuming 98% yield?

Answers to Self-Assessment Exercises

3.51 (d) 3.52 (a) 3.53 (b)

Chapter Summary and Key Terms

CHEMICAL EQUATIONS (INTRODUCTION AND SECTION 3.1) The study of the quantitative relationships between chemical formulas and chemical equations is known as **stoichiometry**. One of the important concepts of stoichiometry is the **law of conservation of mass**, which states that the total mass of the products of a chemical reaction is the same as the total mass of the reactants. The same numbers of atoms of each type are present before and after a chemical reaction. A balanced **chemical equation** shows equal numbers of atoms of each element on each side of the equation. Equations are balanced by placing coefficients in front of the chemical formulas for the **reactants** and **products** of a reaction, *not* by changing the subscripts in chemical formulas.

SIMPLE PATTERNS OF CHEMICAL REACTIVITY (SECTION 3.2) Among the reaction types described in this chapter are (1) **combination reactions**, in which two reactants combine to form one product; (2) **decomposition reactions**, in which a single reactant forms two or more products; and (3) **combustion reactions** in oxygen, in which a substance, typically a hydrocarbon, reacts rapidly with O_2 to form CO_2 and H_2O.

FORMULA WEIGHTS (SECTION 3.3) Much quantitative information can be determined from chemical formulas and balanced chemical equations by using atomic weights. The **formula weight** of a compound equals the sum of the atomic weights of the atoms in its formula. If the formula is a molecular formula, the formula weight is also called the **molecular weight**. Atomic weights and formula weights can be used to determine the **elemental composition** of a compound.

AVOGADRO'S NUMBER AND THE MOLE (SECTION 3.4) A mole of any substance contains **Avogadro's number** (6.02×10^{23}) of formula units of that substance. The mass of a **mole** of atoms, molecules, or ions (the **molar mass**) equals the formula weight of that material expressed in grams. The mass of 1 molecule of H_2O, for example, is 18.0 u, so the mass of 1 mol of H_2O is 18.0 g. That is, the molar mass of H_2O is 18.0 g/mol.

EMPIRICAL FORMULAS FROM ANALYSIS (SECTION 3.5) The empirical formula of any substance can be determined from its percent composition by calculating the relative number of moles of each atom in 100 g of the substance. If the substance is molecular in nature, its molecular formula can be determined from the empirical formula if the molecular weight is also known. Combustion analysis is a special technique for determining the empirical formulas of compounds containing only carbon, hydrogen, and/or oxygen.

QUANTITATIVE INFORMATION FROM BALANCED EQUATIONS AND LIMITING REACTANTS (SECTIONS 3.6 AND 3.7) The mole concept can be used to calculate the relative quantities of reactants and products in chemical reactions. The coefficients in a balanced equation give the relative numbers of moles of the reactants and products. To calculate the number of grams of a product from the number of grams of a reactant, first convert grams of reactant to moles of reactant. Then use the coefficients in the balanced equation to convert the number of moles of reactant to moles of product. Finally, convert moles of product to grams of product.

A **limiting reactant** is completely consumed in a reaction. When it is used up, the reaction stops, thus limiting the quantities of products formed. The **theoretical yield** of a reaction is the quantity of product calculated to form when all of the limiting reactant reacts. The actual yield of a reaction is always less than the theoretical yield. The **percent yield** compares the actual and theoretical yields.

Learning Outcomes After studying this chapter, you should be able to:

- Balance chemical equations. (Section 3.1) *Related Exercises: 3.5, 3.70*
- Predict the products of simple combination, decomposition, and combustion reactions. (Section 3.2) *Related Exercises: 3.12, 3.74*
- Calculate formula weights. (Section 3.3) *Related Exercises: 3.17, 3.76*
- Convert grams to moles and vice versa using molar masses. (Section 3.4) *Related Exercises: 3.25, 3.81*
- Convert number of molecules to moles and vice versa using Avogadro's number. (Section 3.4) *Related Exercises: 3.27, 3.83*
- Calculate the empirical and molecular formulas of a compound from percentage composition and molecular weight. (Section 3.5) *Related Exercises: 3.37, 3.90*
- Identify limiting reactants and calculate amounts, in grams or moles, of reactants consumed and products formed for a reaction. (Section 3.6) *Related Exercises: 3.47, 3.96*
- Calculate the percent yield of a reaction. (Section 3.7) *Related Exercises: 3.59, 3.105*

Key Equations

- $$\text{\% mass composition of element} = \frac{\left(\begin{array}{c}\text{number of atoms}\\ \text{of element}\end{array}\right)\left(\begin{array}{c}\text{atomic weight}\\ \text{of element}\end{array}\right)}{\text{formula weight of compound}} \times 100\% \quad [3.15]$$

  This is the formula to calculate the mass percentage of each element in a compound. The sum of all the percentages of all the elements in a compound should add up to 100%.

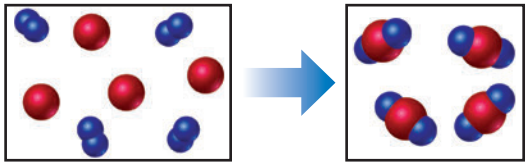
- $$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

  This is the formula to calculate the percent yield of a reaction. The percent yield can never be more than 100%.

Exercises

Visualizing Concepts

3.61 The reaction between reactant A (blue spheres) and reactant B (red spheres) is shown in the following diagram:



Based on this diagram, which equation best describes the reaction? [Section 3.1]

(**a**) $A_2 + B \longrightarrow A_2B$

(**b**) $A_2 + 4\,B \longrightarrow 2\,AB_2$

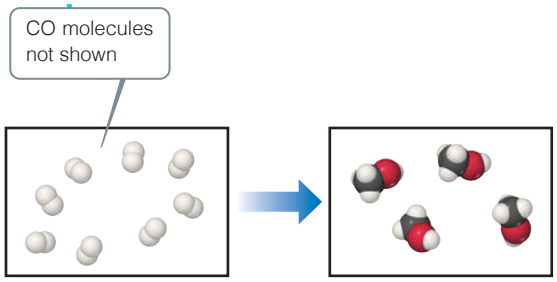
(**c**) $2\,A + B_4 \longrightarrow 2\,AB_2$

(**d**) $A + B_2 \longrightarrow AB_2$

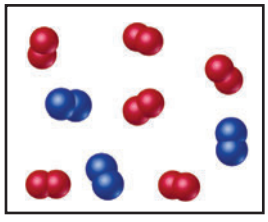
3.62 The following diagram shows the combination reaction between hydrogen, H_2, and carbon monoxide, CO, to produce methanol, CH_3OH (white spheres are H, black spheres are C, red spheres are O). The correct number of CO molecules involved in this reaction is not shown. [Section 3.1]

(**a**) Determine the number of CO molecules that should be shown in the left (reactants) box.

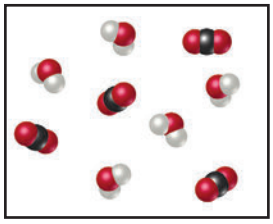
(**b**) Write a balanced chemical equation for the reaction.



3.63 The following diagram represents the collection of elements formed by a decomposition reaction. (**a**) If the blue spheres represent N atoms and the red ones represent O atoms, what was the empirical formula of the original compound? (**b**) Could you draw a diagram representing the molecules of the compound that had been decomposed? Why or why not? [Section 3.2]



3.64 The following diagram represents the collection of CO_2 and H_2O molecules formed by complete combustion of a hydrocarbon. What is the empirical formula of the hydrocarbon? [Section 3.2]



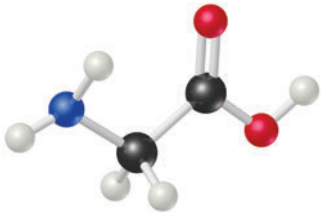
3.65 Glycine, an amino acid used by organisms to make proteins, is represented by the following molecular model.

(**a**) Write its molecular formula.

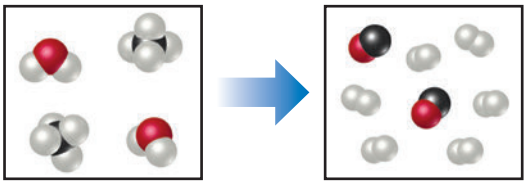
(**b**) Determine its molar mass.

(**c**) Calculate how many moles of glycine are in a 100.0-g sample of glycine.

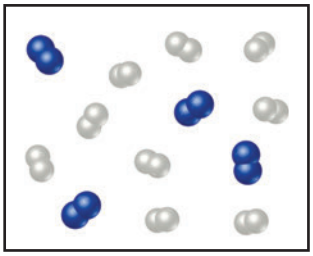
(**d**) Calculate the percent nitrogen by mass in glycine. [Sections 3.3 and 3.5]



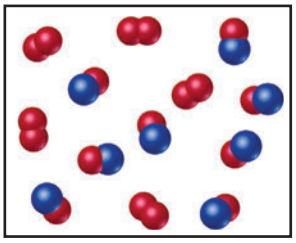
3.66 The following diagram represents a high-temperature reaction between CH_4 and H_2O. Based on this reaction, find how many moles of each product can be obtained starting with 4.0 mol CH_4. [Section 3.6]



3.67 Nitrogen (N_2) and hydrogen (H_2) react to form ammonia (NH_3). Consider the mixture of N_2 and H_2 shown in the accompanying diagram. The blue spheres represent N, and the white ones represent H. (**a**) Write the balanced chemical equation for the reaction. (**b**) What is the limiting reactant? (**c**) How many molecules of ammonia can be made, assuming the reaction goes to completion, based on the diagram? (**d**) Are any reactant molecules left over, based on the diagram? If so, how many of which type are left over? [Section 3.7]



3.68 Nitrogen monoxide and oxygen react to form nitrogen dioxide. Consider the mixture of NO and O_2 shown in the accompanying diagram. The blue spheres represent N, and the red ones represent O. (**a**) How many molecules of NO_2 can be formed, assuming the reaction goes to completion? (**b**) What is the limiting reactant? (**c**) If the actual yield of the reaction was 75% instead of 100%, how many molecules of each kind would be present after the reaction was over?



Chemical Equations and Simple Patterns of Chemical Reactivity (Section 3.1)

3.69 A key step in balancing chemical equations is correctly identifying the formulas of the reactants and products. For example, consider the reaction between calcium oxide, CaO(*s*), and $H_2O(l)$ to form aqueous calcium hydroxide. (**a**) Write a balanced chemical equation for this combination reaction, having correctly identified the product as $Ca(OH)_2(aq)$. (**b**) Is it possible to balance the equation if you incorrectly identify the product as CaOH(*aq*), and if so, what is the equation?

3.70 Balance the following equations:

(**a**) $HClO_4(aq) + P_4O_{10}(s) \longrightarrow HPO_3(aq) + Cl_2O_7(l)$

(**b**) $Au_2S_3(s) + H_2(g) \longrightarrow Au(s) + H_2S(g)$

(**c**) $Ba_3N_2(s) + H_2O(aq) \longrightarrow Ba(OH)_2(aq) + NH_3(g)$

(**d**) $Na_2CO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g)$

3.71 Balance the following equations:

(**a**) $CF_4(l) + Br_2(g) \longrightarrow CBr_4(l) + F_2(g)$

(**b**) $Cu(s) + HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + NO_2(g) + H_2O(l)$

(**c**) $MnO_2(s) + HCl(aq) \longrightarrow MnCl_2(s) + H_2O(l) + Cl_2(g)$

(**d**) $KOH(aq) + H_3PO_4(aq) \longrightarrow K_3PO_4(aq) + H_2O(l)$

3.72 Write balanced chemical equations to correspond to each of the following descriptions: (**a**) When sulfur trioxide gas reacts with water, a solution of sulfuric acid forms.(**b**) Boron sulfide, $B_2S_3(s)$, reacts violently with water to form dissolved boric acid, H_3BO_3, and hydrogen sulfide gas. (**c**) Phosphine, $PH_3(g)$, combusts in oxygen gas to form water vapor and solid tetraphosphorus decaoxide. (**d**) When solid mercury(II) nitrate is heated, it decomposes to form solid mercury(II) oxide, gaseous nitrogen dioxide, and oxygen. (**e**) Copper metal reacts with hot concentrated sulfuric acid solution to form aqueous copper(II) sulfate, sulfur dioxide gas, and water.

Patterns of Chemical Reactivity (Section 3.2)

3.73 (**a**) When a compound containing C, H, and O is completely combusted in air, what reactant besides the hydrocarbon is involved in the reaction? (**b**) What products form in this reaction? (**c**) What is the sum of the coefficients in the balanced chemical equation for the combustion of one mole of acetone, $C_3H_6O(l)$, in air?

3.74 Write a balanced chemical equation for the reaction that occurs when (**a**) titanium metal reacts with $O_2(g)$; (**b**) silver(I) oxide decomposes into silver metal and oxygen gas when heated; (**c**) propanol, $C_3H_7OH(l)$ burns in air; (**d**) methyl *tert*-butyl ether, $C_5H_{12}O(l)$, burns in air.

3.75 Balance the following equations and indicate whether they are combination, decomposition, or combustion reactions:

(**a**) $NaClO_3(s) \longrightarrow NaCl(s) + O_2(g)$

(**b**) $NH_4OH(aq) \longrightarrow H_2O(l) + NH_3(g)$

(**c**) $K(s) + Cl_2(g) \longrightarrow KCl(s)$

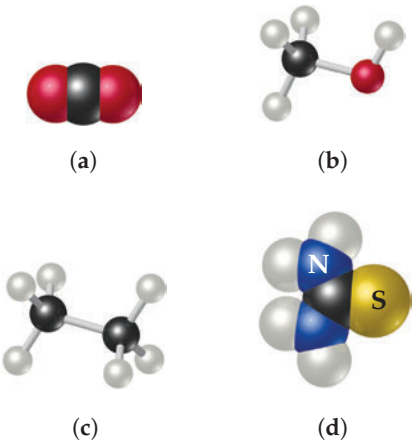
(**d**) $C_2H_5OH(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$

Formula Weights (Section 3.3)

3.76 Determine the formula weights of each of the following compounds: (**a**) Butyric acid, $CH_3CH_2CH_2COOH$, which is responsible for the rotten smell of spoiled food; (**b**) sodium perborate, $NaBO_3$, a substance used as bleach; (**c**) calcium carbonate, $CaCO_3$, a substance found in marble. (c) CF_2Cl_2, a refrigerant known as Freon; (**d**) $NaHCO_3$, known as baking soda and used in bread and pastry baking; (**e**) iron pyrite, FeS_2, which has a golden appearance and is known as "Fool's Gold."

3.77 Calculate the percentage by mass of the indicated element in the following compounds: (**a**) hydrogen in methane, CH_4, the major hydrocarbon in natural gas; (**b**) oxygen in vitamin E, $C_{29}H_{50}O_2$; (**c**) sulphur in magnesium sulphate, $MgSO_4$, a substance used as a drying agent; (**d**) nitrogen in epinephrine, $C_9H_{13}NO_3$, also known as adrenalin, a hormone that is important for the fight-or-flight response; (**e**) oxygen in the insect pheromone sulcatol, $C_8H_{16}O$; (**f**) carbon in sucrose, $C_{12}H_{22}O_{11}$, the compound that is responsible for the sweet taste of table sugar.

3.78 Calculate the percentage of carbon by mass in each of the compounds represented by the following models:



(**a**) (**b**) (**c**) (**d**)

Avogadro's Number and the Mole (Section 3.4)

3.79 (**a**) What is the mass, in grams, of one mole of ^{79}Br? (b) How many bromine atoms are present in one mole of ^{79}Br?

3.80 Without doing any detailed calculations (but using a periodic table to give atomic weights), rank the following samples in order of increasing numbers of atoms: 0.2 mol PCl_5 molecules, 80 g Fe_2O_3, 3.0×10^{23} CO molecules.

3.81 Calculate the following quantities:

(**a**) mass, in grams, of 1.50×10^{-2} mol CdS

(**b**) number of moles of NH_4Cl in 86.6 g of this substance

(**c**) number of molecules in 8.447×10^{-2} mol C_6H_6

(**d**) number of O atoms in 6.25×10^{-3} mol $Al(NO_3)_3$

3.82 (**a**) What is the mass, in grams, of 1.223 mol of iron(III) sulfate?

(**b**) How many moles of ammonium ions are in 6.955 g of ammonium carbonate?

(**c**) What is the mass, in grams, of 1.50×10^{21} molecules of aspirin, $C_9H_8O_4$?

(**d**) What is the molar mass of diazepam (Valium®) if 0.05570 mol has a mass of 15.86 g?

3.83 The molecular formula of salicylic acid, a compound commonly found in facial cleanser, is $C_7H_6O_3$. (**a**) What is the molar mass of salicylic acid? (**b**) How many moles of salicylic acid are present in 0.5 mg of this substance? (**c**) How many molecules of salicylic acid are in 0.5 mg of this substance? (**d**) How many oxygen atoms are present in 0.5 mg of salicylic acid?

3.84 A sample of the male sex hormone testosterone, $C_{19}H_{28}O_2$, contains 3.88×10^{21} hydrogen atoms. (**a**) How many atoms of carbon does it contain? (**b**) How many molecules of testosterone does it contain? (**c**) How many moles of testosterone does it contain? (**d**) What is the mass of this sample in grams?

3.85 At least 25 μg of tetrahydrocannabinol (THC), the active ingredient in marijuana, is required to produce intoxication. The molecular formula of THC is $C_{21}H_{30}O_2$. How many moles of THC does this 25 μg represent? How many molecules?

Empirical Formulas from Analyses (Section 3.5)

3.86 Determine the empirical formula of each of the following compounds if a sample contains (**a**) 3.92 mol C, 5.99 mol H, and 2.94 mol O; (**b**) 12.0 g calcium and 2.8 g nitrogen; (**c**) 89.14% Au and 10.86% O by mass.

3.87 Determine the empirical formulas of the compounds with the following compositions by mass:

(**a**) 42.1% Na, 18.9% P, and 39.0% O

(**b**) 18.7% Li, 16.3% C, and 65.0% O

(**c**) 60.0% C, 4.4% H, and the remainder O

3.88 The compound XCl_4 contains 75.0% Cl by mass. What is the element X?

3.89 What is the molecular formula of each of the following compounds?

(**a**) empirical formula CH_3O, molar mass = 62.0 g/mol

(**b**) empirical formula NH_2, molar mass = 32.0 g/mol

3.90 Determine the empirical and molecular formulas of each of the following substances:

(**a**) Ibuprofen, a headache remedy, contains 75.69% C, 8.80% H, and 15.51% O by mass and has a molar mass of 206 g/mol.

(**b**) Cadaverine, a foul-smelling substance produced by the action of bacteria on meat, contains 58.55% C, 13.81% H, and 27.40% N by mass; its molar mass is 102.2 g/mol.

(**c**) Epinephrine (adrenaline), a hormone secreted into the bloodstream in times of danger or stress, contains 59.0% C, 7.1% H, 26.2% O, and 7.7% N by mass; its molar mass is about 180 u.

3.91 (**a**) The characteristic odor of pineapple is due to ethyl butyrate, a compound containing carbon, hydrogen, and oxygen. Combustion of 2.78 mg of ethyl butyrate produces 6.32 mg of CO_2 and 2.58 mg of H_2O. What is the empirical formula of the compound? (**b**) Nicotine, a component of tobacco, is composed of C, H, and N. A 5.250-mg sample of nicotine was combusted, producing 14.242 mg of CO_2 and 4.083 mg of H_2O. What is the empirical formula for nicotine? If nicotine has a molar mass of 160 $\pm$ 5 g/mol, what is its molecular formula?

3.92 Propenoic acid, $C_3H_4O_2$, is a reactive organic liquid that is used in the manufacturing of plastics, coatings, and adhesives. An unlabeled container is thought to contain this liquid. A 0.275-g sample of the liquid is combusted to produce 0.102 g of water and 0.374 g carbon dioxide. Is the unknown liquid propenoic acid? Support your reasoning with calculations.

3.93 Epsom salts, a strong laxative used in veterinary medicine, is a hydrate, which means that a certain number of water molecules are included in the solid structure. The formula for Epsom salts can be written as $MgSO_4 \cdot xH_2O$, where x indicates the number of moles of H_2O per mole of $MgSO_4$. When 5.061 g of this hydrate is heated to 250 °C, all the water of hydration is lost, leaving 2.472 g of $MgSO_4$. What is the value of x?

Reaction Stoichiometry (Section 3.6)

3.94 The reaction between potassium superoxide, KO_2, and CO_2,

$$4\,KO_2 + 2\,CO_2 \longrightarrow 2K_2CO_3 + 3\,O_2$$

is used as a source of O_2 and absorber of CO_2 in self-contained breathing equipment used by rescue workers.

(**a**) How many moles of O_2 are produced when 0.400 mol of KO_2 reacts in this fashion?

(**b**) How many grams of KO_2 are needed to form 7.50 g of O_2?



(**c**) How many grams of CO_2 are used when 7.50 g of O_2 are produced?

3.95 An iron ore sample contains Fe_2O_3 together with other substances. Reaction of the ore with CO produces iron metal:

$$Fe_2O_3(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$$

(**a**) Balance this equation.

(**b**) Calculate the number of grams of CO that can react with 0.350 kg of Fe_2O_3.

(**c**) Calculate the number of grams of Fe and the number of grams of CO_2 formed when 0.350 kg of Fe_2O_3 reacts.

(**d**) Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.96 Calcium hydride reacts with water to form calcium hydroxide and hydrogen gas. (**a**) Write a balanced chemical equation for the reaction. (**b**) How many grams of calcium hydride are needed to form 4.500 g of hydrogen?

3.97 The complete combustion of octane, C_8H_{18}, a component of gasoline, proceeds as follows:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

(**a**) How many moles of O_2 are needed to burn 1.50 mol of C_8H_{18}?

(**b**) How many grams of O_2 are needed to burn 10.0 g of C_8H_{18}?

(**c**) Octane has a density of 0.692 g/mL at 20 °C. How many grams of O_2 are required to burn 15.0 gal of C_8H_{18} (the capacity of an average fuel tank)?

(**d**) How many grams of CO_2 are produced when 15.0 gal of C_8H_{18} are combusted?

3.98 Detonation of nitroglycerin proceeds as follows:

$$4\,C_3H_5N_3O_9(l) \longrightarrow 12\,CO_2(g) + 6\,N_2(g) + O_2(g) + 10\,H_2O(g)$$

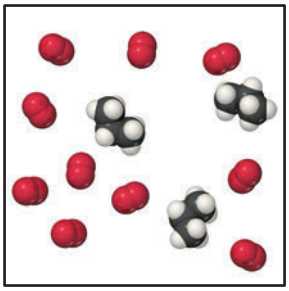
(**a**) If a sample containing 2.00 mL of nitroglycerin (density = 1.592 g/mL) is detonated, how many moles of gas are produced? (**b**) If each mole of gas occupies 55 L under the conditions of the explosion, how many liters of gas are produced? (**c**) How many grams of N_2 are produced in the detonation?

3.99 The combustion of one mole of liquid octane, $CH_3(CH_2)_6CH_3$, produces 5470 kJ of heat. Calculate how much heat is produced if 1.000 gallon of octane is combusted. See Exercise 3.97 for necessary information about octane.

Limiting Reactants (Section 3.7)

3.100 Define the terms *theoretical yield, actual yield, and percent yield.* (**b**) Why is the actual yield in a reaction almost always less than the theoretical yield? (**c**) Can a reaction ever have 110% actual yield?

3.101 Consider the mixture of propane, C_3H_8, and O_2 shown here. (**a**) Write a balanced equation for the combustion reaction that occurs between propane and oxygen. (**b**) Which reactant is the limiting reactant? (**c**) How many molecules of CO_2, H_2O, C_3H_8, and O_2 will be present if the reaction goes to completion?



3.102 Aluminum hydroxide reacts with sulfuric acid as follows:

$$2\,Al(OH)_3(s) + 3\,H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 6\,H_2O(l)$$

Which is the limiting reactant when 0.500 mol $Al(OH)_3$ and 0.500 mol H_2SO_4 are allowed to react? How many moles of $Al_2(SO_4)_3$ can form under these conditions? How many moles of the excess reactant remain after the completion of the reaction?

3.103 One of the steps in the commercial process for converting ammonia to nitric acid is the conversion of NH_3 to NO:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$

In a certain experiment, 2.00 g of NH_3 reacts with 2.50 g of O_2. (**a**) Which is the limiting reactant? (**b**) How many grams of NO and H_2O form? (**c**) How many grams of the excess reactant remain after the limiting reactant is completely consumed? (**d**) Show that your calculations in parts (b) and (c) are consistent with the law of conservation of mass.

3.104 Solutions of sulfuric acid and lead(II) acetate react to form solid lead(II) sulfate and a solution of acetic acid. If 5.00 g of sulfuric acid and 5.00 g of lead(II) acetate are mixed, calculate the number of grams of sulfuric acid, lead(II) acetate, lead(II) sulfate, and acetic acid present in the mixture after the reaction is complete.

3.105 When ethane (C_2H_6) reacts with chlorine (Cl_2), the main product is C_2H_5Cl, but other products containing Cl, such as $C_2H_4Cl_2$, are also obtained in small quantities. The formation of these other products reduces the yield of C_2H_5Cl. (**a**) Calculate the theoretical yield of C_2H_5Cl when 125 g of C_2H_6 reacts with 255 g of Cl_2, assuming that C_2H_6 and Cl_2 react only to form C_2H_2Cl and HCl. (**b**) Calculate the percent yield of C_2H_5Cl if the reaction produces 206 g of C_2H_5Cl.

3.106 When hydrogen sulfide gas is bubbled into a solution of sodium hydroxide, the reaction forms sodium sulfide and water. How many grams of sodium sulfide are formed if 1.25 g of hydrogen sulfide is bubbled into a solution containing 2.00 g of sodium hydroxide, assuming that the sodium sulfide is made in 92.0% yield?

Additional Exercises

3.107 Write balanced chemical equations for (**a**) the complete combustion of acetone (CH_3COCH_3), a common organic solvent; (**b**) the decomposition of solid mercury (I) carbonate into carbon dioxide gas, mercury, and solid mercury oxide; (**c**) the combination reaction between sulphur dioxide gas and liquid water to produce sulfurous acid.

3.108 If 2.0 mol $CH_3CH_2CH_2COOH$, 2.0 mol C_4H_{10}, and 2.0 mol C_6H_6 are completely combusted in oxygen, which one produces the largest number of moles of H_2O? Which one produces the least? Explain.

3.109 Calcium is an essential nutrient in our body. It is important for bone health. Four common calcium-containing supplements are calcium carbonate ($CaCO_3$), calcium citrate ($Ca_3C_{12}H_{10}O_{14}$), calcium gluconate ($CaC_{12}H_{22}O_{14}$), and calcium lactate ($CaC_6H_{10}O_6$). Rank these calcium supplements in terms of the mass percentage of calcium they contain.

3.110 (**a**) Ibuprofen is a common over-the-counter analgesic with the formula $C_{13}H_{18}O_2$. How many moles of $C_{13}H_{18}O_2$ are in a 500-mg tablet of ibuprofen? Assume the tablet is composed entirely of ibuprofen. (**b**) How many molecules of $C_{13}H_{18}O_2$ are in this tablet? (**c**) How many oxygen atoms are in the tablet?

3.111 Very small semiconductor crystals, composed of approximately 1000 to 10,000 atoms, are called quantum dots. Quantum dots made of the semiconductor CdSe are now being used in electronic reader and tablet displays because they emit light efficiently and in multiple colors, depending on dot size. The density of CdSe is 5.82 g/cm^3.

(**a**) What is the mass of one 2.5-nm CdSe quantum dot?

(**b**) CdSe quantum dots that are 2.5 nm in diameter emit blue light upon stimulation. Assuming that the dot is a perfect sphere and that the empty space in the dot can be neglected, calculate how many Cd atoms are in one quantum dot of this size.

(**c**) What is the mass of one 6.5-nm CdSe quantum dot?

(**d**) CdSe quantum dots that are 6.5 nm in diameter emit red light upon stimulation. Assuming that the dot is a perfect sphere, calculate how many Cd atoms are in one quantum dot of this size.

(**e**) If you wanted to make one 6.5-nm dot from multiple 2.5-nm dots, how many 2.5-nm dots would you need, and how many CdSe formula units would be left over, if any?

3.112 (**a**) One molecule of the antibiotic penicillin G has a mass of 5.342×10^{-21} g. What is the molar mass of penicillin G? (**b**) Hemoglobin, the oxygen-carrying protein in red blood cells, has four iron atoms per molecule and contains 0.340% iron by mass. Calculate the molar mass of hemoglobin.

3.113 Cinnamaldehyde is a compound that is responsible for the characteristic aroma of cinnamon. It contains 81.79% C, 6.10% H, and the remaining is oxygen. Its molar mass is 132 g/mol. Determine its molecular formula.

3.114 Fructose, commonly called fruit sugar, is a monosaccharide found in many plants. It contains 40% C, 6.71% H, and the remainder O. (**a**) What is the empirical formula for fructose? (**b**) A mass spectrum of fructose shows a peak at about 180 u. What is the molecular formula of the substance?

3.115 Vanillin, the dominant flavoring in vanilla, contains C, H, and O. When 1.05 g of this substance is completely combusted, 2.43 g of CO_2 and 0.50 g of H_2O are produced. What is the empirical formula of vanillin?

3.116 An organic compound was found to contain only C, H, and Cl. When a 1.50-g sample of the compound was completely combusted in air, 3.52 g of CO_2 was formed. In a separate experiment, the chlorine in a 1.00-g sample of the compound was converted to 1.27 g of AgCl. Determine the empirical formula of the compound.

3.117 A compound, $Na_2Cr_2O_x$, where x is unknown, is analyzed and found to contain 39.70% Cr. What is the value of x?

3.118 An element X forms an iodide (XI_3) and a chloride (XCl_3). The iodide is quantitatively converted to the chloride when it is heated in a stream of chlorine:

$$2\,XI_3 + 3\,Cl_2 \longrightarrow 2\,XCl_3 + 3\,I_2$$

If 0.5000 g of XI_3 is treated with chlorine, 0.2360 g of XCl_3 is obtained. (**a**) Calculate the atomic weight of the element X. (**b**) Identify the element X.

3.119 A method used by the U.S. Environmental Protection Agency (EPA) for determining the concentration of ozone in air is to pass the air sample through a "bubbler" containing sodium iodide, which removes the ozone according to the following equation:

$$O_3(g) + 2\,NaI(aq) + H_2O(l) \longrightarrow O_2(g) + I_2(s) + 2\,NaOH(aq)$$

(**a**) How many moles of sodium iodide are needed to remove 5.95×10^{-6} mol of O_3? (**b**) How many grams of sodium iodide are needed to remove 1.3 mg of O_3?

3.120 A chemical plant uses electrical energy to decompose aqueous solutions of NaCl to give Cl_2, H_2, and NaOH:

$$2\,NaCl(aq) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g) + Cl_2(g)$$

If the plant produces 1.5×10^6 kg (1500 metric tons) of Cl_2 daily, estimate the quantities of H_2 and NaOH produced.

3.121 The fat stored in a camel's hump is a source of both energy and water. Calculate the mass of H_2O produced by the metabolism of 1.0 kg of fat, assuming the fat consists entirely of tristearin ($C_{57}H_{110}O_6$), a typical animal fat, and assuming that during metabolism, tristearin reacts with O_2 to form only CO_2 and H_2O.

3.122 When hydrocarbons are burned in a limited amount of air, both CO and CO_2 form. When 0.450 g of a particular hydrocarbon was burned in air, 0.467 g of CO, 0.733 g of CO_2, and 0.450 g of H_2O were formed. (**a**) What is the empirical formula of the compound? (**b**) How many grams of O_2 were used in the reaction? (**c**) How many grams would have been required for complete combustion?

3.123 A mixture of $N_2(g)$ and $H_2(g)$ reacts in a closed container to form ammonia, $NH_3(g)$. The reaction ceases before either reactant has been totally consumed. At this stage 3.0 mol N_2, 3.0 mol H_2, and 3.0 mol NH_3 are present. How many moles of N_2 and H_2 were present originally?

3.124 A mixture containing $KClO_3$, K_2CO_3, $KHCO_3$, and KCl was heated, producing CO_2, O_2, and H_2O gases according to the following equations:

$$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$$
$$2\,KHCO_3(s) \longrightarrow K_2O(s) + H_2O(g) + 2\,CO_2(g)$$
$$K_2CO_3(s) \longrightarrow K_2O(s) + CO_2(g)$$

The KCl does not react under the conditions of the reaction. If 100.0 g of the mixture produces 1.80 g of H_2O, 13.20 g of CO_2, and 4.00 g of O_2, what was the composition of the original mixture? (Assume complete decomposition of the mixture.)

3.125 When a mixture of 10.0 g of acetylene (C_2H_2) and 10.0 g of oxygen (O_2) is ignited, the resulting combustion reaction produces CO_2 and H_2O. (**a**) Write the balanced chemical equation for this reaction. (**b**) Which is the limiting reactant? (**c**) How many grams of C_2H_2, O_2, CO_2, and H_2O are present after the reaction is complete?

Integrative Exercises

These exercises require skills from earlier chapters as well as skills from the present chapter.

3.126 Boron nitride, BN, is an electrical insulator with remarkable thermal and chemical stability. Its density is 2.1 g/cm^3. It can be made by reacting boric acid, H_3BO_3, with ammonia. The other product of the reaction is water. (**a**) Write a balanced chemical equation for the synthesis of BN. (**b**) If you made 225 g of boric acid react with 150 g ammonia, what mass of BN could you make? (**c**) Which reactant, if any, would be left over, and how many moles of leftover reactant would remain? (d) One application of BN is as thin film for electrical insulation. If you take the mass of BN from part (a) and make a 0.4 mm thin film from it, what area, in cm^2, would it cover?

3.127 Viridicatumtoxin B, $C_{30}H_{31}NO_{10}$, is a natural antibiotic compound. It requires a synthesis of 12 steps in the laboratory. Assuming all steps have equivalent yields of 85%, which is the final percent yield of the total synthesis?

3.128 Consider a sample of calcium carbonate in the form of a cube measuring 2.005 in. on each edge. If the sample has a density of 2.71 g/cm^3, how many oxygen atoms does it contain?

3.129 (**a**) You are given a cube of silver metal that measures 1.000 cm on each edge. The density of silver is 10.5 g/cm^3. How many atoms are in this cube? (**b**) Because atoms are spherical, they cannot occupy all of the space of the cube. The silver atoms pack in the solid in such a way that 74% of the volume of the solid is actually filled with the silver atoms. Calculate the volume of a single silver atom. (**c**) Using the volume of a silver atom and the formula for the volume of a sphere, calculate the radius in angstroms of a silver atom.

3.130 (**a**) If an automobile travels 350 km with a gas mileage of 9.0 km/L, how many kilograms of CO_2 are produced? Assume that the gasoline is composed of octane, $C_8H_{18}(l)$, whose density is 0.692 g/mL. (**b**) Repeat the calculation for a truck that has a gas mileage of 2 km/L.

3.131 Section 2.9 introduced the idea of structural isomerism, with 1-propanol and 2-propanol as examples. Determine which of these properties would distinguish these two substances: (**a**) boiling point, (**b**) combustion analysis results, (**c**) molecular weight, (**d**) density at a given temperature and pressure. You can check on the properties of these two compounds in

Wolfram Alpha (http://www.wolframalpha.com/) or the *CRC Handbook of Chemistry and Physics*.

3.132 NO_x is a generic term for the nitrogen oxides, NO and NO_2. NO_x gases are air pollutants that react to form smog and acid rain. In order to reduce NO_x emission from vehicle, catalytic converters are installed in car exhausts to decompose NO and NO_2 respectively into N_2 and O_2 (**a**) Write the balanced chemical equations for the decomposition of NO and NO_2 respectively. (**b**) If the car produces 100 g NO_x a day, with equal mole ratio of NO and NO_2, how many grams of NO and NO_2 are produced respectively?

3.133 Hydrogen cyanide, HCN, is a poisonous gas. The lethal dose is approximately 300 mg HCN per kilogram of air when inhaled. (**a**) Calculate the amount of HCN that gives the lethal dose in a small laboratory room measuring 3.5 × 4.5 × 2.5 m. The density of air at 26 °C is 0.00118 g/cm^3. (**b**) If the HCN is formed by reaction of NaCN with an acid such as H_2SO_4, what mass of NaCN gives the lethal dose in the room?

$$2\,NaCN(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2\,HCN(g)$$

(**c**) HCN forms when synthetic fibers containing Orlon® or Acrilan® burn. Acrilan® has an empirical formula of CH_2CHCN, so HCN is 50.9% of the formula by mass. A rug measures 3.5 × 4.5 m and contains 850 g of Acrilan® fibers per square yard of carpet. If the rug burns, will a lethal dose of HCN be generated in the room? Assume that the yield of HCN from the fibers is 20% and that the carpet is 50% consumed.

3.134 The source of oxygen that drives the internal combustion engine in an automobile is air. Air is a mixture of gases, principally N_2(~79%) and O_2(~20%). In the cylinder of an automobile engine, nitrogen can react with oxygen to produce nitric oxide gas, NO. As NO is emitted from the tailpipe of the car, it can react with more oxygen to produce nitrogen dioxide gas. (**a**) Write balanced chemical equations for both reactions. (**b**) Both nitric oxide and nitrogen dioxide are pollutants that can lead to acid rain and global warming; collectively, they are called "NO_x" gases. In 2009, the United States emitted an estimated 19 million tons of nitrogen dioxide into the atmosphere. How many grams of nitrogen dioxide is this? (**c**) The production of NO_x gases is an unwanted side reaction of the main engine combustion process that turns octane, C_8H_{18}, into CO_2 and water. If 85% of the oxygen in an engine is used to combust octane and the remainder used to produce nitrogen dioxide, calculate how many grams of nitrogen dioxide would be produced during the combustion of 500 g of octane.

3.135 The thermite reaction,

$$Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$$

produces so much heat that the Fe product melts. This reaction is used industrially to weld metal parts under water, where a torch cannot be employed. It is also a favorite chemical demonstration in the lecture hall (on a small scale).

(**a**) Balance the chemical equation for the thermite reaction, and include the proper states of matter.

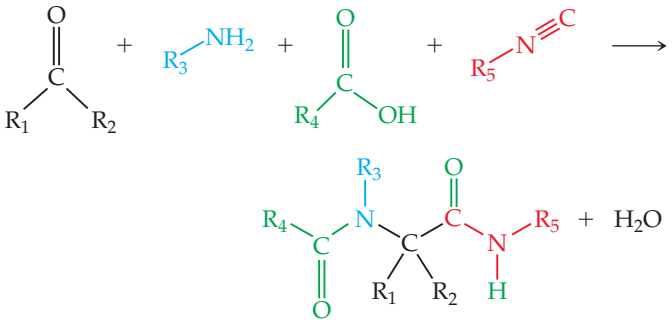
(**b**) Calculate how many grams of aluminum are needed to completely react with 500.0 g of Fe_2O_3 in this reaction.

(**c**) This reaction produces 852 kJ of heat per mole of Fe_2O_3 reacted. How many grams of Fe_2O_3 are needed to produce 1.00 × 10^4 kJ of heat?

(**d**) If you performed the reverse reaction— aluminum oxide plus iron makes iron oxide plus aluminum—would that reaction have heat as a reactant or a product?

3.136 One of the most bizarre reactions in chemistry is called the Ugi reaction:

$$R_1C(=O)R_2 + R_3 - NH_2 + R_4COOH + R_5NC \rightarrow R_4C(=O)N(R_3)C(R_1R_2)C{=}ONHR_5 + H_2O$$



(**a**) Write out the balanced chemical equation for the Ugi reaction, for the case where R = $CH_3CH_2CH_2CH_2CH_2CH_2$— (this is called the *hexyl* group) for all compounds. (**b**) What mass of the "hexyl Ugi product" would you form if 435.0 mg of $CH_3\,CH_2CH_2CH_2CH_2CH_2NH_2$ was the limiting reactant?

Design an Experiment

You will learn later in this book that sulfur is capable of forming two common oxides, SO_2 and SO_3. One question that we might ask is whether the direct reaction between sulfur and oxygen leads to the formation of SO_2, SO_3, or a mixture of the two. This question has practical significance because SO_3 can go on to react with water to form sulfuric acid, H_2SO_4, which is produced industrially on a very large scale. Consider also that the answer to this question may depend on the relative amount of each element that is present and the temperature at which the reaction is carried out. For example, on the one hand, carbon and oxygen normally react to form CO_2, but when not enough oxygen is present, CO can form. On the other hand, under normal reaction conditions H_2 and O_2 react to form water, H_2O (rather than hydrogen peroxide H_2O_2), regardless of the starting ratio of hydrogen to oxygen.

Suppose you are given a bottle of sulfur, which is a yellow solid, a cylinder of O_2, a transparent reaction vessel that can be evacuated and sealed so that only sulfur, oxygen, and the product(s) of the reaction between the two are present, an analytical balance so that you can determine the masses of the reactants and/or products, and a furnace that can be used to heat the reaction vessel to 200 °C where the two elements react. (**a**) If you start with 0.10 mol of sulfur in the reaction vessel how many moles of oxygen would need to be added to form SO_2, assuming SO_2 forms exclusively? (**b**) How many moles of oxygen would be needed to form SO_3, assuming SO_3 forms exclusively? (**c**) Given the available equipment, how would you determine you had added the correct number of moles of each reactant to the reaction vessel? (**d**) What observation or experimental technique would you use to determine the identity of the reaction product(s)? Could differences in the physical properties of SO_2 and SO_3 be used to help identify the product(s)? Have any instruments been described in Chapters 1–3 that would allow you to identify the product(s)? (**e**) What experiments would you conduct to determine if the product(s) of this reaction (either SO_2 or SO_3 or a mixture of the two) can be controlled by varying the ratio of sulfur and oxygen that are added to the reaction vessel? What ratio(s) of S to O_2 would you test to answer this question?

4

REACTIONS IN AQUEOUS SOLUTION

WHAT'S AHEAD

4.1 ▶ General Properties of Aqueous Solutions

4.2 ▶ Precipitation Reactions

4.3 ▶ Acids, Bases, and Neutralization Reactions

4.4 ▶ Oxidation–Reduction Reactions

4.5 ▶ Concentrations of Solutions

4.6 ▶ Solution Stoichiometry and Chemical Analysis

4.1 | General Properties of Aqueous Solutions



Water is the most abundant liquid on our planet. It covers nearly two-thirds of our planet, and this simple substance has been the key to much of Earth's evolutionary history. Life almost certainly originated in water, and the need for water by all forms of life has helped determine diverse biological structures. Indeed, most of the mass of our bodies is water, and it has a composition close to that of seawater. The chemical reactions responsible for life occur in water. By the end of this section, you should be able to

- Identify what occurs when a substance dissolves in water

A *solution* is a homogeneous mixture of two or more substances. The substance present in the greatest quantity is usually called the **solvent**, and the other substances are called **solutes**; they are said to be *dissolved in* the solvent. When a small amount of sodium chloride (NaCl) is dissolved in a large quantity of water, for example, water is the solvent and sodium chloride is the solute.

Electrolytes and Nonelectrolytes

At a young age we learn not to bring electrical devices into the bathtub so as not to electrocute ourselves. That is a useful lesson because most of the water we encounter in daily life is electrically conducting. Pure water, however, is a very poor conductor of electricity. The conductivity of bathwater originates from the substances dissolved in the water, not from the water itself.

Not all substances that dissolve in water make the resulting solution conducting. Figure 4.1 shows a simple experiment to test the electrical conductivity of three solutions: pure water, a solution of table sugar (sucrose) in water, and a solution of table salt (sodium chloride) in water. A light bulb is connected to a battery-powered electrical circuit that contains two electrodes submerged in a beaker of each solution. In order for the light bulb to turn on, there must be an electrical current (that is, a flow of electrically charged particles) between the two electrodes immersed in the solution. Because the light bulb does not turn on in pure water, we conclude that there are not enough charged particles in pure water to create a circuit; water must then mostly exist as H_2O molecules. The solution containing sucrose ($C_{12}H_{22}O_{11}$) also does not turn on the light bulb; therefore, we conclude that the sucrose molecules in solution are uncharged. But the solution containing NaCl does provide enough charged particles to create an electrical circuit and turn on the light bulb. This is experimental evidence that Na^+ and Cl^- ions are formed in aqueous solution.

A substance (such as NaCl) whose aqueous solutions contain ions is called an **electrolyte**. A substance (such as $C_{12}H_{22}O_{11}$) that does not form ions in solution is called a **nonelectrolyte**. The different classifications of NaCl and $C_{12}H_{22}O_{11}$ arise largely because NaCl is an ionic compound, whereas $C_{12}H_{22}O_{11}$ is a molecular compound.

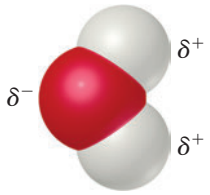


▲ **Figure 4.1** Completion of an electrical circuit with an electrolyte turns on the light.

How Compounds Dissolve in Water

Recall from Figure 2.17 that solid NaCl consists of an orderly arrangement of Na^+ and Cl^- ions. When NaCl dissolves in water, each ion separates from the solid structure and disperses throughout the solution [**Figure 4.2**(**a**)]. The ionic solid *dissociates* into its component ions as it dissolves.

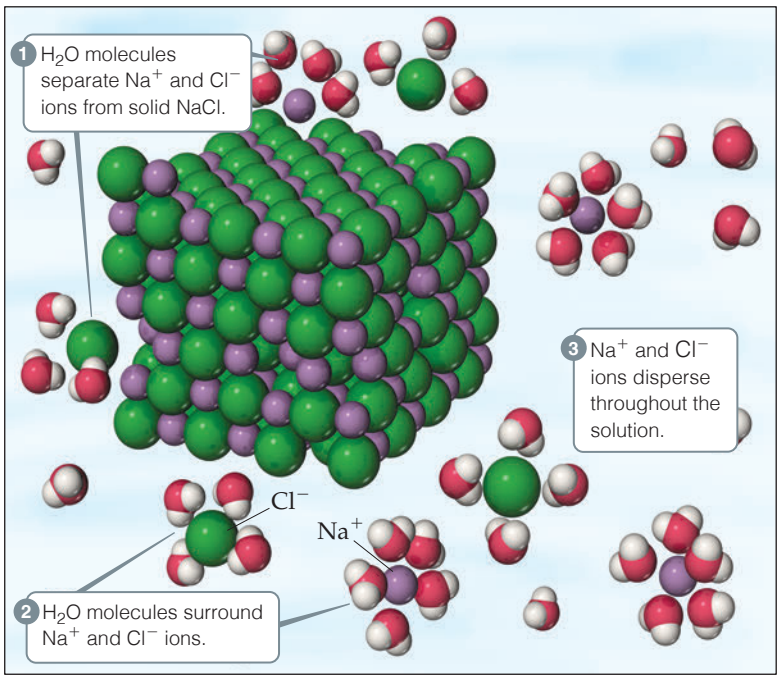
Water is a very effective solvent for ionic compounds. Although H_2O has no overall charge, the O atom is rich in electrons and has a partial negative charge relative to the H atoms, while each H atom has a partial positive charge. The lowercase Greek letter delta (δ) is used to denote partial charge: A partial negative charge is denoted δ^- ("delta minus"), and a partial positive charge is denoted by δ^+ ("delta plus"). Cations are attracted by the negative end of H_2O, and anions are attracted by the positive end.



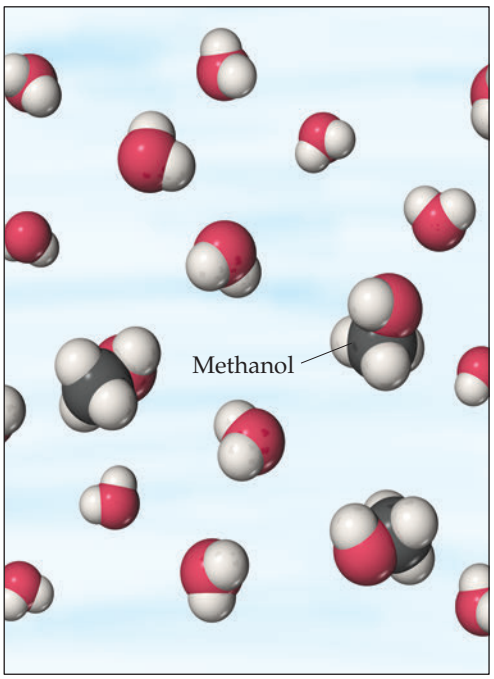
As an ionic compound dissolves, the ions become surrounded by H_2O molecules, as shown in Figure 4.2(a). The ions are said to be *solvated*. In chemical equations, we denote solvated ions by writing them as $Na^+(aq)$ and $Cl^-(aq)$, where *aq* is an abbreviation for "aqueous." **Solvation** helps stabilize the ions in solution and prevents cations and anions from recombining. Furthermore, because the ions and their shells of surrounding water molecules are free to move about, the ions become dispersed uniformly throughout the solution.

We can usually predict the nature of the ions in a solution of an ionic compound from the chemical name of the substance. Sodium sulfate (Na_2SO_4), for example,

Go Figure Do both, just one, or neither of the following solutions conduct electricity? If just one, which one?



(a) Ionic compounds like sodium chloride, NaCl, form ions when they dissolve.



(b) Molecular substances like methanol, CH_3OH, dissolve without forming ions.

▲ **Figure 4.2** **Dissolution in water.** (**a**) When an ionic compound, such as sodium chloride, NaCl, dissolves in water, H_2O molecules separate, surround, and uniformly disperse the ions into the liquid. (**b**) Molecular substances that dissolve in water, such as methanol, CH_3OH, usually do so without forming ions. We can think of methanol in water as a simple mixing of two molecular species. In both (a) and (b) the water molecules have been moved apart so that the solute particles can be seen clearly.

dissociates into sodium ions (Na^+) and sulfate ions (SO_4^{2-}). You must remember the formulas and charges of common ions (Tables 2.4 and 2.5) to understand the forms in which ionic compounds exist in aqueous solution.

When a molecular compound such as sucrose or methanol [Figure 4.2(**b**)] dissolves in water, the solution usually consists of intact molecules dispersed throughout the solution. Consequently, most molecular compounds are nonelectrolytes. A few molecular substances do have aqueous solutions that contain ions. Acids are the most important of these solutions. For example, when HCl(*g*) dissolves in water to form HCl(*aq*), the molecule *ionizes*; that is, it dissociates into $H^+(aq)$ and $Cl^-(aq)$ ions.

Strong and Weak Electrolytes

Electrolytes differ in the extent to which they conduct electricity. **Strong electrolytes** are those solutes that exist in solution completely or nearly completely as ions. Essentially all water-soluble ionic compounds (such as NaCl) and a few molecular compounds (such as HCl) are strong electrolytes. **Weak electrolytes** are those solutes that exist in solution mostly in the form of neutral molecules with only a small fraction in the form of ions. For example, in a solution of acetic acid (CH_3COOH), most of the solute is present as $CH_3COOH(aq)$ molecules. Only a small fraction (about 1%) of the CH_3COOH has dissociated into $H^+(aq)$ and $CH_3COO^-(aq)$ ions.*

We must be careful not to confuse the extent to which an electrolyte dissolves (its solubility) with whether it is strong or weak. For example, CH_3COOH is extremely soluble in water but is a weak electrolyte. $Ca(OH)_2$, in contrast, is not very soluble in water, but the amount that does dissolve dissociates almost completely. Thus, $Ca(OH)_2$ is a strong electrolyte.

When a weak electrolyte, such as acetic acid, ionizes in solution, we write the reaction in the form

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \qquad [4.1]$$

The half-arrows pointing in opposite directions mean that the reaction is significant in both directions. At any given moment some CH_3COOH molecules are ionizing to form H^+ and CH_3COO^- ions, and some of the H^+ and CH_3COO^- ions are recombining to form CH_3COOH. The balance between these opposing processes determines the relative numbers of ions and neutral molecules. This balance produces a state of **chemical equilibrium** in which the relative numbers of each type of ion or molecule in the reaction are constant over time. Chemists use half-arrows pointing in opposite directions to represent reactions that go both forward and backward to achieve equilibrium, such as the ionization of weak electrolytes. In contrast, a single reaction arrow is used for reactions that largely go forward, such as the ionization of strong electrolytes. Because HCl is a strong electrolyte, we write the equation for the ionization of HCl as

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq) \qquad [4.2]$$

The absence of a left-pointing half-arrow indicates that the H^+ and Cl^- ions have no tendency to recombine to form HCl molecules in aqueous solution.

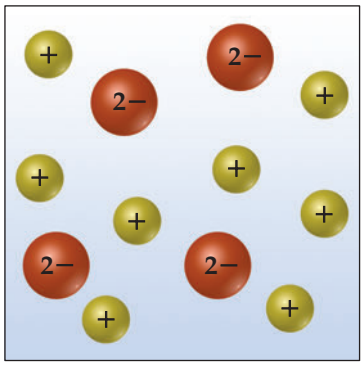
In the following sections, we will look at how a compound's composition lets us predict whether it is a strong electrolyte, weak electrolyte, or nonelectrolyte. For the moment, you need only to remember that *water-soluble ionic compounds are strong electrolytes*. Ionic compounds can usually be identified by the presence of both metals and nonmetals [for example, NaCl, $FeSO_4$, and $Al(NO_3)_3$]. Ionic compounds containing the ammonium ion, NH_4^+ [for example, NH_4Br and $(NH_4)_2CO_3$], are exceptions to this rule of thumb.

*The chemical formula of acetic acid is sometimes written $HC_2H_3O_2$ so that the formula looks like that of other common acids such as HCl. The formula (CH_3COOH) conforms to the molecular structure of acetic acid, with the acidic H on the O atom at the end of the formula.

Sample Exercise 4.1

Relating Relative Numbers of Anions and Cations to Chemical Formulas

The accompanying diagram represents an aqueous solution of either $MgCl_2$, KCl, or K_2SO_4 with the water molecules left out for clarity. Which solution does the drawing best represent?



SOLUTION

Analyze We are asked to associate the charged spheres in the diagram with ions present in a solution of an ionic substance.

Plan We examine each ionic substance given to determine the relative numbers and charges of its ions. We then correlate these ionic species with the ones shown in the diagram.

Solve The diagram shows twice as many cations as anions, consistent with the formulation K_2SO_4.

Check Notice that the net charge in the diagram is zero, as it must be if it is to represent an ionic substance.

Practice Exercise

If you were to draw diagrams representing aqueous solutions of (**a**) $NiSO_4$, (**b**) $Ca(NO_3)_2$, (**c**) Na_3PO_4, (**d**) $Al_2(SO_4)_3$, how many anions would you show if each diagram contained six cations?

Self-Assessment Exercise

4.1 Which of the following groups of substances contain only strong electrolytes?

(a) KBr, SO_2, $CaCl_2$

(b) HCl, NH_3, NaOH

(c) $NaNO_3$, HCl, Rb_2SO_4

Exercises

4.2 State whether each of the following statements is true or false. Justify your answer in each case.

(**a**) Electrolyte solutions conduct electricity because electrons are moving through the solution.

(**b**) If you add a nonelectrolyte to an aqueous solution that already contains an electrolyte, the electrical conductivity will not change.

4.3 We have learned in this chapter that many ionic solids dissolve in water as strong electrolytes; that is, as separated ions in solution. Which statement is most correct about this process? (**a**) Water is a strong acid and therefore is good at dissolving ionic solids. (**b**) Water is good at solvating ions because the hydrogen and oxygen atoms in water molecules bear partial charges. (**c**) The hydrogen and oxygen bonds of water are easily broken by ionic solids.

4.4 Ignoring protolysis reactions (i.e. proton transfer reaction), specify what ions are present in a solution upon dissolving each of the following substances in water: (**a**)Li_2CO_3, (**b**)$(NH_4)_3PO_4$, (**c**) $Na_2Cr_2O_7$, (**d**) $NaPF_6$.

4.5 When carbon dioxide dissolves in water, it is in equilibrium with carbonic acid H_2CO_3, which is a weak electrolyte. What solutes are present in an aqueous solution of this compound? Write the chemical equation for the ionization of H_2CO_3.

Answers to Self-Assessment Exercises

4.1 (c)

4.2 | Precipitation Reactions



"Hard" water contains calcium and magnesium ions. These ions can react with soap to form a white solid that forms around baths, showers and basins. This is an example of a chemical reaction between two soluble materials to form an insoluble product. Scum, as it is called, is harmless, though unsightly, and there are many cleaning products designed to remove it.

By the end of this section, you should be able to

- Predict if a precipitate forms when two aqueous solutions are mixed

Figure 4.3 shows two clear solutions being mixed. One solution contains potassium iodide, KI, dissolved in water, and the other contains lead nitrate, $Pb(NO_3)_2$, dissolved in water. The reaction between these two solutes produces a water-insoluble yellow solid. Reactions that result in the formation of an insoluble product are called **precipitation reactions**. A **precipitate** is an insoluble solid formed by a reaction in solution. In Figure 4.3 the precipitate is lead iodide (PbI_2), a compound that has a very low solubility in water:

$$Pb(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow PbI_2(s) + 2\,KNO_3(aq) \qquad [4.3]$$

The other product of this reaction, potassium nitrate (KNO_3), remains in solution.

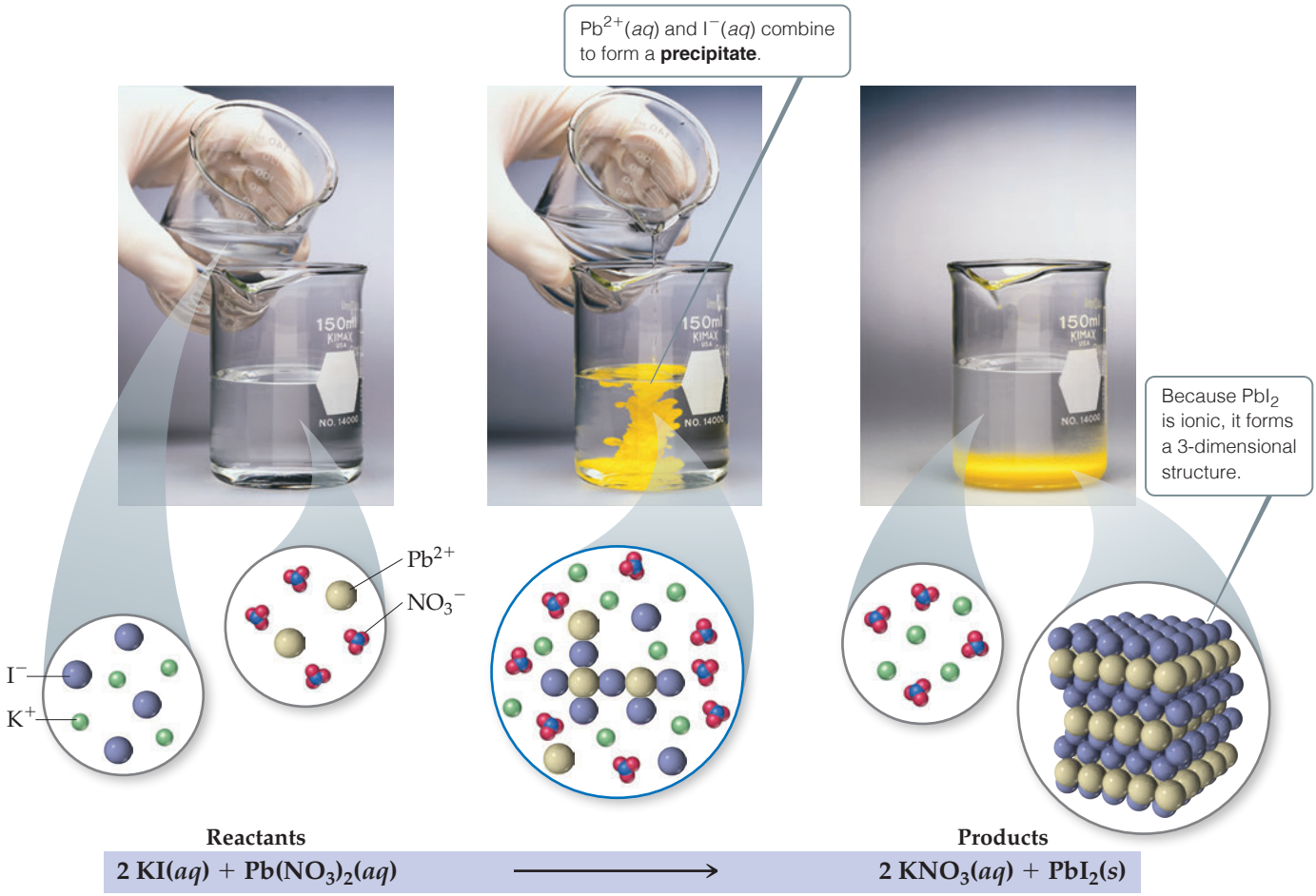
Precipitation reactions occur when pairs of oppositely charged ions attract each other so strongly that they form an insoluble ionic solid. To predict whether certain combinations of ions form insoluble compounds, we must consider some guidelines concerning the solubilities of common ionic compounds.

Solubility Guidelines for Ionic Compounds

The **solubility** of a substance at a given temperature is the amount of the substance that can be dissolved in a given quantity of solvent at that temperature. Any substance with a solubility less than 0.01 mol/L will be considered *insoluble*. In these cases, the attraction between the oppositely charged ions in the solid is too great for the water molecules to separate the ions to any significant extent; the substance remains largely undissolved.

Unfortunately, there are no rules based on simple physical properties such as ionic charge to guide us in predicting whether a particular ionic compound will be soluble. Experimental observations, however, have led to guidelines for predicting solubility for ionic compounds. For example, experiments show that all common ionic compounds that contain the nitrate anion, NO_3^-, are soluble in water. **Table 4.1** summarizes the

Go Figure Which ions remain in solution after PbI_2 precipitation is complete?



▲ **Figure 4.3** A precipitation reaction.

TABLE 4.1 Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+}, and Ba^{2+}

solubility guidelines for common ionic compounds. The table is organized according to the anion in the compound, but it also reveals many important facts about cations. Note that *all common ionic compounds of the alkali metal ions (group 1 of the periodic table) and of the ammonium ion* (NH_4^+) *are soluble in water.*

How to Predict Whether a Precipitate Forms When Strong Electrolytes Mix

1. Note the ions present in the reactants.
2. Consider the possible cation–anion combinations.
3. Use Table 4.1 to determine if any of the combinations is insoluble.

For example, will a precipitate form when solutions of $Mg(NO_3)_2$ and NaOH are mixed? Both substances are soluble ionic compounds and strong electrolytes. Mixing the solutions first produces a solution containing Mg^{2+}, NO_3^-, Na^+, and OH^- ions. Will either cation interact with either anion to form an insoluble compound? Knowing from Table 4.1 that $Mg(NO_3)_2$ and NaOH are both soluble in water, our only possibilities are Mg^{2+} with OH^- and Na^+ with NO_3^-. From Table 4.1 we see that hydroxides are generally insoluble. Because Mg^{2+} is not an exception, $Mg(OH)_2$ is insoluble and thus forms a precipitate. $NaNO_3$, however, is soluble, so Na^+ and NO_3^- remain in solution. The balanced equation for the precipitation reaction is

$$Mg(NO_3)_2(aq) + 2\,NaOH(aq) \longrightarrow Mg(OH)_2(s) + 2\,NaNO_3(aq) \qquad [4.4]$$

Exchange (Metathesis) Reactions

Notice in Equation 4.4 that the reactant cations exchange anions—Mg^{2+} ends up with OH^-, and Na^+ ends up with NO_3^-. The chemical formulas of the products are based on the charges of the ions—two OH^- ions are needed to give a neutral compound with Mg^{2+}, and one NO_3^- ion is needed to give a neutral compound with Na^+. *The equation can be balanced only after the chemical formulas of the products have been determined.*

Reactions in which cations and anions appear to exchange partners conform to the general equation

$$AX + BY \longrightarrow AY + BX \qquad [4.5]$$

Example: $$AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$$

Such reactions are called either **exchange reactions** or **metathesis reactions** (meh-TATH-eh-sis, Greek for "to transpose"). Precipitation reactions conform to this pattern, as do many neutralization reactions between acids and bases, as we will see in Section 4.3.

How To Balance a Metathesis Reaction

1. Use the chemical formulas of the reactants to determine which ions are present.
2. Write the chemical formulas of the products by combining the cation from one reactant with the anion of the other, using the ionic charges to determine the subscripts in the chemical formulas.
3. Check the water solubilities of the products. For a precipitation reaction to occur, at least one product must be insoluble in water.
4. Balance the equation.

Sample Exercise 4.2

Using Solubility Rules

Classify these ionic compounds as soluble or insoluble in water: (**a**) sodium carbonate, Na_2CO_3, (**b**) lead sulfate, $PbSO_4$.

SOLUTION

Analyze We are given the names and formulas of two ionic compounds and asked to predict whether they are soluble or insoluble in water.

Plan We can use Table 4.1 to answer the question. Thus, we need to focus on the anion in each compound because the table is organized by anions.

Solve

(**a**) According to Table 4.1, most carbonates are insoluble. But carbonates of the alkali metal cations (such as sodium ion) are an exception to this rule and are soluble. Thus, Na_2CO_3 is soluble in water.

(**b**) Table 4.1 indicates that although most sulfates are water soluble, the sulfate of Pb^{2+} is an exception. Thus, $PbSO_4$ is insoluble in water.

Practice Exercise

Which of the following compounds is insoluble in water?
(**a**) $(NH_4)_2S$ (**b**) $CaCO_3$ (**c**) NaOH (**d**) Ag_2SO_4 (**e**) $Pb(CH_3COO)_2$

Sample Exercise 4.3

Predicting a Metathesis Reaction

(**a**) Predict the identity of the precipitate that forms when aqueous solutions of $BaCl_2$ and K_2SO_4 are mixed. (**b**) Write the balanced chemical equation for the reaction.

SOLUTION

Analyze We are given two ionic reactants and asked to predict the insoluble product that they form.

Plan We need to write the ions present in the reactants and exchange the anions between the two cations. Once we have written the chemical formulas for these products, we can use Table 4.1 to determine which is insoluble in water. Knowing the products also allows us to write the equation for the reaction.

Solve

(**a**) The reactants contain Ba^{2+}, Cl^-, K^+, and SO_4^{2-} ions. Exchanging the anions gives us $BaSO_4$ and KCl. According to Table 4.1, most compounds of SO_4^{2-} are soluble but those of Ba^{2+} are not. Thus, $BaSO_4$ is insoluble and will precipitate from solution. KCl is soluble.

(**b**) From part (a) we know the chemical formulas of the products, $BaSO_4$ and KCl. The balanced equation is

$$BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,KCl(aq)$$

Practice Exercise

(**a**) What compound precipitates when aqueous solutions of $Fe_2(SO_4)_3$ and LiOH are mixed? (**b**) Write a balanced equation for the reaction.

Ionic Equations and Spectator Ions

In writing equations for reactions in aqueous solution, it is often useful to indicate whether the dissolved substances are present predominantly as ions or as molecules. Let's reconsider the precipitation reaction between $Pb(NO_3)_2$ and 2 KI (Eq. 4.3):

$$Pb(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow PbI_2(s) + 2\,KNO_3(aq)$$

An equation written in this fashion, showing the complete chemical formulas of reactants and products, is called a **molecular equation** because it shows chemical formulas without indicating ionic character. Because $Pb(NO_3)_2$, KI, and KNO_3 are all water-soluble ionic compounds and therefore strong electrolytes, we can write the equation in a form that indicates which species exist as ions in the solution:

$$Pb^{2+}(aq) + 2\,NO_3^-(aq) + 2\,K^+(aq) + 2\,I^-(aq) \longrightarrow PbI_2(s) + 2\,K^+(aq) + 2\,NO_3^-(aq) \quad [4.6]$$

An equation written in this form, with all soluble strong electrolytes shown as ions, is called a **complete ionic equation**.

Notice that $K^+(aq)$ and $NO_3^-(aq)$ appear on both sides of Equation 4.6. Ions that appear in identical forms on both sides of a complete ionic equation, called **spectator ions**, play no direct role in the reaction. Spectator ions can be canceled, like algebraic quantities, on either side of the reaction arrow, since they are not reacting with anything. Once we cancel the spectator ions, we are left with the **net ionic equation**, which is one that includes only the ions and molecules directly involved in the reaction:

$$Pb^{2+}(aq) + 2\,I^-(aq) \longrightarrow PbI_2(s) \quad [4.7]$$

Because charge is conserved in reactions, the sum of the ionic charges must be the same on both sides of a balanced net ionic equation. In this case, the 2+ charge of the cation and the two 1− charges of the anions add to zero, the charge of the electrically neutral product. *If every ion in a complete ionic equation is a spectator, no reaction occurs.*

Net ionic equations illustrate the similarities between various reactions involving electrolytes. For example, Equation 4.7 expresses the essential feature of the precipitation reaction between any strong electrolyte containing $Pb^{2+}(aq)$ and any strong electrolyte containing $I^-(aq)$: The ions combine to form a precipitate of PbI_2. Thus, a net ionic

equation demonstrates that more than one set of reactants can lead to the same net reaction. For example, aqueous solutions of KI and MgI_2 share many chemical similarities because both contain I^- ions. Either solution when mixed with a $Pb(NO_3)_2$ solution produces $PbI_2(s)$. The complete ionic equation, however, identifies the actual reactants that participate in a reaction.

How to Write a Net Ionic Equation

1. Write a balanced molecular equation for the reaction.
2. Rewrite the equation to show the ions that form in solution when each soluble strong electrolyte dissociates into its ions. *Only strong electrolytes dissolved in aqueous solution are written in ionic form.*
3. Identify and cancel spectator ions.

Sample Exercise 4.4

Writing a Net Ionic Equation

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of calcium chloride and sodium carbonate are mixed.

SOLUTION

Analyze Our task is to write a net ionic equation for a precipitation reaction, given the names of the reactants present in solution.

Plan We write the chemical formulas of the reactants and products and then determine which product is insoluble. We then write and balance the molecular equation. Next, we write each soluble strong electrolyte as separated ions to obtain the complete ionic equation. Finally, we eliminate the spectator ions to obtain the net ionic equation.

Solve Calcium chloride is composed of calcium ions, Ca^{2+}, and chloride ions, Cl^-; hence, an aqueous solution of the substance is $CaCl_2(aq)$. Sodium carbonate is composed of Na^+ ions and CO_3^{2-} ions; hence, an aqueous solution of the compound is $Na_2CO_3(aq)$. In the molecular equations for precipitation reactions, the anions and cations appear to exchange partners. Thus, we put Ca^{2+} and CO_3^{2-} together to give $CaCO_3$ and Na^+ and Cl^- together to give NaCl. According to the solubility guidelines in Table 4.1, $CaCO_3$ is insoluble and NaCl is soluble. The balanced molecular equation is

$$CaCl_2(aq) + Na_2CO_3(aq) \longrightarrow CaCO_3(s) + 2\,NaCl(aq)$$

In a complete ionic equation, *only* dissolved strong electrolytes (such as soluble ionic compounds) are written as separate ions. As the (*aq*) designations remind us, $CaCl_2$, Na_2CO_3, and NaCl are all dissolved in the solution. Furthermore, they are all strong electrolytes. $CaCO_3$ is an ionic compound, but it is not soluble. We do not write the formula of any insoluble compound as its component ions. Thus, the complete ionic equation is

$$Ca^{2+}(aq) + 2\,Cl^-(aq) + 2\,Na^+(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)$$

The spectator ions are Na^+ and Cl^-. Canceling them gives the following net ionic equation:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

Check We can check our result by confirming that both the elements and the electric charge are balanced. Each side has one Ca, one C, and three O, and the net charge on each side equals 0.

Comment If none of the ions in an ionic equation is removed from solution or changed in some way, all ions are spectator ions and a reaction does not occur.

Practice Exercise

Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of silver nitrate and potassium phosphate are mixed.

Self-Assessment Exercise

4.6 Which combination of solutions will form a precipitate?

(a) $KOH(aq)$ and $MgSO_4(aq)$

(b) $NaOH(aq)$ and $KNO_3(aq)$

(c) $NH_4Cl(aq)$ and $Rb_2CO_3(aq)$

Exercises

4.7 Using solubility guidelines, predict whether each of the following compounds is soluble or insoluble in water: (**a**) Hg_2SO_4, (**b**) NH_4OH, (**c**) $Ni(CH_3COO)_2$, (**d**) $AgNO_3$, (**e**) $FeCO_3$.

4.8 Will precipitation occur when the following solutions are mixed? If so, write a balanced chemical equation for the reaction. (**a**) $Ca(CH_3COO)_2$ and NaOH, (**b**) K_2CO_3 and NH_4NO_3, (**c**) Na_2S and $FeCl_3$.

4.9 Write balanced net ionic equations for the reactions that occur in each of the following cases. Identify the spectator ion or ions in each reaction.

(**a**) $Ba(OH)_2(aq) + FeCl_3(aq) \longrightarrow$

(**b**) $ZnCl_2(aq) + Cs_2CO_3(aq) \longrightarrow$

(**c**) $Na_2S(aq) + CoSO_4(aq) \longrightarrow$

4.10 Separate samples of a solution of an unknown salt are treated with dilute solutions of HBr, H_2SO_4, and NaOH. A precipitate forms in all three cases. Which of the following cations could be present in the unknown salt solution: K^+, Pb^{2+}, Ba^{2+}?

4.11 You know that an unlabeled bottle contains an aqueous solution of one of the following: $AgNO_3$, $CaCl_2$, or $Al_2(SO_4)_3$. A friend suggests that you test a portion of the solution with $Ba(NO_3)_2$ and then with NaCl solutions. According to your friend's logic, which of these chemical reactions could occur, thus helping you identify the solution in the bottle? (**a**) Barium sulfate could precipitate. (**b**) Silver chloride could precipitate. (**c**) Silver sulfate could precipitate. (**d**) More than one, but not all, of the reactions described in answers a–c could occur. (**e**) All three reactions described in answers a–c could occur.

Answers to Self-Assessment Exercises

4.6 (a)

4.3 Acids, Bases, and Neutralization Reactions



Many acids and bases are industrial and household substances, and some are important components of biological fluids. Hydrochloric acid, for example, is an important industrial chemical and the main constituent of gastric juice in your stomach. Vinegar and lemon juice are common household acids. Ammonia and baking soda (sodium hydrogen carbonate) are common household bases. Acids and bases are also common electrolytes.

By the end of this section, you should be able to

- Recognize the common types of reaction that acids and bases undergo

Acids

As noted in Section 2.8, **acids** are substances that ionize in aqueous solution to form hydrogen ions $H^+(aq)$. Because a hydrogen atom consists of a proton and an electron, H^+ is simply a proton. Thus, acids are often called *proton donors*. Molecular models of four common acids are shown in **Figure 4.4**.

Protons in aqueous solution are solvated by water molecules, just as other cations are [Figure 4.2(**a**)]. In writing chemical equations involving protons in water, therefore, we write $H^+(aq)$.

Molecules of different acids ionize to form different numbers of H^+ ions. Both HCl and HNO_3 are *monoprotic* acids, yielding one H^+ per molecule of acid. Sulfuric acid, H_2SO_4, is a *diprotic* acid, one that yields two H^+ per molecule of acid. The ionization of H_2SO_4 and other diprotic acids occurs in two steps:

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \qquad [4.8]$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \qquad [4.9]$$

Although H_2SO_4 is a strong electrolyte, only the first ionization (Equation 4.8) is complete. Thus, aqueous solutions of sulfuric acid contain a mixture of $H^+(aq)$, $HSO_4^-(aq)$, and $SO_4^{2-}(aq)$.

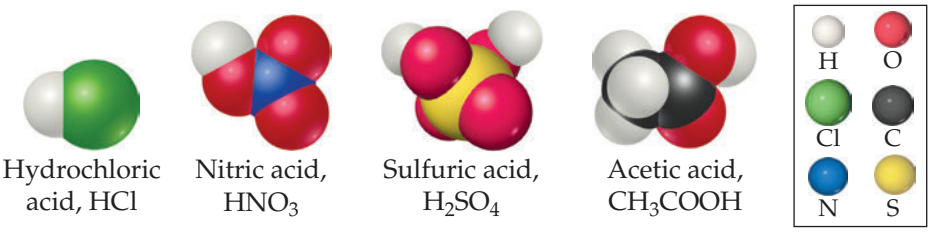
The molecule CH_3COOH (acetic acid) that we have mentioned previously is the primary component in vinegar. Acetic acid has four hydrogens, as Figure 4.4 shows, but only one of them, the H that is bonded to an oxygen in the —COOH group, is ionized in water. Thus, the H in the COOH group breaks its O—H bond in water. The three other hydrogens in acetic acid are bound to carbon and do not break their C—H bonds in water. The reasons for this difference are very interesting and will be discussed in Chapter 16.

Bases

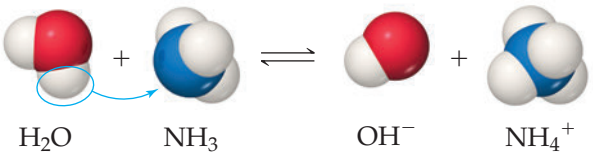
Bases are substances that accept (react with) H^+ ions. Bases produce hydroxide ions (OH^-) when they dissolve in water. Ionic hydroxide compounds, such as NaOH, KOH, and $Ca(OH)_2$, are among the most common bases. When dissolved in water, they dissociate into ions, introducing OH^- ions into the solution.

Compounds that do not contain OH^- ions can also be bases. For example, ammonia (NH_3) is a common base. When added to water, it accepts an H^+ ion from a water molecule and thereby produces an OH^- ion (**Figure 4.5**):

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^-(aq) + NH_4^+(aq) \qquad [4.10]$$



▶ **Figure 4.4** **Molecular models of four common acids.**



▶ **Figure 4.5** **Proton transfer.** An H_2O molecule acts as a proton donor (acid), and NH_3 acts as a proton acceptor (base). In aqueous solutions, only a fraction of the NH_3 molecules react with H_2O. Consequently, NH_3 is a weak electrolyte.

TABLE 4.2 Common Strong Acids and Bases

Strong Acids	Strong Bases
Hydrochloric acid, HCl	Group 1 metal hydroxides [LiOH, NaOH, KOH, RbOH, CsOH]
Hydrobromic acid, HBr	Some Group 2 metal hydroxides [$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$]
Hydroiodic acid, HI	
Chloric acid, $HClO_3$	
Perchloric acid, $HClO_4$	
Nitric acid, HNO_3	
Sulfuric acid (first proton), H_2SO_4	

Ammonia is a weak electrolyte because only about 1% of the NH_3 forms NH_4^+ and OH^- ions.

Strong and Weak Acids and Bases

Acids and bases that are strong electrolytes (completely ionized in solution) are **strong acids** and **strong bases**. Those that are weak electrolytes (partly ionized) are **weak acids** and **weak bases**. When reactivity depends only on $H^+(aq)$ concentration, strong acids are more reactive than weak acids. The reactivity of an acid, however, can depend on the anion as well as on $H^+(aq)$ concentration. For example, hydrofluoric acid (HF) is a weak acid (only partly ionized in aqueous solution), but it is very reactive and vigorously attacks many substances, including glass. This reactivity is due to the combined action of $H^+(aq)$ and $F^-(aq)$.

Table 4.2 lists the strong acids and bases we are most likely to encounter. You need to commit this information to memory in order to correctly identify strong electrolytes and write net ionic equations. The brevity of this list tells us that most acids are weak. (For H_2SO_4, as we noted earlier, only the first proton completely ionizes.) The only common strong bases are the common soluble metal hydroxides. The most common weak base is NH_3, which reacts with water to form OH^- ions (Equation 4.10).

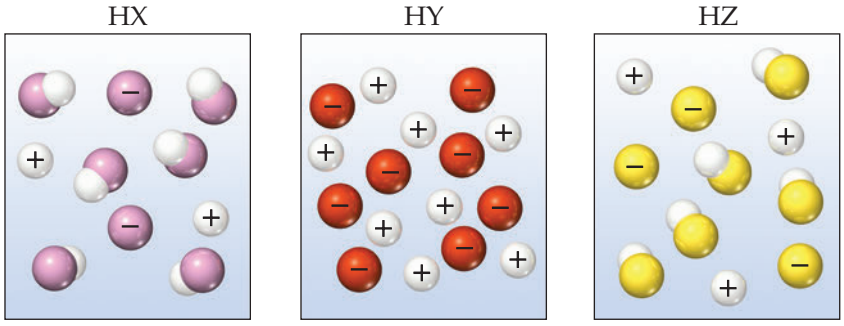
Identifying Strong and Weak Electrolytes

If we remember the common strong acids and bases (Table 4.2) and also remember that NH_3 is a weak base, we can make reasonable predictions about the electrolytic strength of

Sample Exercise 4.5

Comparing Acid Strengths

The following diagrams represent aqueous solutions of acids HX, HY, and HZ, with water molecules omitted for clarity. Rank the acids from strongest to weakest.



SOLUTION

Analyze We are asked to rank three acids from strongest to weakest, based on schematic drawings of their solutions.

Plan We can determine the relative numbers of uncharged molecular species in the diagrams. The strongest acid is the one with the most H^+ ions and fewest undissociated molecules in solution. The weakest acid is the one with the largest number of undissociated molecules.

Solve The order is HY > HZ > HX. HY is a strong acid because it is totally ionized (no HY molecules in solution), whereas both HX and HZ are weak acids, whose solutions consist of a mixture of molecules and ions. Because HZ contains more H^+ ions and fewer molecules than HX, it is a stronger acid.

Practice Exercise

A set of aqueous solutions are prepared containing different acids at the same concentration: acetic acid, chloric acid, and hydrobromic acid. Which solution(s) are the most electrically conductive? (**a**) chloric acid (**b**) hydrobromic acid (**c**) acetic acid (**d**) both chloric acid and hydrobromic acid (**e**) all three solutions have the same electrical conductivity

a great number of *water-soluble* substances. Table 4.3 summarizes our observations about electrolytes. We first ask whether the substance is ionic or molecular. If it is ionic, it is a strong electrolyte. If the substance is molecular, we ask whether it is an acid or a base. (It is an acid if it either has H first in the chemical formula or contains a COOH group.) If it is an acid, we use Table 4.2 to determine whether it is a strong or weak electrolyte: All strong acids are strong electrolytes, and all weak acids are weak electrolytes. If an acid is not listed in Table 4.2, it is probably a weak acid and therefore a weak electrolyte.

If our substance is a base, we use Table 4.2 to determine whether it is a strong base. NH_3 is the only molecular base that we consider in this chapter, and it is a weak base; Table 4.3 tells us it is therefore a weak electrolyte. Finally, any molecular substance that we encounter in this chapter that is not an acid or NH_3 is probably a nonelectrolyte.

TABLE 4.3 Summary of the Electrolytic Behavior of Common Soluble Ionic and Molecular Compounds

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids, weak bases	All other compounds

Sample Exercise 4.6

Identifying Strong, Weak, and Nonelectrolytes

Classify these dissolved substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: $CaCl_2$, HNO_3, C_2H_5OH (ethanol), HCOOH (formic acid), KOH.

SOLUTION

Analyze We are given several chemical formulas and asked to classify each substance as a strong electrolyte, weak electrolyte, or nonelectrolyte.

Plan The approach we take is outlined in Table 4.3. We can predict whether a substance is ionic or molecular based on its composition. As we saw in Section 2.7, most ionic compounds we encounter in this text are composed of a metal and a nonmetal, whereas most molecular compounds are composed only of nonmetals.

Solve Two compounds fit the criteria for ionic compounds: $CaCl_2$ and KOH. Because Table 4.3 tells us that all ionic compounds are strong electrolytes, that is how we classify these two substances. The three remaining compounds are molecular. Two of these molecular substances, HNO_3 and HCOOH, are acids. Nitric acid, HNO_3, is a common strong acid, as shown in Table 4.2, and therefore is a strong electrolyte. Because most acids are weak acids, our best guess would be that HCOOH is a weak acid (weak electrolyte), which is in fact the case. The remaining molecular compound, C_2H_5OH, is neither an acid nor a base, so it is a nonelectrolyte.

Comment Although ethanol, C_2H_5OH, has an OH group, it is not a metal hydroxide and therefore not a base. Rather, ethanol is a member of a class of organic compounds that have C—OH bonds, which are known as alcohols. Organic compounds containing the COOH group are called carboxylic acids (Chapter 16). Molecules that have this group are weak acids.

Practice Exercise

Which of these substances, when dissolved in water, is a strong electrolyte? (**a**) ammonia (**b**) hydrofluoric acid (**c**) folic acid (**d**) sodium nitrate (**e**) sucrose

Neutralization Reactions and Salts

The properties of acidic solutions are quite different from those of basic solutions. Acids have a sour taste, whereas bases have a bitter taste.* Acids change the colors of certain dyes in a way that differs from the way bases affect the same dyes. This is the principle behind the indicator known as litmus paper (**Figure 4.6**). Acid–base chemistry is an important theme throughout all of chemistry that we begin to explore here.

When a solution of an acid and a solution of a base are mixed, a **neutralization reaction** occurs. The products of the reaction have none of the characteristic properties of either the acidic solution or the basic solution. For example, when hydrochloric acid is mixed with a solution of sodium hydroxide, the reaction is

$$\underset{\text{(acid)}}{HCl(aq)} + \underset{\text{(base)}}{NaOH(aq)} \longrightarrow \underset{\text{(water)}}{H_2O(l)} + \underset{\text{(salt)}}{NaCl(aq)} \qquad [4.11]$$

Water and table salt, NaCl, are the products of the reaction. By analogy to this reaction, the term **salt** has come to mean any ionic compound whose cation comes from a base (for example, Na^+ from NaOH) and whose anion comes from an acid (for example, Cl^- from HCl). In general, *a neutralization reaction between an acid and a metal hydroxide produces water and a salt.*

Because HCl, NaOH, and NaCl are all water-soluble strong electrolytes, the complete ionic equation associated with Equation 4.11 is

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq) \qquad [4.12]$$

Therefore, the net ionic equation is

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad [4.13]$$

Equation 4.13 summarizes the main feature of the neutralization reaction between any strong acid and any strong base: $H^+(aq)$ and $OH^-(aq)$ ions combine to form $H_2O(l)$.

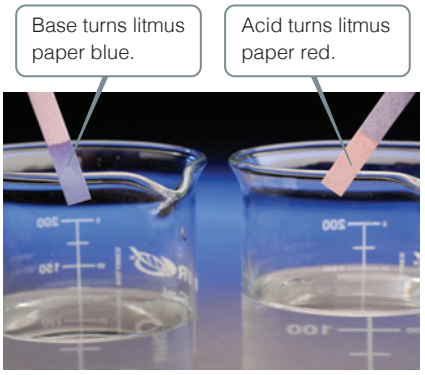
Figure 4.7 shows the neutralization reaction between hydrochloric acid and the water-insoluble base $Mg(OH)_2$:

Molecular equation:

$$Mg(OH)_2(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + 2\,H_2O(l) \qquad [4.14]$$

Net ionic equation:

$$Mg(OH)_2(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,H_2O(l) \qquad [4.15]$$



▲ **Figure 4.6 Litmus paper.** Litmus paper is coated with dyes that change color in response to exposure to either acids or bases.

Sample Exercise 4.7

Writing Chemical Equations for a Neutralization Reaction

For the reaction between aqueous solutions of acetic acid (CH_3COOH) and barium hydroxide, $Ba(OH)_2$, write (**a**) the balanced molecular equation, (**b**) the complete ionic equation, (**c**) the net ionic equation.

SOLUTION

Analyze We are given the chemical formulas for an acid and a base and asked to write a balanced molecular equation, a complete ionic equation, and a net ionic equation for their neutralization reaction.

Plan As Equation 4.11 and the italicized statement that follows it indicate, neutralization reactions form two products, H_2O and a salt. We examine the cation of the base and the anion of the acid to determine the composition of the salt.

Solve

(**a**) The salt contains the cation of the base (Ba^{2+}) and the anion of the acid (CH_3COO^-). Thus, the salt formula is $Ba(CH_3COO)_2$. According to Table 4.1, this compound is soluble in water. The unbalanced molecular equation for the neutralization reaction is:

$$CH_3COOH(aq) + Ba(OH)_2(aq) \longrightarrow H_2O(l) + Ba(CH_3COO)_2(aq)$$

*Tasting chemical solutions is not a good practice. However, we have all had acids such as ascorbic acid (vitamin C), acetylsalicylic acid (aspirin), and citric acid (in citrus fruits) in our mouths, and we are familiar with their characteristic sour taste. Soaps, which are basic, have the characteristic bitter taste of bases.

To balance this equation, we must provide two molecules of CH_3COOH to furnish the two CH_3COO^- ions and to supply the two H^+ ions needed to combine with the two OH^- ions of the base. The balanced molecular equation is:

$$2\,CH_3COOH(aq) + Ba(OH)_2(aq) \longrightarrow 2\,H_2O(l) + Ba(CH_3COO)_2(aq)$$

(b) To write the complete ionic equation, we identify the strong electrolytes and break them into ions. In this case $Ba(OH)_2$ and $Ba(CH_3COO)_2$ are both water-soluble ionic compounds and hence strong electrolytes. Thus, the complete ionic equation is:

$$2\,CH_3COOH(aq) + Ba^{2+}(aq) + 2OH^-(aq) \longrightarrow 2\,H_2O(l) + Ba^{2+}(aq) + 2\,CH_3COO^-(aq)$$

(c) Eliminating the spectator ion, Ba^{2+}, and simplifying coefficients give the net ionic equation:

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$

Check We can determine whether the molecular equation is balanced by counting the number of atoms of each kind on both sides of the arrow (10 H, 6 O, 4 C, and 1 Ba on each side). However, it is often easier to check equations by counting groups: There are 2 CH_3COO groups, as well as 1 Ba, and 4 additional H atoms and 2 additional O atoms on each side of the equation. The net ionic equation checks out because the numbers of each kind of element and the net charge are the same on both sides of the equation.

Practice Exercise

Which is the correct net ionic equation for the reaction of aqueous ammonia with nitric acid?

(a) $NH_4^+(aq) + H^+(aq) \longrightarrow NH_5^{2+}(aq)$

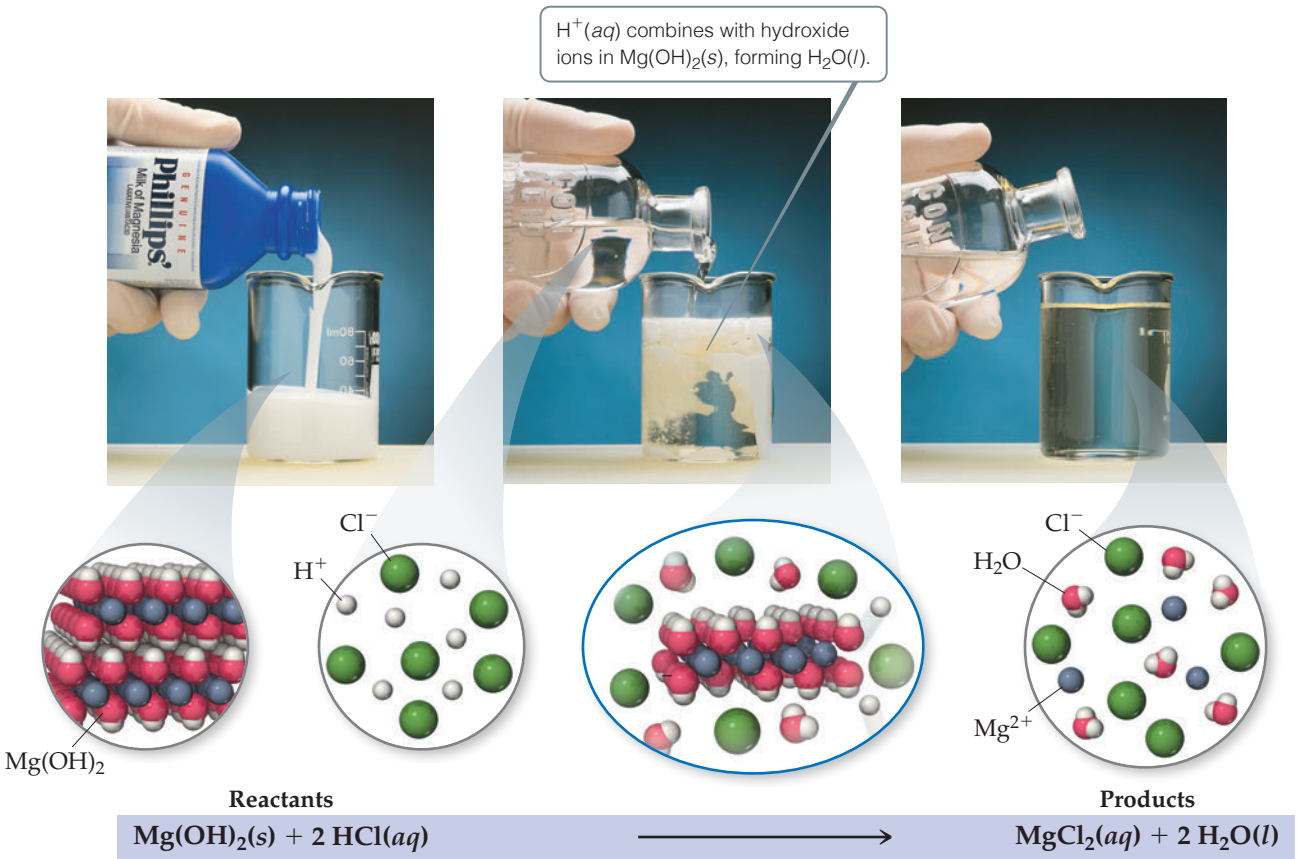
(b) $NH_3(aq) + NO_3^-(aq) \longrightarrow NH_2^-(aq) + HNO_3(aq)$

(c) $NH_2^-(aq) + H^+(aq) \longrightarrow NH_3(aq)$

(d) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

(e) $NH_4^+(aq) + NO_3^-(aq) \longrightarrow NH_4NO_3(aq)$

Go Figure If you used nitric acid instead of hydrochloric acid in this reaction, what products would form?



▲ **Figure 4.7 Neutralization reaction between $Mg(OH)_2(s)$ and hydrochloric acid.** Milk of magnesia is a suspension of water-insoluble magnesium hydroxide, $Mg(OH)_2(s)$, in water. When sufficient hydrochloric acid, $HCl(aq)$, is added, a reaction ensues that leads to an aqueous solution containing $Mg^{2+}(aq)$ and $Cl^-(aq)$ ions.

Notice that the OH^- ions (this time in a solid reactant) and H^+ ions combine to form H_2O. Because the ions exchange partners, neutralization reactions between acids and metal hydroxides are metathesis reactions.

Neutralization Reactions with Gas Formation

Many bases besides OH^- react with H^+ to form molecular compounds. Two of these that you might encounter in the laboratory are the sulfide ion and the carbonate ion. Both of these anions react with acids to form gases that have low solubilities in water.

Hydrogen sulfide (H_2S), the substance that gives rotten eggs their foul odor, forms when an acid such as $HCl(aq)$ reacts with a metal sulfide such as Na_2S:

Molecular equation:

$$2\,HCl(aq) + Na_2S(aq) \longrightarrow H_2S(g) + 2\,NaCl(aq) \qquad [4.16]$$

Net ionic equation:

$$2\,H^+(aq) + S^{2-}(aq) \longrightarrow H_2S(g) \qquad [4.17]$$

Carbonates and hydrogen carbonates react with acids to form $CO_2(g)$. Reaction of CO_3^{2-} or HCO_3^- with an acid first gives carbonic acid (H_2CO_3). For example, when hydrochloric acid is added to sodium hydrogen carbonate, the reaction is

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2CO_3(aq) \qquad [4.18]$$

Carbonic acid is unstable. If present in solution in sufficient concentrations, it decomposes to H_2O and CO_2, which escapes from the solution as a gas:

$$H_2CO_3(aq) \longrightarrow H_2O(l) + CO_2(g) \qquad [4.19]$$

The overall reaction is summarized by the following equations:

Molecular equation:

$$HCl(aq) + NaHCO_3(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g) \qquad [4.20]$$

Net ionic equation:

$$H^+(aq) + HCO_3^-(aq) \longrightarrow H_2O(l) + CO_2(g) \qquad [4.21]$$

Both $NaHCO_3(s)$ and $Na_2CO_3(s)$ are used as neutralizers in acid spills; either salt is added until the fizzing caused by $CO_2(g)$ formation stops. Sometimes sodium hydrogen carbonate is used as an antacid to soothe an upset stomach. In that case the HCO_3^- reacts with stomach acid to form $CO_2(g)$.

CHEMISTRY PUT TO WORK Antacids

Your stomach secretes acids to help digest foods. These acids, which include hydrochloric acid, contain about 0.1 mol of H^+ per liter of solution. The stomach and digestive tract are normally protected from the corrosive effects of stomach acid by a mucosal lining. Holes can develop in this lining, however, allowing the acid to attack the underlying tissue, causing painful damage. These holes, known as ulcers, can be caused by the secretion of excess acids and/or by a weakness in the digestive lining. Many peptic ulcers are caused by infection by the bacterium *Helicobacter pylori*. Many people suffer from ulcers at some point in their lives. Many others experience occasional indigestion, heartburn, or reflux due to digestive acids entering the esophagus.

The problem of excess stomach acid can be addressed by (1) removing the excess acid or (2) decreasing the production of acid. Substances that remove excess acid are called *antacids*, whereas those that decrease acid production are called *acid inhibitors*. **Figure 4.8** shows several common over-the-counter antacids, which usually contain hydroxide, carbonate, or bicarbonate ions (**Table 4.4**). Antiulcer drugs, such as Tagamet® and Zantac®, are acid inhibitors. They act on acid-producing cells in the lining of the stomach. Formulations that control acid in this way are now available as over-the-counter drugs.

Related Exercise: 4.99



▲ **Figure 4.8 Antacids.** These products all serve as acid-neutralizing agents in the stomach.

TABLE 4.4 Some Common Antacids

Commercial Name	Acid-Neutralizing Agents
Alka-Seltzer®	$NaHCO_3$
Amphojel®	$Al(OH)_3$
Di-Gel®	$Mg(OH)_2$ and $CaCO_3$
Milk of Magnesia	$Mg(OH)_2$
Maalox®	$Mg(OH)_2$ and $Al(OH)_3$
Mylanta®	$Mg(OH)_2$ and $Al(OH)_3$
Rolaids®	$Mg(OH)_2$ and $CaCO_3$
Tums®	$CaCO_3$

Self-Assessment Exercise

4.12 What is the net ionic equation for the reaction between stomach acid and an antacid containing $Al(OH)_3$?

(a) $HCl(aq) + Al(OH)_3(s) \rightarrow H_2O(l) + AlCl_3(aq)$

(b) $3HCl(aq) + Al(OH)_3(s) \rightarrow 3H_2O(l) + AlCl_3(aq)$

(c) $3H^+(aq) + Al(OH)_3(s) \rightarrow 3H_2O(l) + Al^{3+}(aq)$

Exercises

4.13 State whether each of the following statements is true or false. Justify your answer in each case.

(**a**) Sulfuric acid is a monoprotic acid.

(**b**) HCl is a weak acid.

(**c**) Methanol is a base.

4.14 Label each of the following substances as an acid, base, salt, or none of these. Indicate whether the substance exists in aqueous solution entirely in molecular form, entirely as ions, or as a mixture of molecules and ions. (**a**) HF, (**b**) acetonitrile, CH_3CN, (**c**) $NaClO_4$, (**d**) $Ba(OH)_2$.

4.15 Classify each of the following substances as a nonelectrolyte, weak electrolyte, or strong electrolyte in water: (**a**) HF, (**b**) C_6H_5COOH (benzoic acid), (**c**) C_6H_6 (benzene), (**d**) $CoCl_3$, (**e**) $AgNO_3$.

4.16 Complete and balance the following molecular equations, and then write the net ionic equation for each:

(**a**) $HBr(aq) + Ca(OH)_2(aq) \longrightarrow$

(**b**) $Cu(OH)_2(s) + HClO_4(aq) \longrightarrow$

(**c**) $Al(OH)_3(s) + HNO_3(aq) \longrightarrow$

4.17 Write balanced molecular and net ionic equations for the following reactions, and identify the gas formed in each: (**a**) solid cadmium sulfide reacts with an aqueous solution of sulfuric acid; (**b**) solid magnesium carbonate reacts with an aqueous solution of perchloric acid.

4.18 Magnesium carbonate, magnesium oxide, and magnesium hydroxide are all white solids that react with acidic solutions. (**a**) Write a balanced molecular equation and a net ionic equation for the reaction that occurs when each substance reacts with a hydrochloric acid solution. (**b**) By observing the reactions in part (a), how could you distinguish any of the three magnesium substances from the other two?

Answers to Self-Assessment Exercises

4.12 (c)

4.4 Oxidation–Reduction Reactions



Almost all metals will corrode when exposed to the atmosphere, a process in which the metal reacts to form a compound and loses its characteristic luster. Gold and platinum are exceptions, making these metals highly prized for jewelry. In a few cases, a surface coating of corrosion is just unsightly, but in many cases, it is associated with an undesirable economic impact. Forming a compound from a metal is nearly always accompanied by an increase in volume that can compromise the integrity of a structure. In extreme situations, this has resulted in the catastrophic failure of the structure: the collapse of the Morandi bridge in Genova, Italy on 14 August 2018 resulted in 43 fatalities.

By the end of this section, you should be able to

- Understand the processes involved in redox reactions

In precipitation reactions, cations and anions come together to form an insoluble ionic compound. In neutralization reactions, protons are transferred from one reactant to another. Now let's consider a third kind of reaction, one in which electrons are transferred from one reactant to another. Such reactions are called either **oxidation-reduction reactions** or **redox reactions**. In this section, we concentrate on redox reactions where one of the reactants is a metal in its elemental form. Redox reactions are critical in understanding many biological and geological processes in the world around us; they also form the basis for energy-related technologies such as batteries and fuel cells (Chapter 20).

Oxidation and Reduction

One of the most familiar redox reactions is *corrosion* of a metal (**Figure 4.9**). In some instances, corrosion is limited to the surface of the metal, as is the case with the green coating that forms on copper roofs and statues. In other instances, the corrosion goes deeper, eventually compromising the structural integrity of the metal, as happens with the rusting of iron.

Corrosion is the conversion of a metal into a metal compound, by a reaction between the metal and some substance in its environment. When a metal corrodes, each metal atom loses one or more electrons to form a cation, which can combine with an anion to form an ionic compound. The green coating on the Statue of Liberty contains Cu^{2+} combined with carbonate and hydroxide anions; rust contains Fe^{3+} combined with oxide and hydroxide anions; and silver tarnish contains Ag^{+} combined with sulfide anions.

When an atom, ion, or molecule becomes more positively charged (that is, when it loses electrons), we say that it has been *oxidized*. Loss of electrons by a substance is called **oxidation**. The term *oxidation* is used because the first reactions of this sort to be studied were reactions with oxygen. Many metals react directly with O_2 in air to form metal oxides. In these reactions, the metal loses electrons to oxygen, forming an ionic



(a) (b) (c)

▲ **Figure 4.9 Familiar corrosion products.** (**a**) A green coating forms when copper is oxidized. (**b**) Rust forms when iron corrodes. (**c**) A black tarnish forms as silver corrodes.

compound of the metal ion and oxide ion. The familiar example of rusting involves the reaction between iron metal and oxygen in the presence of water. In this process, Fe is *oxidized* (loses electrons) to form Fe^{3+}.

The reaction between iron and oxygen tends to be relatively slow, but other metals, such as the alkali and alkaline earth metals, react quickly upon exposure to air. **Figure 4.10** shows how the bright metallic surface of calcium tarnishes as CaO forms in the reaction

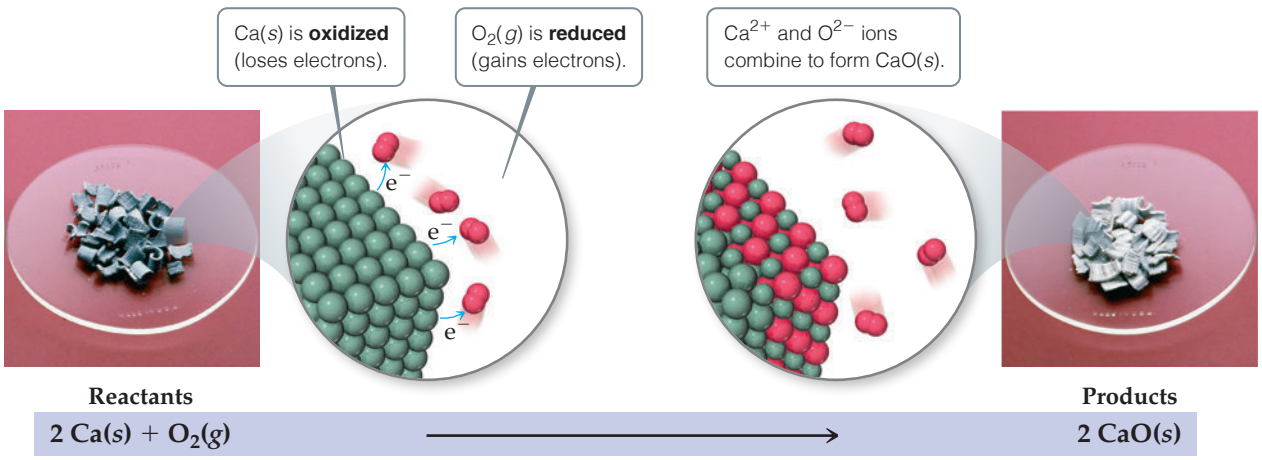
$$2\,Ca(s) + O_2(g) \longrightarrow 2\,CaO(s) \qquad [4.22]$$

In this reaction, Ca is oxidized to Ca^{2+} and neutral O_2 is transformed to O^{2-} ions. In Equation 4.22, the oxidation involves transfer of electrons from the calcium metal to the O_2, leading to formation of CaO. When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is *reduced*. The gain of electrons by a substance is called **reduction**. When one reactant loses electrons (that is, when it is oxidized), another reactant must gain them. In other words, oxidation of one substance must be accompanied by reduction of some other substance. In Equation 4.22, then, molecular oxygen is reduced to oxide (O^{2-}) ions.

Oxidation Numbers

Before we can identify an oxidation-reduction reaction, we must have a bookkeeping system—a way of keeping track of electrons gained by the substance being reduced and electrons lost by the substance being oxidized. The concept of oxidation numbers (also called *oxidation states*) was devised as a way of doing this. Each atom in a neutral substance or ion is assigned an **oxidation number** (also known as an **oxidation state**). For monatomic ions, the oxidation number is the same as the charge. For neutral molecules

Go Figure How many electrons does each oxygen atom gain during the course of this reaction?



▲ **Figure 4.10 Oxidation of calcium metal by molecular oxygen.**

and polyatomic ions, the oxidation number of a given atom is a hypothetical charge. This charge is assigned by artificially dividing up the electrons among the atoms in the molecule or ion. We use the following rules for assigning oxidation numbers:

1. *For an atom in its **elemental form**, the oxidation number is always zero.* Thus, each H atom in the H_2 molecule has an oxidation number of 0, and each P atom in the P_4 molecule has an oxidation number of 0.
2. *For any **monatomic ion**, the oxidation number equals the ionic charge.* Thus, K^+ has an oxidation number of +1, S^{2-} has an oxidation number of −2, and so forth.
   In ionic compounds the alkali metal ions (Group 1) always have a 1+ charge and therefore an oxidation number of +1. The alkaline earth metals (Group 2) are always +2, and aluminum (Group 13) is always +3 in ionic compounds. (In writing oxidation numbers, we will write the sign before the number to distinguish them from the actual electronic charges, which we write with the number first.)
3. ***Nonmetals*** usually have negative oxidation numbers, although they can sometimes be positive:
   (**a**) *The oxidation number of **oxygen** is usually −2 in both ionic and molecular compounds.* The major exception is in compounds called peroxides, which contain the O_2^{2-} ion, giving each oxygen an oxidation number of −1.
   (**b**) *The oxidation number of **hydrogen** is usually +1 when bonded to nonmetals and −1 when bonded to metals* (for example, metal hydrides such as sodium hydride, NaH).
   (**c**) *The oxidation number of **fluorine** is −1 in all compounds.* The other ***halogens*** have an oxidation number of −1 in most binary compounds. When combined with oxygen, as in oxyanions, however, they have positive oxidation states.
4. ***The sum of the oxidation numbers** of all atoms in a neutral compound is zero. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.* For example, in the hydronium ion H_3O^+, which is a more accurate description of $H^+(aq)$, the oxidation number of each hydrogen is +1 and that of oxygen is −2. Thus, the sum of the oxidation numbers is $3(+1) + (-2) = +1$, which equals the net charge of the ion. This rule is useful in obtaining the oxidation number of one atom in a compound or ion if you know the oxidation numbers of the other atoms, as illustrated in Sample Exercise 4.8.

Sample Exercise 4.8

Determining Oxidation Numbers

Determine the oxidation number of sulfur in (**a**) H_2S, (**b**) S_8, (**c**) SCl_2, (**d**) Na_2SO_3, (**e**) SO_4^{2-}.

SOLUTION

Analyze We are asked to determine the oxidation number of sulfur in two molecular species, in the elemental form, and in two substances containing ions.

Plan In each species, the sum of oxidation numbers of all the atoms must equal the charge on the species. We will use the rules outlined previously to assign oxidation numbers.

Solve

(**a**) When bonded to a nonmetal, hydrogen has an oxidation number of +1. Because the H_2S molecule is neutral, the sum of the oxidation numbers must equal zero. Letting x equal the oxidation number of S, we have $2(+1) + x = 0$. Thus, S has an oxidation number of −2.

(**b**) Because S_8 is an elemental form of sulfur, the oxidation number of S is 0.

(**c**) Because SCl_2 is a binary compound, we expect chlorine to have an oxidation number of −1. The sum of the oxidation numbers must equal zero. Letting x equal the oxidation number of S, we have $x + 2(-1) = 0$. Consequently, the oxidation number of S must be +2.

(**d**) Sodium, an alkali metal, always has an oxidation number of +1 in its compounds. Oxygen commonly has an oxidation number of −2. Letting x equal the oxidation number of S, we have $2(+1) + x + 3(-2) = 0$. Therefore, the oxidation number of S in this compound (Na_2SO_3) is +4.

(**e**) The oxidation number of O is −2. The sum of the oxidation numbers equals −2, the net charge of the SO_4^{2-} ion. Thus, we have $x + 4(-2) = -2$. From this relation we conclude that the oxidation number of S in this ion is +6.

Comment These examples illustrate that the oxidation number of a given element depends on the compound in which it occurs. The oxidation numbers of sulfur, as seen in these examples, range from −2 to +6.

Practice Exercise

In which compound is the oxidation state of oxygen −1?
(**a**) O_2 (**b**) H_2O (**c**) H_2SO_4 (**d**) H_2O_2 (**e**) KCH_3COO

Oxidation of Metals by Acids and Salts

The reaction between a metal and either an acid or a metal salt conforms to the general pattern

$$A + BX \longrightarrow AX + B \qquad [4.23]$$

Examples:

$$Zn(s) + 2\,HBr(aq) \longrightarrow ZnBr_2(aq) + H_2(g)$$

$$Mn(s) + Pb(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Pb(s)$$

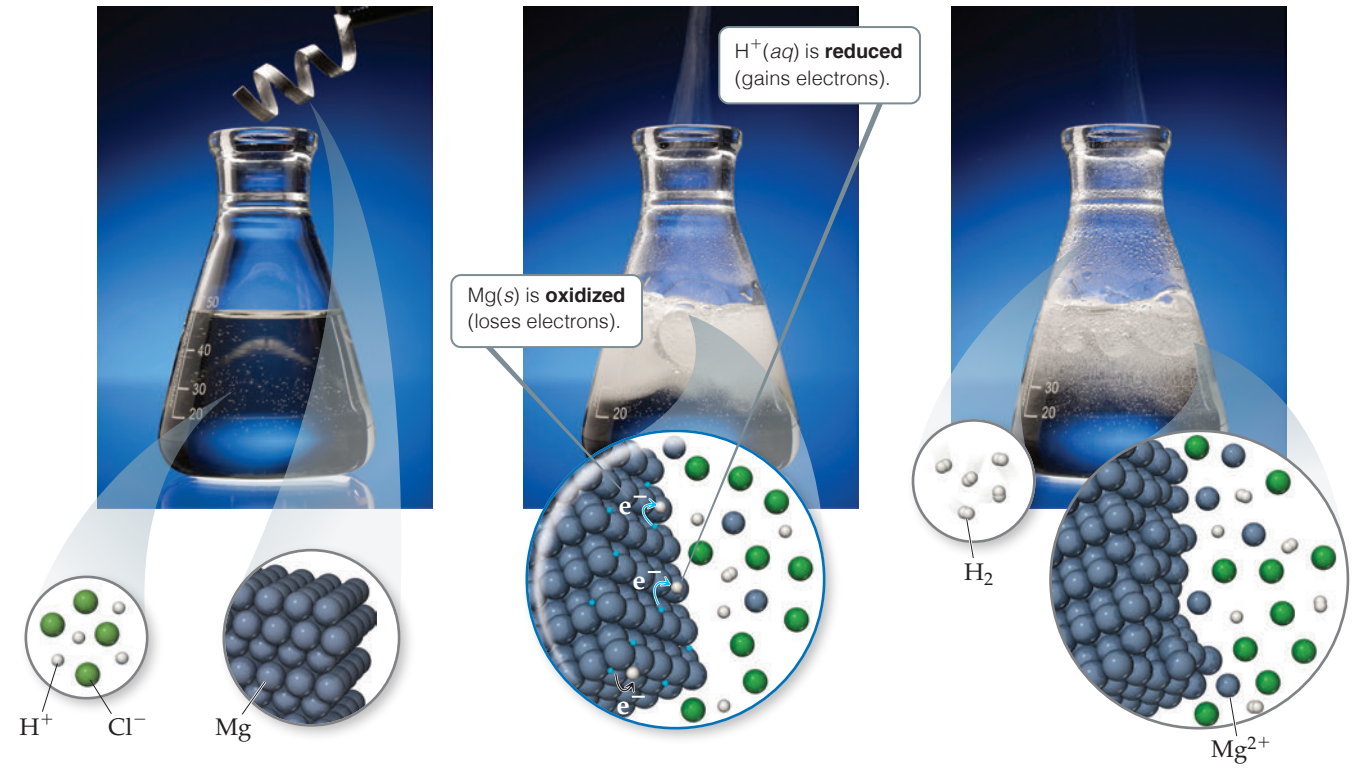
These reactions are called **displacement reactions** because the ion in solution is *displaced* (replaced) through oxidation of an element.

Many metals undergo displacement reactions with acids, producing salts and hydrogen gas. For example, magnesium metal reacts with hydrochloric acid to form magnesium chloride and hydrogen gas (**Figure 4.11**):

$$\underset{\text{Oxidation number}}{\overset{\overset{0}{\downarrow}\quad\overset{+1\ -1}{\downarrow}\qquad\overset{+2\ -1}{\uparrow}\qquad\overset{0}{\uparrow}}{Mg(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)}} \qquad [4.24]$$

The oxidation number of Mg changes from 0 to +2, an increase that indicates the atom has lost electrons and has therefore been oxidized. The oxidation number of H^+ in the acid decreases from +1 to 0, indicating that this ion has gained electrons and has therefore

Go Figure How many moles of hydrogen gas would be produced for every mole of magnesium added into the HCl solution?



▲ **Figure 4.11 Reaction of magnesium metal with hydrochloric acid.** The metal is readily oxidized by the acid, producing hydrogen gas, $H_2(g)$, and $MgCl_2(aq)$.

been reduced. Chlorine has an oxidation number of −1 both before and after the reaction, indicating that it is neither oxidized nor reduced. In fact, the Cl^- ions are spectator ions, dropping out of the net ionic equation:

$$Mg(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2(g) \qquad [4.25]$$

Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to Fe^{2+} by aqueous solutions of Ni^{2+} such as $Ni(NO_3)_2(aq)$:

Molecular equation:
$$Fe(s) + Ni(NO_3)_2(aq) \longrightarrow Fe(NO_3)_2(aq) + Ni(s) \qquad [4.26]$$

Net ionic equation:
$$Fe(s) + Ni^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Ni(s) \qquad [4.27]$$

The oxidation of Fe to Fe^{2+} in this reaction is accompanied by the reduction of Ni^{2+} to Ni. Remember: *Whenever one substance is oxidized, another substance must be reduced.*

Sample Exercise 4.9

Writing Equations for Oxidation-Reduction Reactions

Write the balanced molecular and net ionic equations for the reaction of aluminum with hydrobromic acid.

SOLUTION

Analyze We must write two equations—molecular and net ionic—for the redox reaction between a metal and an acid.

Plan Metals react with acids to form salts and H_2 gas. To write the balanced equations, we must write the chemical formulas for the two reactants and then determine the formula of the salt, which is composed of the cation formed by the metal and the anion of the acid.

Solve The reactants are Al and HBr. The cation formed by Al is Al^{3+}, and the anion from hydrobromic acid is Br^-. Thus, the salt formed in the reaction is $AlBr_3$. Writing the reactants and products and then balancing the equation gives the molecular equation:

$$2\,Al(s) + 6\,HBr(aq) \longrightarrow 2\,AlBr_3(aq) + 3\,H_2(g)$$

Both HBr and $AlBr_3$ are soluble strong electrolytes. Thus, the complete ionic equation is

$$2\,Al(s) + 6\,H^+(aq) + 6\,Br^-(aq) \longrightarrow 2\,Al^{3+}(aq) + 6\,Br^-(aq) + 3\,H_2(g)$$

Because Br^- is a spectator ion, the net ionic equation is

$$2\,Al(s) + 6\,H^+(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)$$

Comment The substance oxidized is the aluminum metal because its oxidation state changes from 0 in the metal to +3 in the cation, thereby increasing in oxidation number. The H^+ is reduced because its oxidation state changes from +1 in the acid to 0 in H_2.

Practice Exercise

Which of the following statements is true about the reaction between zinc and copper sulfate? (**a**) Zinc is oxidized, and copper ion is reduced. (**b**) Zinc is reduced, and copper ion is oxidized. (**c**) All reactants and products are soluble strong electrolytes. (**d**) The oxidation state of copper in copper sulfate is 0. (**e**) More than one of the previous choices are true.

The Activity Series

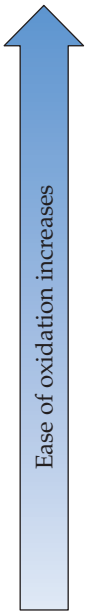
Can we predict whether a certain metal will be oxidized either by an acid or by a particular salt? This question is of practical importance as well as chemical interest. According to Equation 4.26, for example, it would be unwise to store a solution of nickel nitrate in an iron container because the solution would dissolve the container. When a metal is oxidized, it forms various compounds. Extensive oxidation can lead to the failure of metal machinery parts or the deterioration of metal structures.

Different metals vary in the ease with which they are oxidized. Zn is oxidized by aqueous solutions of Cu^{2+}, for example, but Ag is not. Zn, therefore, loses electrons more readily than Ag; that is, Zn is easier to oxidize than Ag.

A list of metals arranged in order of decreasing ease of oxidation, such as in Table 4.5, is called an **activity series**. The metals at the top of the table, such as the alkali metals and the alkaline earth metals, are most easily oxidized; that is, they react most readily to form compounds. They are called the *active metals*. The metals at the bottom of the activity series, such as the transition elements from Groups 8 to 11, are very stable and form compounds less readily. These metals, which are used to make coins and jewelry, are called *noble metals* because of their low reactivity.

TABLE 4.5 Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2\,H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$



The activity series can be used to predict the outcome of reactions between metals and either metal salts or acids. *Any metal on the list can be oxidized by the ions of elements below it.* For example, copper is above silver in the series. Thus, copper metal is oxidized by silver ions:

$$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s) \qquad [4.28]$$

The oxidation of copper to copper ions is accompanied by the reduction of silver ions to silver metal. The silver metal is evident on the surface of the copper wire in **Figure 4.12**. The copper(II) nitrate produces a blue color in the solution, as can be seen most clearly in the photograph on the right of Figure 4.12.

Only metals above hydrogen in the activity series are able to react with acids to form H_2. For example, Ni reacts with HCl(*aq*) to form H_2:

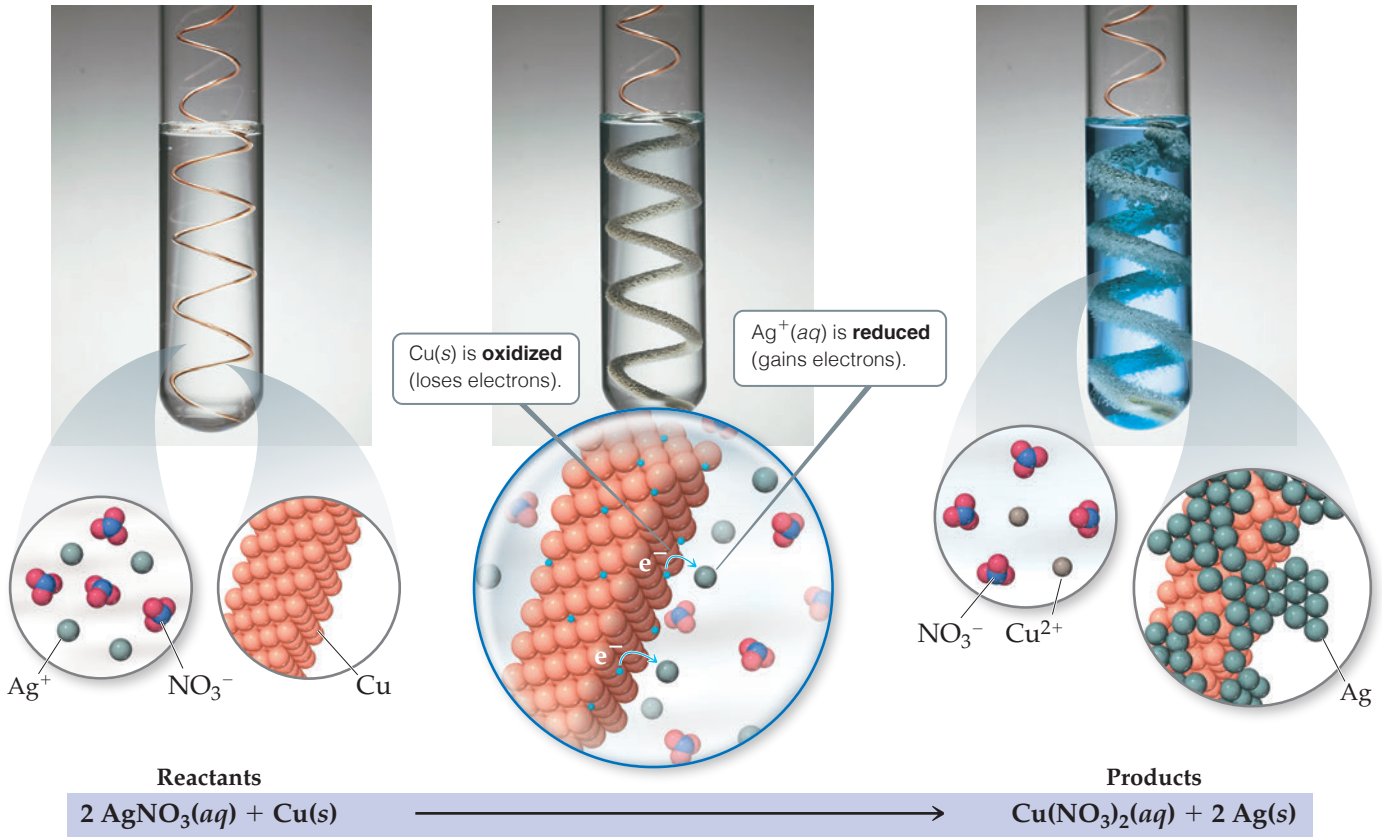
$$Ni(s) + 2\,HCl(aq) \longrightarrow NiCl_2(aq) + H_2(g) \qquad [4.29]$$

Because elements below hydrogen in the activity series are not oxidized by H^+, Cu does not react with HCl(*aq*). Interestingly, copper does react with nitric acid, as shown in Figure 1.11, but the reaction is not oxidation of Cu by H^+ ions. Instead, the metal is oxidized to Cu^{2+} by the nitrate ion, accompanied by the formation of brown nitrogen dioxide, $NO_2(g)$:

$$Cu(s) + 4\,HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g) \qquad [4.30]$$

As the copper is oxidized in this reaction, NO_3^-, where the oxidation number of nitrogen is +5, is reduced to NO_2, where the oxidation number of nitrogen is +4. We will examine reactions of this type in Chapter 20.

Go Figure Why does this solution turn blue?



▲ **Figure 4.12 Reaction of copper metal with silver ion.** When copper metal is placed in a solution of silver nitrate, a redox reaction forms silver metal and a blue solution of copper(II) nitrate.

Sample Exercise 4.10

Determining If an Oxidation-Reduction Reaction Will Occur

Will an aqueous solution of iron(II) chloride oxidize magnesium metal? If so, write the balanced molecular and net ionic equations for the reaction.

SOLUTION

Analyze We are given two substances—an aqueous salt, $FeCl_2$, and a metal, Mg—and asked if they react with each other.

Plan A reaction occurs if the reactant that is a metal in its elemental form (Mg) is located above the reactant that is a metal in its oxidized form (Fe^{2+}) in Table 4.5. If the reaction occurs, the Fe^{2+} ion in $FeCl_2$ is reduced to Fe, and the Mg is oxidized to Mg^{2+}.

Solve Because Mg is above Fe in the table, the reaction occurs. To write the formula for the salt produced in the reaction, we must remember the charges on common ions. Magnesium is always present in compounds as Mg^{2+}; the chloride ion is Cl^-. The magnesium salt formed in the reaction is $MgCl_2$, meaning the balanced molecular equation is

$$Mg(s) + FeCl_2(aq) \longrightarrow MgCl_2(aq) + Fe(s)$$

Both $FeCl_2$ and $MgCl_2$ are soluble strong electrolytes and can be written in ionic form, which shows us that Cl^- is a spectator ion in the reaction. The net ionic equation is

$$Mg(s) + Fe^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Fe(s)$$

The net ionic equation shows that Mg is oxidized and Fe^{2+} is reduced in this reaction.

Check Note that the net ionic equation is balanced with respect to both charge and mass.

Practice Exercise

Which of these metals is the easiest to oxidize?
(**a**) gold (**b**) lithium (**c**) iron (**d**) sodium (**e**) aluminum

STRATEGIES FOR SUCCESS Analyzing Chemical Reactions

In this chapter, you have been introduced to a great number of chemical reactions. It's not easy to get a "feel" for what happens when chemicals react. One goal of this textbook is to help you become more adept at predicting the outcomes of reactions. The key to gaining this "chemical intuition" is to learn how to categorize reactions.

Attempting to memorize individual reactions would be a futile task. It is far more fruitful to recognize patterns to determine the general category of a reaction, such as metathesis or oxidation-reduction. When faced with the challenge of predicting the outcome of a chemical reaction, ask yourself the following questions:

- What are the reactants?
- Are they electrolytes or nonelectrolytes?
- Are they acids or bases?
- If the reactants are electrolytes, will metathesis produce a precipitate? Water? A gas?
- If metathesis cannot occur, can the reactants engage in an oxidation-reduction reaction? This requires that there be both a reactant that can be oxidized and a reactant that can be reduced.

Being able to predict what happens during a reaction follows from asking basic questions like these. Each question narrows the set of possible outcomes, steering you ever closer to a likely outcome. Your prediction might not always be entirely correct, but if you keep your wits about you, you will not be far off. As you gain experience, you will begin to look for reactants that might not be immediately obvious, such as water from the solution or oxygen from the atmosphere. Because proton transfer (acid–base) and electron transfer (oxidation-reduction) are involved in a huge number of chemical reactions, knowing the hallmarks of such reactions will mean you are well on your way to becoming an excellent chemist!

Self-Assessment Exercise

4.19 Which combination of metal and metal ion do you expect to undergo a redox reaction?

(a) $Ca(s)$ and $K^+(aq)$

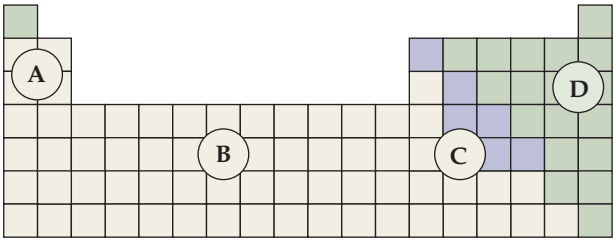
(b) $Fe(s)$ and $Al^{3+}(aq)$

(c) $Ag(s)$ and $Cu^{2+}(aq)$

(d) $Fe(s)$ and $Pb^{2+}(aq)$

Exercises

4.20 (**a**) Which region of the periodic table shown here contains elements that are easiest to oxidize? (**b**) Which region contains the least readily oxidized elements?



4.21 Determine the oxidation number of sulfur in each of the following substances: (**a**) barium sulfate, $BaSO_4$, (**b**) sulfurous acid, H_2SO_3, (**c**) strontium sulfide, SrS, (**d**) hydrogen sulfide, H_2S. (**e**) Locate sulfur in the periodic table in Exercise 4.20; what region is it in? (**f**) Which region(s) of the periodic table contains elements that can adopt both positive and negative oxidation numbers?

4.22 Determine the oxidation number for the indicated element in each of the following substances: (**a**) S in SO_3, (**b**) Ti in $TiCl_4$, (**c**) P in $AgPF_6$, (**d**) N in HNO_3, (**e**) S in H_2SO_3, (**f**) O in OF_2.

4.23 Which element is oxidized and which is reduced in the following reactions?

(**a**) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

(**b**) $3\,Fe(NO_3)_2(aq) + 2\,Al(s) \longrightarrow 3\,Fe(s) + 2\,Al(NO_3)_3(aq)$

(**c**) $Cl_2(aq) + 2\,NaI(aq) \longrightarrow I_2(aq) + 2\,NaCl(aq)$

(**d**) $PbS(s) + 4\,H_2O_2(aq) \longrightarrow PbSO_4(s) + 4\,H_2O(l)$

4.24 Write balanced molecular and net ionic equations for the reactions of (**a**) manganese with dilute sulfuric acid, (**b**) chromium with hydrobromic acid, (**c**) tin with hydrochloric acid, (**d**) aluminum with formic acid, HCOOH.

4.25 Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, write NR. (**a**) Iron metal is added to a solution of copper(II) nitrate, (**b**) zinc metal is added to a solution of magnesium sulfate, (**c**) hydrobromic acid is added to tin metal, (**d**) hydrogen gas is bubbled through an aqueous solution of nickel(II) chloride, (**e**) aluminum metal is added to a solution of cobalt(II) sulfate.

Answers to Self-Assessment Exercises

4.19 (d)

4.5 Concentrations of Solutions



In recent years, we have seen an explosion in the marketing of dietary supplements. Many of these involve "trace elements"—substances we require in small quantities for the healthy functioning of our bodies. While a diet deficient in such essential elements can cause undesirable physiological effects, so too can an excess of the element. For example, there is around 2.3 g of iron in the body of an adult woman and 3.8 g in an adult man. A deficiency of iron can lead to conditions such as anemia, characterized by fatigue among other symptoms, while too much iron can lead to stomach pain and metabolic acidosis. Body chemistry is essentially solution chemistry and an ability to quantify the amount of substance in a solution is essential to its understanding.

By the end of this section, you should be able to

- Convert between mass, moles, and concentration of a soluble substance

Scientists use the term **concentration** to designate the amount of solute dissolved in a given quantity of solvent or quantity of solution. The greater the amount of solute dissolved in a certain amount of solvent, the more concentrated the resulting solution. In chemistry we often need to express the concentrations of solutions quantitatively.

Molarity

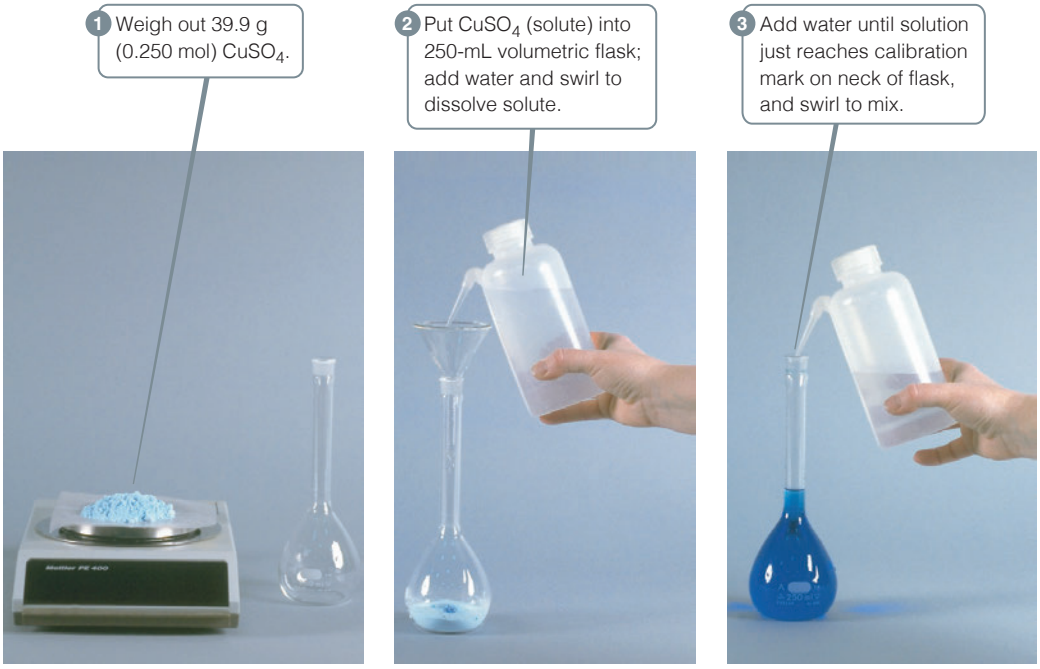
Molarity (symbol *M*) expresses the concentration of a solution as the number of moles of solute in a liter of solution (soln):

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \qquad [4.31]$$

A 1.00 molar solution (written 1.00 *M*) contains 1.00 mol of solute in every liter of solution. **Figure 4.13** shows the preparation of 0.250 L of a 1.00 *M* solution of $CuSO_4$. The molarity of the solution is $(0.250 \text{ mol } CuSO_4)/(0.250 \text{ L soln}) = 1.00\ M$. Note that we use the abbreviation "soln" for "solution."

Expressing the Concentration of an Electrolyte

In biology, the total concentration of ions in solution is very important in metabolic and cellular processes. When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound. For example, a 1.0 *M* solution of NaCl is 1.0 *M* in Na^+ ions and 1.0 *M* in Cl^- ions, and a 1.0 *M* solution of



▲ **Figure 4.13** **Preparing 0.250 L of a 1.00 *M* solution of $CuSO_4$.**

Sample Exercise 4.11

Calculating Molarity

Calculate the molarity of a solution made by dissolving 23.4 g of sodium sulfate (Na_2SO_4) in enough water to form 125 mL of solution.

SOLUTION

Analyze We are given the number of grams of solute (23.4 g), its chemical formula (Na_2SO_4), and the volume of the solution (125 mL) and asked to calculate the molarity of the solution.

Plan We can calculate molarity using Equation 4.31. To do so, we must convert the number of grams of solute to moles and the volume of the solution from milliliters to liters.

Solve

The number of moles of Na_2SO_4 is obtained by using its molar mass:

$$\text{Moles } Na_2SO_4 = (23.4 \text{ g } \cancel{Na_2SO_4})\left(\frac{1 \text{ mol } Na_2SO_4}{142.1 \text{ g } \cancel{Na_2SO_4}}\right) = 0.165 \text{ mol } Na_2SO_4$$

Converting the volume of the solution to liters:

$$\text{Liters soln} = (125 \text{ } \cancel{\text{mL}})\left(\frac{1 \text{ L}}{1000 \text{ } \cancel{\text{mL}}}\right) = 0.125 \text{ L}$$

Thus, the molarity is:

$$\text{Molarity} = \frac{0.165 \text{ mol } Na_2SO_4}{0.125 \text{ L soln}} = 1.32 \frac{\text{mol } Na_2SO_4}{\text{L soln}} = 1.32\,M$$

Check Because the numerator is only slightly larger than the denominator, it is reasonable for the answer to be a little over 1 *M*. The units (mol/L) are appropriate for molarity, and three significant figures are appropriate for the answer because each of the initial pieces of data had three significant figures.

▶ Practice Exercise

What is the molarity of a solution that is made by dissolving 3.68 g of sucrose ($C_{12}H_{22}O_{11}$) in sufficient water to form 275.0 mL of solution? (**a**) 13.4 *M* (**b**) $7.43 \times 10^{-2}\,M$ (**c**) $3.91 \times 10^{-2}\,M$ (**d**) $7.43 \times 10^{-5}\,M$ (**e**) $3.91 \times 10^{-5}\,M$

Sample Exercise 4.12

Calculating Molar Concentrations of Ions

What is the molar concentration of each ion present in a 0.025 *M* aqueous solution of calcium nitrate?

SOLUTION

Analyze We are given the concentration of the ionic compound used to make the solution and asked to determine the concentrations of the ions in the solution.

Plan We can use the subscripts in the chemical formula of the compound to determine the relative ion concentrations.

Solve Calcium nitrate is composed of calcium ions (Ca^{2+}) and nitrate ions (NO_3^-), so its chemical formula is $Ca(NO_3)_2$. Because there are two NO_3^- ions for each Ca^{2+} ion, each mole of $Ca(NO_3)_2$ that dissolves dissociates into 1 mol of Ca^{2+} and 2 mol of NO_3^-. Thus, a solution that is 0.025 *M* in $Ca(NO_3)_2$ is 0.025 *M* in Ca^{2+} and $2 \times 0.025\ M = 0.050\ M$ in NO_3^-:

Check The concentration of NO_3^- ions is twice that of Ca^{2+} ions, as the subscript 2 after the NO_3^- in the chemical formula $Ca(NO_3)_2$ suggests.

Practice Exercise

What is the ratio of the concentration of potassium ions to the concentration of carbonate ions in a 0.015 *M* solution of potassium carbonate? (**a**) 1:0.015 (**b**) 0.015:1 (**c**) 1:1 (**d**) 1:2 (**e**) 2:1

Na_2SO_4 is 2.0 *M* in Na^+ ions and 1.0 *M* in SO_4^{2-} ions. Thus, the concentration of an electrolyte solution can be specified either in terms of the compound used to make the solution (1.0 *M* Na_2SO_4) or in terms of the ions in the solution (2.0 *M* Na^+ and 1.0 *M* SO_4^{2-}).

Interconverting Molarity, Moles, and Volume

If we know any two of the three quantities in the definition of molarity (Equation 4.31), we can calculate the third. For example, if we know the molarity of an HNO_3 solution to be 0.200 *M*, which means 0.200 mol of HNO_3 per liter of solution, we can calculate the number of moles of solute in a given volume, say 2.0 L. Molarity therefore is a conversion factor between volume of solution and moles of solute:

$$\text{Moles } HNO_3 = (2.0\ \cancel{\text{L soln}})\left(\frac{0.200\ \text{mol } HNO_3}{1\ \cancel{\text{L soln}}}\right) = 0.40\ \text{mol } HNO_3$$

To illustrate the conversion of moles to volume, let's calculate the volume of 0.30 *M* HNO_3 solution required to supply 2.0 mol of HNO_3:

$$\text{Liters soln} = (2.0\ \cancel{\text{mol } HNO_3})\left(\frac{1\ \text{L soln}}{0.30\ \cancel{\text{mol } HNO_3}}\right) = 6.7\ \text{L soln}$$

Note that in this case we used the reciprocal of molarity in the conversion:

$$\text{Liters} = \text{mol} \times 1/M = \cancel{\text{mol}} \times \text{liters}/\cancel{\text{mol}}$$

If one of the solutes is a liquid, we can use its density to convert its mass to volume and vice versa. For example, a typical American beer contains 5.0% ethanol (CH_3CH_2OH) by volume in water (along with other components). The density of ethanol is 0.789 g/mL. Therefore, if we wanted to calculate the molarity of ethanol (usually just called "alcohol" in everyday language) in beer, we would first consider 1.00 L of beer.

This 1.00 L of beer contains 0.950 L of water and 0.050 L of ethanol:

$$5\% = 5/100 = 0.050$$

Then we can calculate the moles of ethanol by proper cancellation of units, taking into account the density of ethanol and its molar mass (46.0 g/mol):

$$\text{Moles ethanol} = (0.050\ \cancel{\text{L}})\left(\frac{1000\ \cancel{\text{mL}}}{\cancel{\text{L}}}\right)\left(\frac{0.789\ \cancel{\text{g}}}{\cancel{\text{mL}}}\right)\left(\frac{1\ \text{mol}}{46.0\ \cancel{\text{g}}}\right) = 0.858\ \text{mol}$$

Because there are 0.858 moles of ethanol in 1.00 L of beer, the concentration of ethanol in beer is 0.86 *M* (taking into account significant figures).

Sample Exercise 4.13

Using Molarity to Calculate Grams of Solute

How many grams of Na_2SO_4 are required to make 0.350 L of 0.500 *M* Na_2SO_4?

SOLUTION

Analyze We are given the volume of the solution (0.350 L), its concentration (0.500 *M*), and the identity of the solute Na_2SO_4 and asked to calculate the number of grams of the solute in the solution.

Plan We can use the definition of molarity (Equation 4.31) to determine the number of moles of solute, and then convert moles to grams using the molar mass of the solute.

$$M_{Na_2SO_4} = \frac{\text{moles } Na_2SO_4}{\text{liters soln}}$$

Solve Calculating the moles of Na_2SO_4 using the molarity and volume of solution gives

$$M_{Na_2SO_4} = \frac{\text{moles } Na_2SO_4}{\text{liters soln}}$$

$$\text{Moles } Na_2SO_4 = \text{liters soln} \times M_{Na_2SO_4}$$

$$= (0.350 \cancel{\text{ L soln}})\left(\frac{0.500 \text{ mol } Na_2SO_4}{1 \cancel{\text{ L soln}}}\right)$$

$$= 0.175 \text{ mol } Na_2SO_4$$

Because each mole of Na_2SO_4 has a mass of 142.1 g, the required number of grams of Na_2SO_4 is

$$\text{Grams } Na_2SO_4 = (0.175 \cancel{\text{ mol } Na_2SO_4})\left(\frac{142.1 \text{ g } Na_2SO_4}{1 \cancel{\text{ mol } Na_2SO_4}}\right)$$

$$= 24.9 \text{ g } Na_2SO_4$$

Check The magnitude of the answer, the units, and the number of significant figures are all appropriate.

Practice Exercise

(**a**) How many grams of Na_2SO_4 are there in 15 mL of 0.50 *M* Na_2SO_4? (**b**) How many milliliters of 0.50 *M* Na_2SO_4 solution are needed to provide 0.038 mol of this salt?

Dilution

Solutions used routinely in the laboratory are often purchased or prepared in concentrated form (called *stock solutions*). Aqueous solutions of lower concentrations can then be obtained by adding water, a process called **dilution**.*

Let's see how we can prepare a dilute solution from a concentrated one. Suppose we want to prepare 250.0 mL (that is, 0.2500 L) of 0.100 *M* $CuSO_4$ solution by diluting a 1.00 *M* $CuSO_4$ stock solution. The main point to remember is that when solvent is added to a solution, the number of moles of solute remains unchanged:

$$\text{Moles solute before dilution} = \text{moles solute after dilution} \qquad [4.32]$$

Because we know both the volume (250.0 mL) and the concentration (0.100 mol/L) of the dilute solution, we can calculate the number of moles of $CuSO_4$ it contains:

$$\text{Moles } CuSO_4 \text{ in dilute soln} = (0.2500 \cancel{\text{ L soln}})\left(\frac{0.100 \text{ mol } CuSO_4}{1 \cancel{\text{ L soln}}}\right)$$

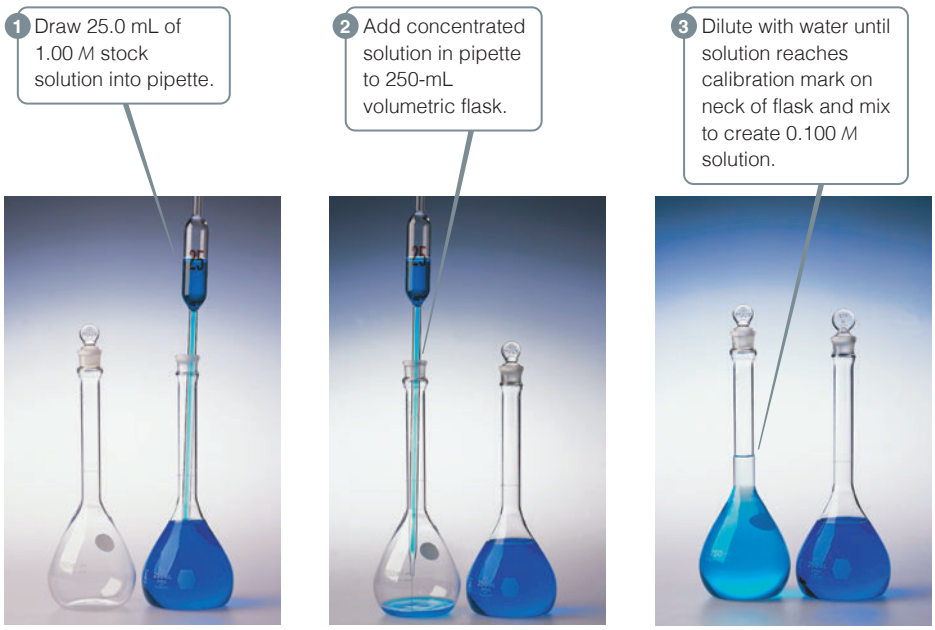
$$= 0.0250 \text{ mol } CuSO_4$$

The volume of stock solution needed to provide 0.0250 mol $CuSO_4$ is therefore:

$$\text{Liters of conc soln} = (0.0250 \cancel{\text{ mol } CuSO_4})\left(\frac{1 \text{ L soln}}{1.00 \cancel{\text{ mol } CuSO_4}}\right) = 0.0250 \text{ L}$$

Figure 4.14 shows the dilution carried out in the laboratory. Notice that the diluted solution is less intensely colored than the concentrated one.

*In diluting a concentrated acid or base, the acid or base should be added to water and then further diluted by adding more water. Adding water directly to concentrated acid or base can cause spattering because of the intense heat generated.



▲ **Figure 4.14** **Preparing 250.0 mL of 0.100 *M* $CuSO_4$ by dilution of 1.00 *M* $CuSO_4$.**

In laboratory situations, calculations of this sort are often made with an equation derived by remembering that the number of moles of solute is the same in both the concentrated and dilute solutions and that moles = molarity × liters:

$$\text{Moles solute in conc soln} = \text{moles solute in dilute soln}$$

$$M_{conc} \times V_{conc} = M_{dil} \times V_{dil} \qquad [4.33]$$

Although we derived Equation 4.33 in terms of liters, any volume unit can be used as long as it is used on both sides of the equation. For example, in the calculation we did for the $CuSO_4$ solution, we have

$$(1.00\,M)(V_{conc}) = (0.100\,M)(250.0\,\text{mL})$$

Solving for V_{conc} gives $V_{conc} = 25.0$ mL as before.

Sample Exercise 4.14

Preparing a Solution by Dilution

How many milliliters of 3.0 *M* H_2SO_4 are needed to make 450 mL of 0.10 *M* H_2SO_4?

SOLUTION

Analyze We need to dilute a concentrated solution. We are given the molarity of a more concentrated solution (3.0 *M*) and the volume and molarity of a more dilute one containing the same solute (450 mL of 0.10 *M* solution). We must calculate the volume of the concentrated solution needed to prepare the dilute solution.

Plan We can calculate the number of moles of solute, H_2SO_4, in the dilute solution and then calculate the volume of the concentrated solution needed to supply this amount of solute. Alternatively, we can directly apply Equation 4.33. Let's compare the two methods.

Solve

Calculate the moles of H_2SO_4 in the dilute solution:

$$\text{Moles } H_2SO_4 \text{ in dilute solution} = (0.450\,\cancel{\text{L soln}})\left(\frac{0.10\text{ mol } H_2SO_4}{1\,\cancel{\text{L soln}}}\right)$$

$$= 0.045\text{ mol } H_2SO_4$$

Calculate the volume of the concentrated solution that contains 0.045 mol H_2SO_4:

$$\text{Liters conc soln} = (0.045\,\cancel{\text{mol } H_2SO_4})\left(\frac{1\text{ L soln}}{3.0\,\cancel{\text{mol } H_2SO_4}}\right) = 0.015\text{ L soln}$$

Converting liters to milliliters gives 15 mL.

If we apply Equation 4.33, we get the same result:

$$(3.0\,M)(V_{conc}) = (0.10\,M)(450\,\text{mL})$$

$$(V_{conc}) = \frac{(0.10\,\cancel{M})(450\,\text{mL})}{3.0\,\cancel{M}} = 15\text{ mL}$$

Either way, we see that if we start with 15 mL of 3.0 M H_2SO_4 and dilute it to a total volume of 450 mL, the desired 0.10 M solution will be obtained.

Check The calculated volume seems reasonable because a small volume of concentrated solution is used to prepare a large volume of dilute solution.

Comment The first approach can also be used to find the final concentration when two solutions of different concentrations are mixed, whereas the second approach, using Equation 4.33, can be used only for diluting a concentrated solution with pure solvent.

Practice Exercise

What volume of a 1.00 M stock solution of glucose must be used to make 500.0 mL of a 1.75×10^{-2} M glucose solution in water?

(**a**) 1.75 mL (**b**) 8.75 mL (**c**) 48.6 mL (**d**) 57.1 mL (**e**) 28,570 mL

Self-Assessment Exercise

4.26 Which solution has the greatest number of molecules or ions present?

(a) 1.00 M $FeCl_3$

(b) 1.50 M HCl

(c) 2.00 M $C_6H_{12}O_6$

Exercises

4.27 (**a**) Calculate the molarity of a solution that contains 0.175 mol $ZnCl_2$ in exactly 150 mL of solution. (**b**) How many moles of protons are present in 35.0 mL of a 4.50 M solution of nitric acid? (**c**) How many milliliters of a 6.00 M NaOH solution are needed to provide 0.350 mol of NaOH?

4.28 The average adult human male has a total blood volume of 5.0 L. If the concentration of sodium ion in this average individual is 0.135 M, what is the mass of sodium ion circulating in the blood?

4.29 The concentration of alcohol (CH_3CH_2OH) in blood, called the "blood alcohol concentration" or BAC, is given in units of grams of alcohol per 100 mL of blood. What is the concentration of alcohol, in terms of molarity, in blood if the BAC is 0.08?

4.30 (**a**) Which will have the highest concentration of sodium ions: 0.25 M NaCl, 0.15 M Na_2CO_3, or 0.075 M Na_3PO_4? (**b**) Which will contain the greater number of moles of sodium ion: 20.0 mL of 0.15 M $NaHCO_3$ or 15.0 mL of 0.04 M Na_2S?

4.31 Ignoring protolysis reactions, indicate the concentration of each ion or molecule present in the following solutions: (**a**) 0.35 M K_3PO_4, (**b**) 5×10^{-4} M $CuCl_2$, (**c**) 0.0184 M CH_3CH_2OH (**d**) a mixture of 35.0 mL of 0.010 M Na_2CO_3 and 50.0 mL of 0.200 M K_2SO_4. Assume the volumes are additive.

4.32 (**a**) You have a stock solution of 14.8 M NH_3. How many milliliters of this solution should you dilute to make 1000.0 mL of 0.250 M NH_3? (**b**) If you take a 10.0-mL portion of the stock solution and dilute it to a total volume of 0.500 L, what will be the concentration of the final solution?

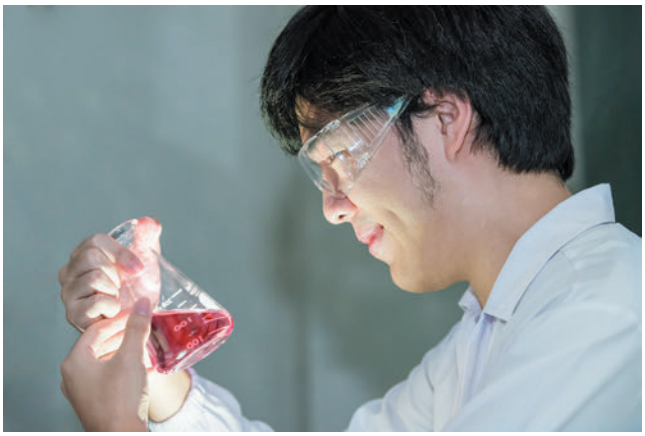
4.33 A medical lab is testing a new anticancer drug on cancer cells. The drug stock solution concentration is 1.5×10^{-9} M, and 1.00 mL of this solution will be delivered to a dish containing 2.0×10^5 cancer cells in 5.00 mL of aqueous fluid. What is the ratio of drug molecules to the number of cancer cells in the dish?

4.34 Pure acetic acid, known as glacial acetic acid, is a liquid with a density of 1.049 g/mL at 25 °C. Calculate the molarity of a solution of acetic acid made by dissolving 20.00 mL of glacial acetic acid at 25 °C in enough water to make 250.0 mL of solution.

Answers to Self-Assessment Exercises

4.26 (a)

4.6 Solution Stoichiometry and Chemical Analysis

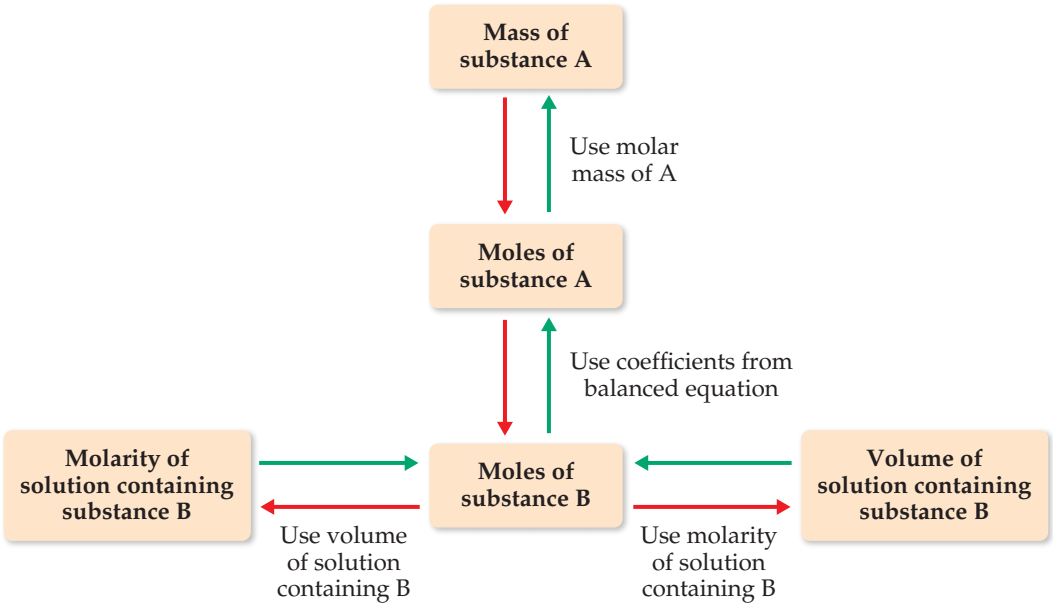


Many reactions occur in solution form. In Chapter 3, we learned that given the chemical equation for a reaction and the amount of one reactant consumed in the reaction, you can calculate the quantities of other reactants and products. In this section we extend this concept to reactions involving solutions.

By the end of this section, you should be able to

- Perform stoichiometric calculations involving solutions.

Recall that the coefficients in a balanced equation give the relative number of moles of reactants and products. To use this information, we must convert the masses of substances involved in a reaction into moles. When dealing with pure substances, as we did in Chapter 3, we use molar mass to convert between grams and moles of the substances. This conversion is not valid when working with a solution because both solute and solvent contribute to its mass. However, if we know the solute concentration, we can use molarity and volume to determine the number of moles (moles solute $= M \times V$). Figure 4.15 summarizes this approach to using stoichiometry for the reaction between a pure substance and a solution.



▲ **Figure 4.15 Procedure for solving stoichiometry problems involving reactions between a pure substance A and a solution containing a known concentration of substance B.** Starting from a known mass of substance A, we follow the red arrows to determine either the volume of the solution containing B (if the molarity of B is known) or the molarity of the solution containing B (if the volume of B is known). Starting from either a known volume or a known molarity of the solution containing B, we follow the green arrows to determine the mass of substance A.

Sample Exercise 4.15

Using Mass Relations in a Neutralization Reaction

How many grams of $Ca(OH)_2$ are needed to neutralize 25.0 mL of 0.100 *M* HNO_3?

SOLUTION

Analyze The reactants are an acid, HNO_3, and a base, $Ca(OH)_2$. The volume and molarity of HNO_3 are given, and we are asked how many grams of $Ca(OH)_2$ are needed to neutralize this quantity of HNO_3.

Plan Following the steps outlined by the green arrows in Figure 4.15, we use the molarity and volume of the HNO_3 solution (substance B in Figure 4.15) to calculate the number of moles of HNO_3. We then use the balanced equation to relate moles of HNO_3 to moles of $Ca(OH)_2$ (substance A). Finally, we use the molar mass to convert moles to grams of $Ca(OH)_2$:

$$V_{HNO_3} \times M_{HNO_3} \Rightarrow \text{mol } HNO_3 \Rightarrow \text{mol } Ca(OH)_2 \Rightarrow \text{g } Ca(OH)_2$$

Solve

The product of the molar concentration of a solution and its volume in liters gives the number of moles of solute:

$$\text{Moles } HNO_3 = V_{HNO_3} \times M_{HNO_3} = (0.0250 \cancel{L})\left(\frac{0.100 \text{ mol } HNO_3}{\cancel{L}}\right)$$
$$= 2.50 \times 10^{-3} \text{ mol } HNO_3$$

Because this is a neutralization reaction, HNO_3 and $Ca(OH)_2$ react to form H_2O and the salt containing Ca^{2+} and NO_3^-:

$$2\,HNO_3(aq) + Ca(OH)_2(s) \longrightarrow 2\,H_2O(l) + Ca(NO_3)_2(aq)$$

Thus, 2 mol $HNO_3 \triangleq$ 1 mol $Ca(OH)_2$. Therefore,

$$\text{Grams } Ca(OH)_2 = (2.50 \times 10^{-3} \cancel{\text{mol } HNO_3}) \times \left(\frac{1 \text{ mol } \cancel{Ca(OH)_2}}{2 \text{ mol } \cancel{HNO_3}}\right)\left(\frac{74.1 \text{ g } Ca(OH)_2}{1 \text{ mol } \cancel{Ca(OH)_2}}\right)$$
$$= 0.0926 \text{ g } Ca(OH)_2$$

Check The answer is reasonable because a small volume of dilute acid requires only a small amount of base to neutralize it.

Practice Exercise

How many milligrams of sodium sulfide are needed to completely react with 25.00 mL of a 0.0100 *M* aqueous solution of cadmium nitrate, to form a precipitate of CdS(*s*)?
(**a**) 13.8 mg (**b**) 19.5 mg (**c**) 23.5 mg (**d**) 32.1 mg (**e**) 39.0 mg

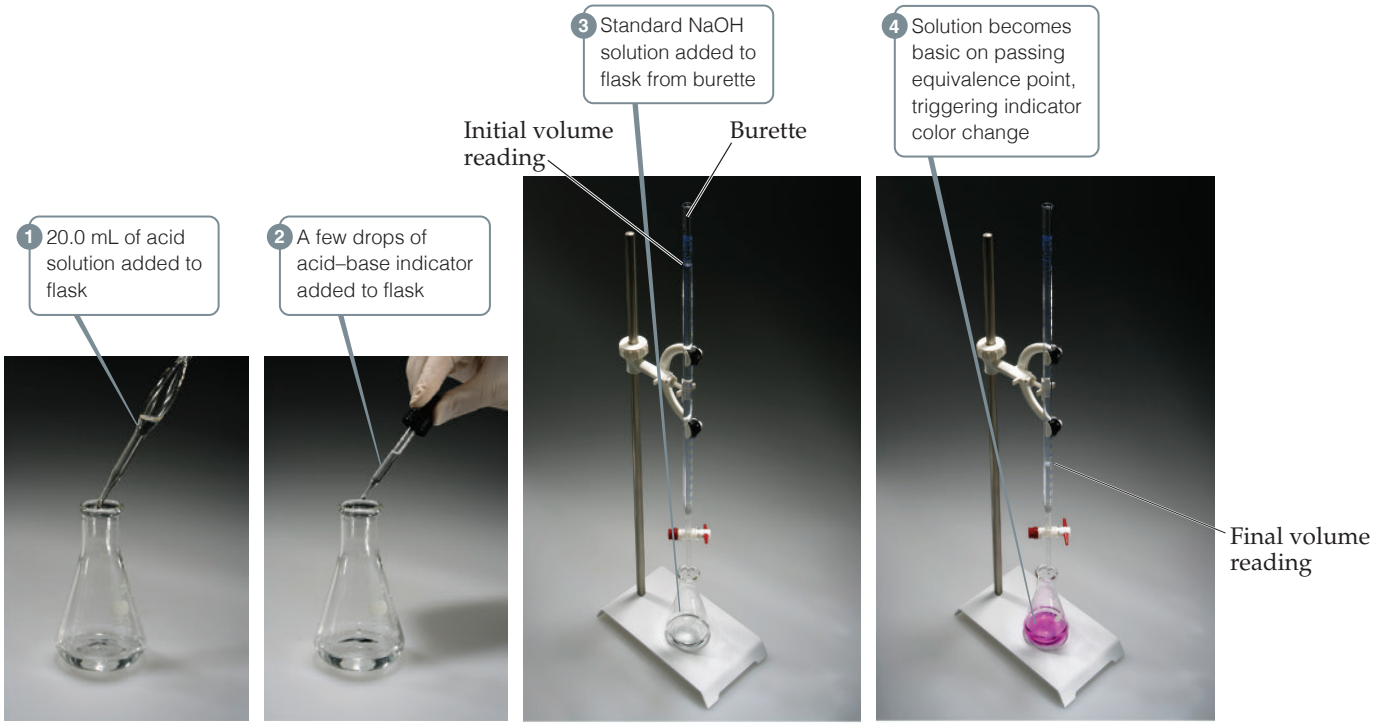
Titrations

To determine the concentration of a particular solute in a solution, chemists often carry out a **titration**, which involves combining a solution where the solute concentration is not known with a reagent solution of known concentration, called a **standard solution**. Just enough standard solution is added to completely react with the solute in the solution of unknown concentration. The point at which stoichiometrically equivalent quantities are brought together is known as the **equivalence point**.

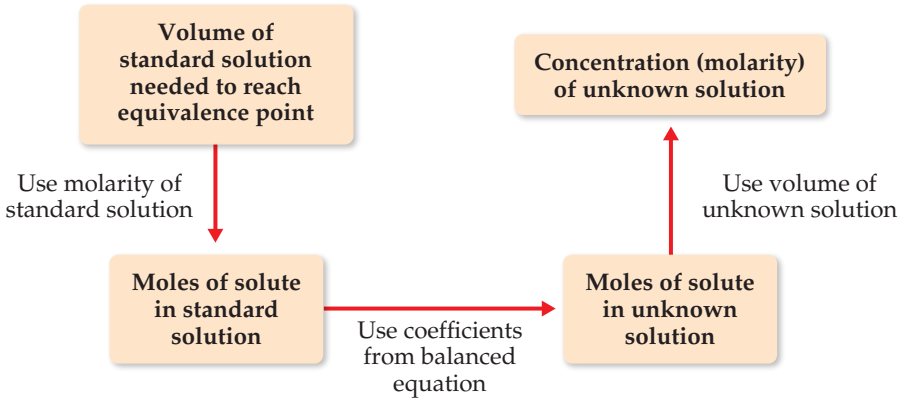
Titrations can be conducted using neutralization, precipitation, or oxidation-reduction reactions. Figure 4.16 illustrates a typical neutralization titration, one between an HCl solution of unknown concentration and a standard NaOH solution. To determine the HCl concentration, we first add a specific volume of the HCl solution, 20.0 mL in this example, to a flask. Next we add a few drops of an acid–base **indicator**. The acid–base indicator is a dye that changes color on passing the equivalence point.* For example, the dye phenolphthalein is colorless in acidic solution but pink in basic solution. The standard solution is then slowly added until the solution turns pink, telling us that the neutralization reaction between HCl and NaOH is complete. The standard solution is added from a *burette* so that we can accurately determine the added volume of NaOH solution. Knowing the volumes of both solutions and the concentration of the standard solution, we can calculate the concentration of the unknown solution as diagrammed in Figure 4.17.

*More precisely, the color change of an indicator signals the end point of the titration, which if the proper indicator is chosen lies very near the equivalence point. Acid–base titrations are discussed in more detail in Section 17.3.

Go Figure How would the volume of standard solution added change if that solution were $Ba(OH)_2(aq)$ instead of $NaOH(aq)$?



▲ **Figure 4.16 Procedure for titrating an acid against a standard solution of NaOH.** The acid–base indicator, phenolphthalein, is colorless in acidic solution but takes on a pink color in basic solution.



◀ **Figure 4.17 Procedure for determining the concentration of a solution from titration with a standard solution.**

Sample Exercise 4.16

Determining Solution Concentration by an Acid–Base Titration

One commercial method used to peel potatoes is to soak them in a NaOH solution for a short time and then remove the potatoes and spray off the peel. The NaOH concentration is normally 3 to 6 *M*, and the solution must be analyzed periodically. In one such analysis, 45.7 mL of 0.500 *M* H_2SO_4 is required to neutralize 20.0 mL of NaOH solution. What is the concentration of the NaOH solution?

SOLUTION

Analyze We are given the volume (45.7 mL) and molarity (0.500 *M*) of an H_2SO_4 solution (the standard solution) that reacts completely with 20.0 mL of NaOH solution. We are asked to calculate the molarity of the NaOH solution.

Plan Following the steps given in Figure 4.17, we use the H_2SO_4 volume and molarity to calculate the number of moles of H_2SO_4. Then we can use this quantity and the balanced equation for the reaction to calculate moles of NaOH. Finally, we can use moles of NaOH and the NaOH volume to calculate NaOH molarity.

Solve

The number of moles of H_2SO_4 is the product of the volume and molarity of this solution:

$$\text{Moles } H_2SO_4 = (45.7 \text{ mL soln})\left(\frac{1 \text{ L soln}}{1000 \text{ mL soln}}\right)\left(\frac{0.500 \text{ mol } H_2SO_4}{\text{L soln}}\right)$$
$$= 2.28 \times 10^{-2} \text{ mol } H_2SO_4$$

Acids react with metal hydroxides to form water and a salt. Thus, the balanced equation for the neutralization reaction is:

$$H_2SO_4(aq) + 2\,NaOH(aq) \longrightarrow 2\,H_2O(l) + Na_2SO_4(aq)$$

According to the balanced equation, 1 mol H_2SO_4 ≃ 2 mol NaOH. Therefore,

$$\text{Moles NaOH} = (2.28 \times 10^{-2} \text{ mol } H_2SO_4)\left(\frac{2 \text{ mol NaOH}}{1 \text{ mol } H_2SO_4}\right)$$
$$= 4.56 \times 10^{-2} \text{ mol NaOH}$$

Knowing the number of moles of NaOH in 20.0 mL of solution allows us to calculate the molarity of this solution:

$$\text{Molarity NaOH} = \frac{\text{mol NaOH}}{\text{L soln}}$$
$$= \left(\frac{4.56 \times 10^{-2} \text{ mol NaOH}}{20.0 \text{ mL soln}}\right)\left(\frac{1000 \text{ mL soln}}{1 \text{ L soln}}\right)$$
$$= 2.28 \frac{\text{mol NaOH}}{\text{L soln}} = 2.28\ M$$

Practice Exercises

What is the molarity of an HCl solution if 27.3 mL of it neutralizes 134.5 mL of 0.0165 *M* $Ba(OH)_2$?

(**a**) 0.0444 *M* (**b**) 0.0813 *M* (**c**) 0.163 *M* (**d**) 0.325 *M* (**e**) 3.35 *M*

Sample Exercise 4.17

Determining the Quantity of Solute by Titration

The quantity of Cl^- in a municipal water supply is determined by titrating the sample with Ag^+. The precipitation reaction taking place during the titration is

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

(**a**) How many grams of chloride ion are in a sample of the water if 20.2 mL of 0.100 *M* Ag^+ is needed to react with all the chloride in the sample? (**b**) If the sample has a mass of 10.0 g, what percentage of Cl^- does it contain?

SOLUTION

Analyze We are given the volume (20.2 mL) and molarity (0.100 *M*) of a solution of Ag^+ and the chemical equation for reaction of this ion with Cl^-. We are asked to calculate the number of grams of Cl^- in the sample and the mass percentage of Cl^- in the sample.

Plan (**a**) We can use the procedure outlined by the green arrows in Figure 4.15. We begin by using the volume and molarity of Ag^+ to calculate the number of moles of Ag^+ used in the titration. We then use the balanced equation to determine the moles of Cl^- in the sample and from that the grams of Cl^-. (**b**) To calculate the percentage of Cl^- in the sample, we compare the number of grams of Cl^- in the sample with the original mass of the sample, 10.0 g.

Solve

(**a**) Calculate the number of moles of Ag^+ used in the titration.

$$\text{Moles } Ag^+ = (20.2 \text{ mL soln})\left(\frac{1 \text{ L soln}}{1000 \text{ mL soln}}\right)\left(\frac{0.100 \text{ mol } Ag^+}{\text{L soln}}\right)$$
$$= 2.02 \times 10^{-3} \text{ mol } Ag^+$$

From the balanced equation we see that 1 mol Ag^+ ≃ 1 mol Cl^-. Using this information and the molar mass of Cl, we have:

$$\text{Grams } Cl^- = (2.02 \times 10^{-3} \text{ mol } Ag^+)\left(\frac{1 \text{ mol Cl}}{1 \text{ mol } Ag^+}\right)\left(\frac{35.5 \text{ g } Cl^-}{\text{mol Cl}}\right)$$
$$= 7.17 \times 10^{-2} \text{ g } Cl^-$$

(**b**) Calculate the percentage of Cl^- used in the sample.

$$\text{Percent } Cl^- = \frac{7.17 \times 10^{-2} \text{ g}}{10.0 \text{ g}} \times 100\% = 0.717\%\ Cl^-$$

Practice Exercise

A mysterious white powder is found at a crime scene. A simple chemical analysis concludes that the powder is a mixture of sugar and morphine ($C_{17}H_{19}NO_3$), a weak base similar to ammonia. The crime lab takes 10.00 mg of the mysterious white powder, dissolves it in 100.00 mL water, and titrates it to the equivalence point with 2.84 mL of a standard 0.0100 *M* HCl solution. What is the percentage of morphine in the white powder?

(**a**) 8.10%
(**b**) 17.3%
(**c**) 32.6%
(**d**) 49.7%
(**e**) 81.0%

Sample Integrative Exercise

Putting Concepts Together

Note: *Integrative exercises require skills from earlier chapters as well as ones from the present chapter.*

A sample of 70.5 mg of potassium phosphate is added to 15.0 mL of 0.050 *M* silver nitrate, resulting in the formation of a precipitate. (**a**) Write the molecular equation for the reaction. (**b**) What is the limiting reactant in the reaction? (**c**) Calculate the theoretical yield, in grams, of the precipitate that forms.

SOLUTION

(**a**) Potassium phosphate and silver nitrate are both ionic compounds. Potassium phosphate contains K^+ and PO_4^{3-} ions, so its chemical formula is K_3PO_4. Silver nitrate contains Ag^+ and NO_3^- ions, so its chemical formula is $AgNO_3$. Because both reactants are strong electrolytes, the solution contains K^+, PO_4^{3-}, Ag^+, and NO_3^- ions before the reaction occurs. According to the solubility guidelines in Table 4.1, Ag^+ and PO_4^{3-} form an insoluble compound, so Ag_3PO_4 will precipitate from the solution. In contrast, K^+ and NO_3^- will remain in solution because KNO_3 is water soluble. Thus, the balanced molecular equation for the reaction is:

$$K_3PO_4(aq) + 3\,AgNO_3(aq) \longrightarrow Ag_3PO_4(s) + 3\,KNO_3(aq)$$

(**b**) To determine the limiting reactant, we must examine the number of moles of each reactant. The number of moles of K_3PO_4 is calculated from the mass of the sample using the molar mass as a conversion factor. The molar mass of K_3PO_4 is $3(39.1) + 31.0 + 4(16.0) = 212.3$ g/mol. Converting milligrams to grams and then to moles, we have:

$$(70.5\ \text{mg}\ K_3PO_4)\left(\frac{10^{-3}\ \text{g}\ K_3PO_4}{1\ \text{mg}\ K_3PO_4}\right)\left(\frac{1\ \text{mol}\ K_3PO_4}{212.3\ \text{g}\ K_3PO_4}\right)$$
$$= 3.32 \times 10^{-4}\ \text{mol}\ K_3PO_4$$

We determine the number of moles of $AgNO_3$ from the volume and molarity of the solution. (Section 4.5) Converting milliliters to liters and then to moles, we have:

$$(15.0\ \text{mL})\left(\frac{10^{-3}\ \text{L}}{1\ \text{mL}}\right)\left(\frac{0.050\ \text{mol}\ AgNO_3}{\text{L}}\right)$$
$$= 7.5 \times 10^{-4}\ \text{mol}\ AgNO_3$$

Comparing the amounts of the two reactants, we find that there are $(7.5 \times 10^{-4})/(3.32 \times 10^{-4}) = 2.3$ times as many moles of $AgNO_3$ as there are moles of K_3PO_4. According to the balanced equation, however, 1 mol K_3PO_4 requires 3 mol $AgNO_3$. Thus, there is insufficient $AgNO_3$ to consume the K_3PO_4, and $AgNO_3$ is the limiting reactant.

(**c**) The precipitate is Ag_3PO_4, whose molar mass is $3(107.9) + 31.0 + 4(16.0) = 418.7$ g/mol. To calculate the number of grams of Ag_3PO_4 that could be produced in this reaction (the theoretical yield), we use the number of moles of the limiting reactant, converting mol $AgNO_3 \Rightarrow$ mol $Ag_3PO_4 \Rightarrow$ g Ag_3PO_4. We use the coefficients in the balanced equation to convert moles of $AgNO_3$ to moles Ag_3PO_4, and we use the molar mass of Ag_3PO_4 to convert the number of moles of this substance to grams.

$$(7.5 \times 10^{-4}\ \text{mol}\ AgNO_3)\left(\frac{1\ \text{mol}\ Ag_3PO_4}{3\ \text{mol}\ AgNO_3}\right)\left(\frac{418.7\ \text{g}\ Ag_3PO_4}{1\ \text{mol}\ Ag_3PO_4}\right)$$
$$= 0.10\ \text{g}\ Ag_3PO$$

The answer has only two significant figures because the quantity of $AgNO_3$ is given to only two significant figures.

Self-Assessment Exercise

4.35 Hard water contains Ca^{2+}, Mg^{2+}, and Fe^{2+} ions, which form a scum with soap. Water softeners replace these ions with Na^+. If 1500 L of hard water contains 0.020 *M* Ca^{2+} and 0.0040 *M* Mg^{2+}, how many grams of NaCl are needed to replace these ions? Keep in mind charge balance must be maintained.

(a) 1800 g
(b) 2100 g
(c) 3500 g
(d) 4200 g

Exercises

4.36 You want to analyze a silver nitrate solution. (**a**) You could add HCl(*aq*) to the solution to precipitate out AgCl(*s*). What volume of a 0.150 *M* HCl(*aq*) solution is needed to precipitate the silver ions from 15.0 mL of a 0.200 *M* $AgNO_3$ solution? (**b**) You could add solid KCl to the solution to precipitate out AgCl(*s*). What mass of KCl is needed to precipitate the silver ions from 15.0 mL of 0.200 *M* $AgNO_3$ solution? (**c**) Given that a 0.150 *M* HCl(*aq*) solution costs $39.95 for 500 mL and that KCl costs $10/ton, which analysis procedure is more cost-effective?

4.37 (**a**) What volume of 0.115 *M* $HClO_4$ solution is needed to neutralize 50.00 mL of 0.0875 *M* NaOH? (**b**) What volume of 0.128 *M* HCl is needed to neutralize 2.87 g of $Mg(OH)_2$? (**c**) If 25.8 mL of an $AgNO_3$ solution is needed to precipitate all the Cl^- ions in a 785-mg sample of KCl (forming AgCl), what is the molarity of the $AgNO_3$ solution? (**d**) If 45.3 mL of a 0.108 *M* HCl solution is needed to neutralize a solution of KOH, how many grams of KOH must be present in the solution?

4.38 Some sulfuric acid is spilled on a lab bench. You can neutralize the acid by sprinkling sodium hydrogen carbonate on it and then mopping up the resulting solution. The sodium hydrogen carbonate reacts with sulfuric acid according to:

$$2\,NaHCO_3(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + 2\,H_2O(l) + 2\,CO_2(g)$$

Sodium hydrogen carbonate is added until the fizzing due to the formation of $CO_2(g)$ stops. If 27 mL of 6.0 *M* H_2SO_4 was spilled, what is the minimum mass of $NaHCO_3$ that must be added to the spill to neutralize the acid?

4.39 A 4.36 g sample of an unknown alkali metal hydroxide is dissolved in 100.0 mL of water. An acid–base indicator is added, and the resulting solution is titrated with 2.50 *M* HCl(*aq*) solution. The indicator changes color, signaling that the equivalence point has been reached, after 17.0 mL of the hydrochloric acid solution has been added. (**a**) What is the molar mass of the metal hydroxide? (**b**) What is the identity of the alkali metal cation: Li^+, Na^+, K^+, Rb^+, or Cs^+?

4.40 A solution of 105.0 mL of 0.300 *M* NaOH is mixed with a solution of 150.0 mL of 0.060 *M* $AlCl_3$. (**a**) Write the balanced chemical equation for the reaction that occurs. (**b**) What precipitate forms? (**c**) What is the limiting reactant? (**d**) How many grams of this precipitate form? (**e**) What is the concentration of each ion that remains in solution?

4.41 A 0.5895 g sample of impure magnesium hydroxide is dissolved in 100.0 mL of 0.2050 *M* HCl solution. The excess acid then needs 19.85 mL of 0.1020 *M* NaOH for neutralization. Calculate the percentage by mass of magnesium hydroxide in the sample, assuming that it is the only substance reacting with the HCl solution.

Answers to Self-Assessment Exercises

4.35 (d)

Chapter Summary and Key Terms

GENERAL PROPERTIES OF AQUEOUS SOLUTIONS (INTRODUCTION AND SECTION 4.1) Solutions in which water is the dissolving medium are called **aqueous solutions**. The component of the solution that is present in the greatest quantity is the **solvent**. The other components are **solutes**.

Any substance whose aqueous solution contains ions is called an **electrolyte**. Any substance that forms a solution containing no ions is a **nonelectrolyte**. Electrolytes that are present in solution entirely as ions are **strong electrolytes**, whereas those that are present partly as ions and partly as molecules are **weak electrolytes**. Ionic compounds dissociate into ions when they dissolve, and they are strong electrolytes. The solubility of ionic substances is made possible by **solvation**, the interaction of ions with polar solvent molecules. Most molecular compounds are nonelectrolytes, although some are weak electrolytes and a few are strong electrolytes. When representing the ionization of a weak electrolyte in solution, half-arrows in both directions are used, indicating that the forward and reverse reactions can achieve a chemical balance called a **chemical equilibrium**.

PRECIPITATION REACTIONS (SECTION 4.2) **Precipitation reactions** are those in which an insoluble product, called a **precipitate**, forms. Solubility guidelines help determine whether an ionic compound will be soluble in water. (The **solubility** of a substance is the amount that dissolves in a given quantity of solvent.) Reactions such as precipitation reactions, in which cations and anions appear to exchange partners, are called **exchange reactions**, or **metathesis reactions**.

Chemical equations can be written to show whether dissolved substances are present in solution predominantly as ions or molecules. When the complete chemical formulas of all reactants and products are used, the equation is called a **molecular equation**. A **complete ionic equation** shows all dissolved strong electrolytes as their component ions. In a **net ionic equation**, those ions that go through the reaction unchanged (**spectator ions**) are omitted.

ACIDS, BASES, AND NEUTRALIZATION REACTIONS (SECTION 4.3) Acids and bases are important electrolytes. **Acids** are proton donors; they increase the concentration of $H^+(aq)$ in aqueous solutions to which they are added. **Bases** are proton acceptors; they increase the concentration of $OH^-(aq)$ in aqueous solutions. Those acids and bases that are strong electrolytes are called **strong acids** and **strong bases**, respectively. Those that are weak electrolytes are **weak acids** and **weak bases**. When solutions of acids and bases are mixed, a neutralization reaction occurs. The **neutralization reaction** between an acid and a metal hydroxide produces water and a **salt**. Gases can also be formed as a result of

neutralization reactions. The reaction of a sulfide with an acid forms $H_2S(g)$; the reaction between a carbonate and an acid forms $CO_2(g)$.

OXIDATION-REDUCTION REACTIONS (SECTION 4.4) **Oxidation** is the loss of electrons by a substance, whereas **reduction** is the gain of electrons by a substance. **Oxidation numbers** keep track of electrons during chemical reactions and are assigned to atoms using specific rules. The oxidation of an element results in an increase in its oxidation number, whereas reduction is accompanied by a decrease in oxidation number. Oxidation is always accompanied by reduction, giving **oxidation-reduction**, or **redox, reactions**.

Many metals are oxidized by O_2, acids, and salts. The redox reactions between metals and acids as well as those between metals and salts are called **displacement reactions**. The products of these displacement reactions are always an element (H_2 or a metal) and a salt. Comparing such reactions allows us to rank metals according to their ease of oxidation. A list of metals arranged in order of decreasing ease of oxidation is called an **activity series**. Any metal on the list can be oxidized by ions of metals (or H^+) below it in the series.

CONCENTRATIONS OF SOLUTIONS (SECTION 4.5) The **concentration** of a solution expresses the amount of a solute dissolved in the solution. One of the common ways to express the concentration of a solute is in terms of molarity. The **molarity** of a solution is the number of moles of solute per liter of solution. Molarity makes it possible to interconvert solution volume and number of moles of solute. If the solute is a liquid, its density can be used in molarity calculations to convert between mass, volume, and moles. Solutions of known molarity can be formed either by weighing out the solute and diluting it to a known volume or by the **dilution** of a more concentrated solution of known concentration (a stock solution). Adding solvent to the solution (the process of dilution) decreases the concentration of the solute without changing the number of moles of solute in the solution ($M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$).

SOLUTION STOICHIOMETRY AND CHEMICAL ANALYSIS (SECTION 4.6) In the process called **titration**, we combine a solution of known concentration (a **standard solution**) with a solution of unknown concentration to determine the unknown concentration or the quantity of solute in the unknown. The point in the titration at which stoichiometrically equivalent quantities of reactants are brought together is called the **equivalence point**. An indicator can be used to show the end point of the titration, which coincides closely with the equivalence point.

Learning Outcomes

After studying this chapter, you should be able to:

- Identify compounds as acids or bases, and as strong, weak, or nonelectrolytes. (Sections 4.1 and 4.3) *Related Exercises: 4.13–4.15, 4.63–4.65*
- Recognize reactions by type and be able to predict the products of simple acid–base, precipitation, and redox reactions. (Sections 4.2–4.4) *Related Exercises: 4.16–4.18, 4.24–4.25, 4.43–4.45, 4.66–4.68, 4.73–4.76*
- Calculate molarity and use it to convert between moles of a substance in solution and volume of the solution. (Section 4.5) *Related Exercises: 4.27–4.31, 4.79–4.85*
- Describe how to carry out a dilution to achieve a desired solution concentration. (Section 4.5) *Related Exercises: 4.32–4.34, 4.86–4.88*
- Describe how to perform and interpret the results of a titration. (Section 4.6) *Related Exercises: 4.38–4.41, 4.91–4.94*

Key Equations

- $$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}} \quad [4.31]$$

  Molarity is the most commonly used unit of concentration in chemistry.

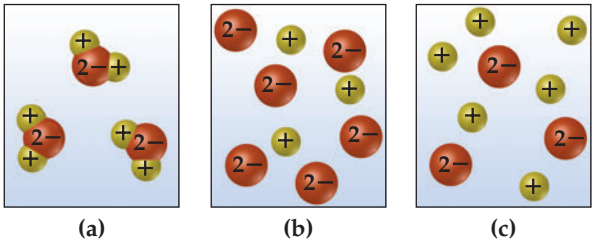
- $$M_{conc} \times V_{conc} = M_{dil} \times V_{dil} \quad [4.33]$$

  When adding solvent to a concentrated solution to make a dilute solution, molarities and volumes of both concentrated and dilute solutions can be calculated if three of the quantities are known.

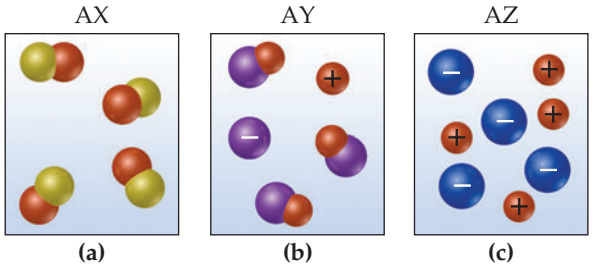
Exercises

Visualizing Concepts

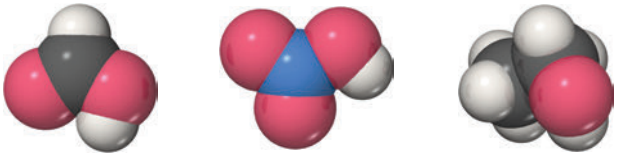
4.42 Which of the following schematic drawings best describes a solution of Li_2SO_4 in water (water molecules not shown for simplicity)? [Section 4.1]



4.43 Aqueous solutions of three different substances, AX, AY, and AZ, are represented by the three accompanying diagrams. Identify each substance as a strong electrolyte, a weak electrolyte, or a nonelectrolyte. [Section 4.1]



4.44 Use the molecular representations shown here to classify each compound as a nonelectrolyte, a weak electrolyte, or a strong electrolyte (see Figure 4.4 for the element color scheme). [Sections 4.1 and 4.3]



4.45 The concept of chemical equilibrium is very important. Which one of the following statements is the most correct way to think about equilibrium?

(**a**) If a system is at equilibrium, nothing is happening.

(**b**) If a system is at equilibrium, the rate of the forward reaction is equal to the rate of the back reaction.

(**c**) If a system is at equilibrium, the product concentration is changing over time. [Section 4.1]

4.46 You are presented with a white solid and told that due to careless labeling it is not clear if the substance is barium chloride, lead chloride, or zinc chloride. When you transfer the solid to a beaker and add water, the solid dissolves to give a clear solution. Next an $Na_2SO_4(aq)$ solution is added and a white precipitate forms. What is the identity of the unknown white solid? [Section 4.2]



4.47 Which of the following ions will *always* be a spectator ion in a precipitation reaction? (**a**) Cl^-, (**b**) NO_3^-, (**c**) NH_4^+, (**d**) S^{2-}, (**e**) SO_4^{2-}. [Section 4.2]

4.48 The labels have fallen off three bottles containing powdered samples of metals; one contains zinc, one lead, and the other platinum. You have three solutions at your disposal: 1 *M* sodium nitrate, 1 *M* nitric acid, and 1 *M* nickel nitrate. How could you use these solutions to determine the identities of each metal powder? [Section 4.4]

4.49 Explain how a redox reaction involves electrons in the same way that a neutralization reaction involves protons. [Sections 4.3 and 4.4]

4.50 What kind of reaction is the "water-splitting" reaction? $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g)$

(**a**) an acid–base reaction

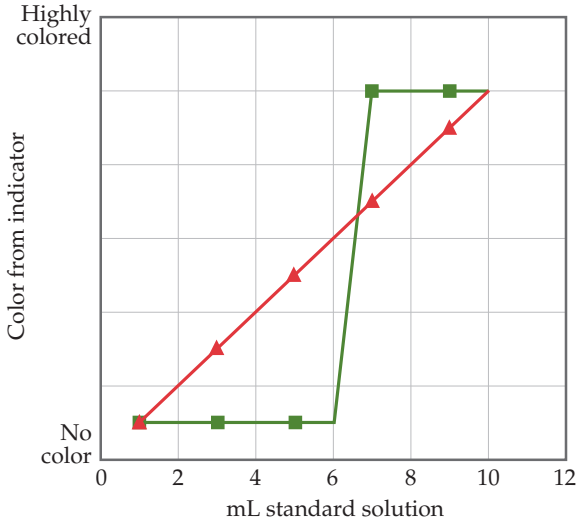
(**b**) a metathesis reaction

(**c**) a redox reaction

(**d**) a precipitation reaction [Section 4.4]

4.51 An aqueous solution contains 1.2 m*M* of total ions. (**a**) If the solution is NaCl(*aq*), what is the concentration of chloride ion? (**b**) If the solution is $FeCl_3(aq)$, what is the concentration of chloride ion? [Section 4.5]

4.52 Which data set, of the two graphed here, would you expect to observe from a titration like that shown in Figure 4.16? [Section 4.6]



4.53 You are titrating an acidic solution with a basic one, and just realized you forgot to add the indicator that tells you when the equivalence point is reached. In this titration, the indicator turns blue at the equivalence point from an initially colorless solution. You quickly grab a bottle of indicator and add some to your titration beaker, and the whole solution turns dark blue. What do you do now? [Section 4.6]

General Properties of Aqueous Solutions (Section 4.1)

4.54 State whether each of the following statements is true or false. Justify your answer in each case.

(**a**) When acetone, CH_3COCH_3, is dissolved in water, a conducting solution results.

(**b**) When ammonium nitrate, NH_4NO_3, dissolves in water, the solution is weakly conducting and basic in nature.

4.55 Would you expect that an anion would be physically closer to the oxygen or to the hydrogens of water molecules that surround it in solution?

4.56 Specify what ions are present upon dissolving each of the following substances in water: (**a**) HIO_3, (**b**) $Ba(OH)_2$, (**c**) HCN, (**d**) $CuSO_4$.

4.57 Acetone, CH_3COCH_3, is a nonelectrolyte; hypochlorous acid, HClO, is a weak electrolyte; and ammonium chloride, NH_4Cl, is a strong electrolyte. (**a**) What are the solutes present in aqueous solutions of each compound? (**b**) If 0.1 mol of each compound is dissolved in solution, which one contains 0.2 mol of solute particles, which contains 0.1 mol of solute particles, and which contains somewhere between 0.1 and 0.2 mol of solute particles?

Precipitation Reactions (Section 4.2)

4.58 Predict whether each of the following compounds is soluble in water: (**a**) MgS, (**b**) $Cr(OH)_3$, (**c**) $ZnCl_2$, (**d**) $Pb_3(PO_4)_2$, (**e**) $Sr(CH_3COO)_2$.

4.59 Identify the precipitate (if any) that forms when the following solutions are mixed, and write a balanced equation for each reaction. (**a**) NH_4I and $CuCl_2$, (**b**) LiOH and $MnCl_2$, (**c**) K_3PO_4 and $CoSO_4$.

4.60 Which ions remain in solution, unreacted, after each of the following pairs of solutions is mixed?

(**a**) potassium carbonate and magnesium sulfate

(**b**) lead nitrate and lithium sulfide

(**c**) ammonium phosphate and calcium chloride

4.61 Separate samples of a solution of an unknown ionic compound are treated with dilute $AgNO_3$, $Pb(NO_3)_2$, and $BaCl_2$. Precipitates form in all three cases. Which of the following could be the anion of the unknown salt: Br^-, CO_3^{2-}, NO_3^-?

4.62 Three solutions are mixed together to form a single solution; in the final solution, there are 0.2 mol $Pb(CH_3COO)_2$, 0.1 mol Na_2S, and 0.1 mol $CaCl_2$ present. What solid(s) will precipitate?

Acids, Bases, and Neutralization Reactions (Section 4.3)

4.63 State whether each of the following statements is true or false. Justify your answer in each case.

(**a**) NH_3 contains no OH^- ions, and yet its aqueous solutions are basic.

(**b**) HF is a strong acid.

(**c**) Although sulfuric acid is a strong electrolyte, an aqueous solution of H_2SO_4 contains more HSO_4^- ions than SO_4^{2-} ions.

4.64 An aqueous solution of an unknown solute is tested with litmus paper and found to be acidic. The solution is weakly conducting compared with a solution of NaCl of the same concentration. Which of the following substances could the unknown be: KOH, NH_3, HNO_3, $KClO_2$, H_3PO_3, CH_3COCH_3 (acetone)?

4.65 Classify each of the following aqueous solutions as a nonelectrolyte, weak electrolyte, or strong electrolyte: (**a**) $PbCl_2$, (**b**) $N(CH_3)_3$, (**c**) CsOH, (**d**) H_2S, (**e**) $CrCl_2$, (**f**) $Ni(CH_3COO)_2$.

4.66 Write the balanced molecular and net ionic equations for each of the following neutralization reactions:

(**a**) Aqueous acetic acid is neutralized by aqueous barium hydroxide.

(**b**) Solid chromium(III) hydroxide reacts with nitrous acid.

(**c**) Aqueous nitric acid and aqueous ammonia react.

4.67 Because the oxide ion is basic, metal oxides react readily with acids. (**a**) Write the net ionic equation for the following reaction:

$$FeO(s) + 2\,HClO_4(aq) \longrightarrow Fe(ClO_4)_2(aq) + H_2O(l)$$

(**b**) Based on the equation in part (a), write the net ionic equation for the reaction that occurs between NiO(*s*) and an aqueous solution of nitric acid.

4.68 As K_2O dissolves in water, the oxide ion reacts with water molecules to form hydroxide ions. (**a**) Write the molecular and net ionic equations for this reaction. (**b**) Based on the definitions of acid and base, what ion is the base in this reaction? (**c**) What is the acid in the reaction? (**d**) What is the spectator ion in the reaction?

Oxidation-Reduction Reactions (Section 4.4)

4.69 True or false:

(**a**) If a substance is oxidized, there must be more oxygen in the substance.

(**b**) If a substance is oxidized, it must lose at least one electron and form an anion.

4.70 True or false:

(**a**) Reduction occurs if the oxidation number of an element increases.

(**b**) Oxidation and reduction must occur together in a reaction.

4.71 Determine the oxidation number for the indicated element in each of the following substances: (**a**) N in N_2H_4, (**b**) N in NO_2, (**c**) Mn in $MnCl_3$, (**d**) Fe in $FeSO_4$, (**e**) Pt in $PtCl_4$, (**f**) Cl in $NaClO_4$.

4.72 Which of the following are redox reactions? For those that are, indicate which element is oxidized and which is reduced. For those that are not, indicate whether they are precipitation or neutralization reactions.

(**a**) $P_4(s) + 10\,HClO(aq) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(aq) + 10\,HCl(aq)$

(**b**) $Br_2(l) + 2\,K(s) \longrightarrow 2\,KBr(s)$

(**c**) $CH_3CH_2OH(l) + 3\,O_2(g) \longrightarrow 3\,H_2O(l) + 2\,CO_2(g)$

(**d**) $ZnCl_2(aq) + 2\,NaOH(aq) \longrightarrow Zn(OH)_2(s) + 2\,NaCl(aq)$

4.73 Write balanced molecular and net ionic equations for the reactions of (**a**) hydrochloric acid with nickel, (**b**) dilute sulfuric acid with iron, (**c**) hydrobromic acid with magnesium, (**d**) acetic acid, CH_3COOH, with zinc.

4.74 Using the activity series (Table 4.5), write balanced chemical equations for the following reactions. If no reaction occurs, write NR. (**a**) Nickel metal is added to a solution of copper(II) nitrate, (**b**) a solution of zinc nitrate is added to a solution of magnesium sulfate, (**c**) hydrochloric acid is added to gold metal, (**d**) chromium metal is immersed in an aqueous solution of cobalt(II) chloride, (**e**) hydrogen gas is bubbled through a solution of silver nitrate.

4.75 The metal cadmium tends to form Cd^{2+} ions. The following observations are made: (i) When a strip of zinc metal is placed in $CdCl_2(aq)$, cadmium metal is deposited on the strip. (ii) When a strip of cadmium metal is placed in $Ni(NO_3)_2(aq)$, nickel metal is deposited on the strip. (**a**) Write net ionic equations to explain each of the preceding observations. (**b**) Which elements more closely define the position of cadmium in the activity series? (**c**) What experiments would you need to perform to locate more precisely the position of cadmium in the activity series?

4.76 The following reactions (note that the arrows are pointing only one direction) can be used to prepare an activity series for the halogens:

$$Br_2(aq) + 2\,NaI(aq) \longrightarrow 2\,NaBr(aq) + I_2(aq)$$
$$Cl_2(aq) + 2\,NaBr(aq) \longrightarrow 2\,NaCl(aq) + Br_2(aq)$$

(**a**) Which elemental halogen would you predict is the most stable, upon mixing with other halides? (**b**) Predict whether a reaction will occur when elemental chlorine and potassium iodide are mixed. (**c**) Predict whether a reaction will occur when elemental bromine and lithium chloride are mixed.

Concentrations of Solutions (Section 4.5)

4.77 (**a**) Is the number of moles of ions present in a solution an intensive or an extensive property? (**b**) Can you identify which one between 0.10 mol $ZnCl_2$ and 0.1*M* $ZnCl_2$ contains more Zn^{2+} ion? Why?

4.78 You make 1.000 L of an aqueous solution that contains 35.0 g of sucrose ($C_{12}H_{22}O_{11}$). (**a**) What is the molarity of sucrose in this solution? (**b**) How many liters of water would you have to add to this solution to reduce the molarity you calculated in part (a) by a factor of two?

4.79 (**a**) Calculate the molarity of a solution made by dissolving 12.5 grams of Na_2CrO_4 in enough water to form exactly 750 mL of solution. (**b**) How many moles of KBr are present in 150 mL of a 0.112 *M* solution? (**c**) How many milliliters of 6.1 *M* HCl solution are needed to obtain 0.150 mol of HCl?

4.80 A person suffering from hyponatremia has a sodium ion concentration in the blood of 0.118 *M* and a total blood volume of 4.6 L. What mass of sodium chloride would need to be added to the blood to bring the sodium ion concentration up to 0.138 *M*, assuming no change in blood volume?

4.81 The average adult male has a total blood volume of 5.0 L. After drinking a few beers, he has the "blood alcohol concentration" or BAC of 0.10 (BAC, is given in units of grams of alcohol per 100 mL of blood). What mass of alcohol is circulating in his blood?

4.82 (**a**) How many grams of ethanol, CH_3CH_2OH, should you dissolve in water to make 1.00 L of vodka (which is an aqueous solution that is 6.86 *M* ethanol)? (**b**) Using the density of ethanol (0.789 g/mL), calculate the volume of ethanol you need to make 1.00 L of vodka.

4.83 In a sugar tolerance test, a patient needs to drink a glucose ($C_6H_{12}O_6$) solution containing 100 g glucose. Given that one cup = 350 mL, calculate the molarity of glucose in the glucose solution.

4.84 In each of the following pairs, indicate which has the higher concentration of Cl^- ion: (**a**) 0.10 *M* $AlCl_3$ solution or a 0.25 *M* LiCl solution, (**b**) 150 mL of a 0.05 *M* $MnCl_3$ solution or 200 mL of 0.10 *M* KCl solution, (**c**) a 2.8 *M* HCl solution or a solution made by dissolving 23.5 g of KCl in water to make 100 mL of solution.

4.85 Calculate the concentration of each ion in the following solutions obtained by mixing: (**a**) 32.0 mL of 0.30 *M* $KMnO_4$ with 15.0 mL of 0.60 *M* $KMnO_4$, (**b**) 60.0 mL of 0.100 *M* $ZnCl_2$ with 5.0 mL of 0.200 *M* $Zn(NO_3)_2$, (**c**) 4.2g of $CaCl_2$ in 150.0mL of 0.02 *M* KCl solution. Assume that the volumes are additive.

4.86 (**a**) How many milliliters of a stock solution of 6.0 *M* HNO_3 would you have to use to prepare 110 mL of 0.500 *M* HNO_3? (**b**) If you dilute 10.0 mL of the stock solution to a final volume of 0.250 L, what will be the concentration of the diluted solution?

4.87 Calicheamicin gamma-1, $C_{55}H_{74}IN_3O_{21}S_4$, is one of the most potent antibiotics known: one molecule kills one bacterial cell. Describe how you would (carefully!) prepare 25.00 mL of an aqueous calicheamicin gamma-1 solution that could kill 1.0×10^8 bacteria, starting from a 5.00×10^{-9}*M* stock solution of the antibiotic.

4.88 Glycerol, $C_3H_8O_3$, is a substance used extensively in the manufacture of cosmetic s, foodstuffs, antifreeze, and plastics. Glycerol is a water-soluble liquid with a density of 1.2656 g/mL at 15 °C. Calculate the molarity of a solution of glycerol made by dissolving 50.000 mL glycerol at 15 °C in enough water to make 250.00 mL of solution.

Solution Stoichiometry and Chemical Analysis (Section 4.6)

4.89 You want to analyze a silver nitrate solution. What mass of NaCl is needed to precipitate Ag^+ ions from 45.0 mL of 0.2500 *M* $AgNO_3$ solution?

4.90 (**a**) How many milliliters of 0.120 *M* HCl are needed to completely neutralize 50.0 mL of 0.101 *M* $Ba(OH)_2$ solution? (**b**) How many milliliters of 0.125 *M* H_2SO_4 are needed to neutralize 0.200 g of NaOH? (**c**) If 55.8 mL of a $BaCl_2$ solution is needed to precipitate all the sulfate ion in a 752-mg sample of Na_2SO_4, what is the molarity of the $BaCl_2$ solution? (**d**) If 42.7 mL of 0.208 *M* HCl solution is needed to neutralize a solution of $Ca(OH)_2$, how many grams of $Ca(OH)_2$ must be in the solution?

4.91 The distinctive odor of vinegar is due to acetic acid, CH_3COOH, which reacts with sodium hydroxide according to:

$$CH_3COOH(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCH_3COO(aq)$$

If 3.45 mL of vinegar needs 42.5 mL of 0.115 *M* NaOH to reach the equivalence point in a titration, how many grams of acetic acid are in a 1.00-qt sample of this vinegar?

4.92 An 8.65 g sample of an unknown Group 2 metal hydroxide is dissolved in 85.0 mL of water. An acid–base indicator is added and the resulting solution is titrated with 2.50 *M* HCl(*aq*) solution. The indicator changes color, signaling that the equivalence point has been reached, after 56.9 mL of the hydrochloric acid solution has been added. (**a**) What is the molar mass of the metal hydroxide? (**b**) What is the identity of the metal cation: Ca^{2+}, Sr^{2+}, or Ba^{2+}?

4.93 A solution is made by mixing 1.5 g of LiOH and 23.5 mL of 1.000 *M* HNO_3. (**a**) Write a balanced equation for the reaction that occurs between the solutes. (**b**) Calculate the concentration of each ion remaining in solution. (**c**) Is the resulting solution acidic or basic?

4.94 A 1.248 g sample of limestone rock is pulverized and then treated with 30.00 mL of 1.035 *M* HCl solution. The excess acid then requires 11.56 mL of 1.010 *M* NaOH for neutralization. Calculate the percentage by mass of calcium carbonate in the rock, assuming that it is the only substance reacting with the HCl solution.

Additional Exercises

4.95 Uranium hexafluoride, UF_6, is processed to produce fuel for nuclear reactors and nuclear weapons. UF_6 can be produced in a two-step reaction. Solid uranium (IV) oxide, UO_2, is first made to react with hydrofluoric acid (HF) solution to form solid UF_4 with water as a by-product. UF_4 further reacts with fluorine gas to form UF_6.

(**a**) Write the balanced molecular equations for the conversion of UO_2 into UF_4 and the conversion of UF_4 to UF_6.

(**b**) Which step is an acid–base reaction?

(**c**) Which step is a redox reaction?

4.96 The accompanying photo shows the reaction between a solution of $Cd(NO_3)_2$ and one of Na_2S. (**a**) What is the identity of the precipitate? (**b**) What ions remain in solution? (**c**) Write the net ionic equation for the reaction. (**d**) Is this a redox reaction?



4.97 Suppose you have a solution that might contain any or all of the following cations: Ni^{2+}, Ag^+, Sr^{2+}, and Mn^{2+}. Addition of HCl solution causes a precipitate to form. After filtering off the precipitate, H_2SO_4 solution is added to the resulting solution and another precipitate forms. This is filtered off, and a solution of NaOH is added to the resulting solution. No precipitate is observed. Which ions are present in each of the precipitates? Which of the four ions listed here must be absent from the original solution?

4.98 You choose to investigate some of the solubility guidelines for two ions not listed in Table 4.1, the chromate ion (CrO_4^{2-}) and the oxalate ion ($C_2O_4^{2-}$). You are given 0.01 *M* solutions (A, B, C, D) of four water-soluble salts:

Solution	Solute	Color of Solution
A	Na_2CrO_4	Yellow
B	$(NH_4)_2C_2O_4$	Colorless
C	$AgNO_3$	Colorless
D	$CaCl_2$	Colorless

When these solutions are mixed, the following observations are made:

Experiment Number	Solutions Mixed	Result
1	A + B	No precipitate, yellow solution
2	A + C	Red precipitate forms
3	A + D	Yellow precipitate forms

Experiment Number	Solutions Mixed	Result
4	B + C	White precipitate forms
5	B + D	White precipitate forms
6	C + D	White precipitate forms

(**a**) Write a net ionic equation for the reaction that occurs in each of the experiments. (**b**) Identify the precipitate formed, if any, in each of the experiments.

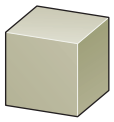
4.99 Antacids are often used to relieve pain and promote healing in the treatment of mild ulcers. Write balanced net ionic equations for the reactions between the aqueous HCl in the stomach and each of the following substances used in various antacids: (**a**) $Al(OH)_3(s)$, (**b**) $Mg(OH)_2(s)$, (**c**) $MgCO_3(s)$, (**d**) $NaAl(CO_3)(OH)_2(s)$, (**e**) $CaCO_3(s)$.

4.100 The commercial production of nitric acid involves the following chemical reactions:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$
$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$$

(**a**) Which of these reactions are redox reactions? (**b**) In each redox reaction identify the element undergoing oxidation and the element undergoing reduction. (**c**) How many grams of ammonia must you start with to make 1000.0 L of a 0.150 *M* aqueous solution of nitric acid? Assume all the reactions give 100% yield.

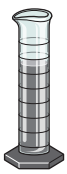
4.101 Consider the following reagents: zinc, copper, mercury (density 13.6 g/mL), silver nitrate solution, nitric acid solution. (**a**) Given a 500-mL Erlenmeyer flask and a balloon, can you combine two or more of the foregoing reagents to initiate a chemical reaction that will inflate the balloon? Write a balanced chemical equation to represent this process. What is the identity of the substance that inflates the balloon? (**b**) What is the theoretical yield of the substance that fills the balloon? (**c**) Can you combine two or more of the foregoing reagents to initiate a chemical reaction that will produce metallic silver? Write a balanced chemical equation to represent this process. What ions are left behind in solution? (**d**) What is the theoretical yield of silver?



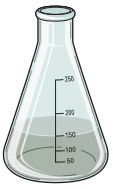
35.0 g Zn



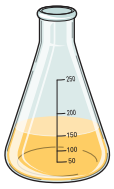
42.0 g Cu



6.55 mL Hg



150 mL of 0.750 *M* $AgNO_3(aq)$

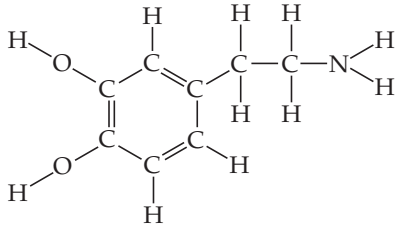


150 mL of 3.00 *M* $HNO_3(aq)$

4.102 Bronze is a *solid solution* of Cu(*s*) and Sn(*s*); solutions of metals like this that are solids are called *alloys*. There is a range of compositions over which the solution is considered a bronze. Bronzes are stronger and harder than either copper or tin alone. (**a**) A 100.0-g sample of a certain bronze is 90.0% copper by mass and 10.0% tin. Which metal can be called the solvent, and which the solute? (**b**) Based on part (a), calculate the concentration of the solute metal in the alloy in units of molarity, assuming a density of 7.9 g/cm^3. (**c**) Suggest a reaction that you could do to remove all the tin from this bronze to leave a pure copper sample. Justify your reasoning.

4.103 A 35.0 mL sample of 1.00 *M* $Co(NO)_3$ and an 80.0-mL sample of 0.600 *M* $Co(NO)_3$ are mixed. The solution is then heated to evaporate water until the total volume is 50.0 mL. Calculate the volume, in mL, of 0.20 *M* H_3PO_4 that is required to precipitate out cobalt (III) phosphate in the final solution.

4.104 Neurotransmitters are molecules that are released by nerve cells to other cells in our bodies, and are needed for muscle motion, thinking, feeling, and memory. Dopamine is a common neurotransmitter in the human brain.



(**a**) Predict what kind of reaction dopamine is most likely to undergo in water: redox, acid–base, precipitation, or metathesis? Explain your reasoning. (**b**) Patients with Parkinson's disease suffer from a shortage of dopamine and may need to take it to reduce symptoms. An IV (intravenous fluid) bag is filled with a solution that contains 400.0 mg dopamine per 250.0 mL of solution. What is the concentration of dopamine in the IV bag in units of molarity? (**c**) Experiments with rats show that if rats are dosed with 3.0 mg/kg of cocaine (that is, 3.0 mg cocaine per kg of animal mass), the concentration of dopamine in their brains increases by 0.75 μM after 60 seconds. Calculate how many molecules of dopamine would be produced in a rat (average brain volume 5.00 mm^3) after 60 seconds of a 3.0 mg/kg dose of cocaine.

4.105 Citric acid, $C_6H_8O_7$, is a triprotic acid. It occurs naturally in citrus fruits like lemons and has applications in food flavouring and preservatives. A solution containing an unknown concentration of the acid is titrated with KOH. It requires 23.20 mL of 0.500 *M* KOH solution to titrate all three acidic protons in 100.00 mL of the citric acid solution. Write a balanced net ionic equation for the neutralization reaction, and calculate the molarity of the citric acid solution.

4.106 (**a**) A caesium hydroxide solution is prepared by dissolving 3.20 g of CsOH in water to make 25.00 mL of solution. What is the molarity of this solution? (**b**) Then, the caesium hydroxide solution prepared in part (a) is used to titrate a hydroiodic acid solution of unknown concentration. Write a balanced chemical equation to represent the reaction between the caesium hydroxide and hydroiodic acid solutions. (**c**) If 18.65 mL of the caesium hydroxide solution was needed to neutralize a 42.3 mL aliquot of the hydroiodic acid solution, what is the concentration (molarity) of the acid?

4.107 A solid sample of $Fe(OH)_3$ is added to 0.500 L of 0.250 *M* aqueous H_2SO_4. The solution that remains is still acidic. It is then titrated with 0.500 *M* NaOH solution, and it takes 12.5 mL of the NaOH solution to reach the equivalence point. What mass of $Fe(OH)_3$ was added to the H_2SO_4 solution?

Integrative Exercises

4.108 Suppose you have 3.00 g of powdered zinc metal, 3.00 g of powdered silver metal and 500.0 mL of a 0.2 *M* copper(II) nitrate solution. (**a**) Which metal will react with the copper(II) nitrate solution? (**b**) What is the net ionic equation that describes this reaction? (**c**) Which is the limiting reagent in the reaction? (**d**) What is the molarity of Cu^{2+} ions in the resulting solution?

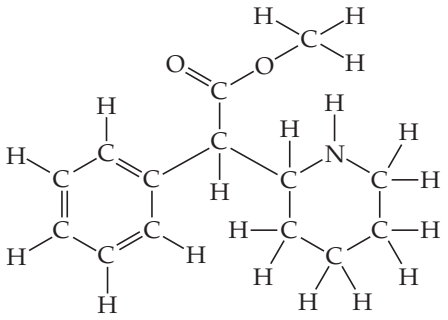
4.109 (**a**) By titration, 15.0 mL of 0.1008 *M* sodium hydroxide is needed to neutralize a 0.2053-g sample of a weak acid. What is the molar mass of the acid if it is monoprotic? (**b**) An elemental analysis of the acid indicates that it is composed of 5.89% H, 70.6% C, and 23.5% O by mass. What is its molecular formula?

4.110 Copper exists in the form of $CuFeS_2$ in copper ore. Copper is isolated in a two-step process. First, $CuFeS_2$ is heated with SiO_2 in the presence of oxygen to form copper(I) sulfide, CuS: $2CuFeS_2 + 2SiO_2(s) + 4O_2(g) \longrightarrow Cu_2S(s) + 2FeSiO_3(s) + 3SO_2(g)$. Cu_2S is then heated with oxygen to form copper and $SO_2(g)$. (**a**) Write the balanced chemical equation for the second reaction. (**b**) Which atoms from which compounds are being oxidized, and which atoms from which compounds are being reduced? (**c**) How many grams of copper would be isolated from 85.36 g of $CuFeS_2$ in copper ore?

4.111 A fertilizer rail car carrying 129,840 L of commercial aqueous ammonia (30% ammonia by mass) tips over and spills. The density of the aqueous ammonia solution is 0.88 g/cm^3. What mass of citric acid, $C(OH)(COOH)(CH_2COOH)_2$, (which contains three acidic protons) is required to neutralize the spill?

4.112 A sample of 8.69 g of $Zn(OH)_2$ is added to 155.0 mL of 0.750 *M* H_2SO_4. (**a**) Write the chemical equation for the reaction that occurs. (**b**) Which is the limiting reactant in the reaction? (**c**) How many moles of $Zn(OH)_2$, H_2SO_4, and $ZnSO_4$ are present after the reaction is complete?

4.113 Ritalin is the trade name of a drug, methylphenidate, used to treat attention-deficit/hyperactivity disorder in young adults. The chemical structure of methylphenidate is



(**a**) Is Ritalin an acid or a base? An electrolyte or a nonelectrolyte? (**b**) A tablet contains a 10.0 mg dose of Ritalin. Assuming all the drug ends up in the bloodstream, and the average man has a total blood volume of 5.0 L, calculate the initial molarity of Ritalin in a man's bloodstream. (**c**) Ritalin has a half-life of 3 hours in the blood, which means that after 3 hours the concentration in the blood has decreased by half of its initial value. For the man in part (b), what is the concentration of Ritalin in his blood after 6 hours?

4.114 A 3.50 g of an alloy which contains only lead and tin is dissolved in hot HNO_3. Excess sulfuric acid is added to this solution and 1.57 g of $PbSO_4(s)$ is obtained. (a) Write the net ionic equation for the formation of $PbSO_4$. (b) Assuming all the lead in the alloy reacted to form $PbSO_4$, what was the amount, in grams, of lead and tin in the alloy respectively?

4.115 The arsenic in a 1.22-g sample of a pesticide was converted to AsO_4^{3-} by suitable chemical treatment. It was then titrated using Ag^+ to form Ag_3AsO_4 as a precipitate. (**a**) What is the oxidation state of As in AsO_4^{3-}? (**b**) Name Ag_3AsO_4 by analogy to the corresponding compound containing phosphorus in place of arsenic. (**c**) If it took 25.0 mL of 0.102 *M* Ag^+ to reach the equivalence point in this titration, what is the mass percentage of arsenic in the pesticide?

4.116 The U.S. standard for arsenate in drinking water requires that public water supplies must contain no greater than 10 parts per billion (ppb) arsenic. If this arsenic is present as arsenate, AsO_4^{3-}, what mass of sodium arsenate would be present in a 1.00 L sample of drinking water that just meets the standard? Parts per billion is defined on a mass basis as

$$\text{ppb} = \frac{\text{g solute}}{\text{g solution}} \times 10^9$$

4.117 Federal regulations in the United States set an upper limit of 50 parts per million (ppm) of NH_3 in the air in a work environment [that is, 50 molecules of $NH_3(g)$ for every million molecules in the air]. Air from a manufacturing operation was drawn through a solution containing 1.00×10^2 mL of 0.0105 *M* HCl. The NH_3 reacts with HCl according to:

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

After drawing air through the acid solution for 10.0 min at a rate of 10.0 L/min, the acid was titrated. The remaining acid needed 13.1 mL of 0.0588 *M* NaOH to reach the equivalence point. (**a**) How many grams of NH_3 were drawn into the acid solution? (**b**) How many ppm of NH_3 were in the air? (Air has a density of 1.20 g/L and an average molar mass of 29.0 g/mol under the conditions of the experiment.) (**c**) Is this manufacturer in compliance with regulations?

Design an Experiment

You are cleaning out a chemistry lab and find three unlabeled bottles, each containing white powder. Near these bottles are three loose labels: "Sodium sulfide," "Sodium bicarbonate," and "Sodium chloride." Let's design an experiment to figure out which label goes with which bottle.

(**a**) You could try to use the physical properties of the three solids to distinguish among them. Using an Internet resource or the *CRC Handbook of Chemistry and Physics*, look up the melting points, aqueous solubilities, or other properties of these salts. Are the differences among these properties for each salt large enough to distinguish among them? If so, design a set of experiments to distinguish each salt and therefore figure out which label goes on which bottle.

(**b**) You could use the chemical reactivity of each salt to distinguish it from the others. Which of these salts, if any, will act as an acid? A base? A strong electrolyte? Can any of these salts be easily oxidized or reduced? Can any of these salts react to produce a gas? Based on your answers to these questions, design a set of experiments to distinguish each salt and thus determine which label goes on which bottle.

5

THERMOCHEMISTRY

WHAT'S AHEAD

5.1 The Nature of Chemical Energy
5.2 The First Law of Thermodynamics
5.3 Enthalpy
5.4 Enthalpies of Reaction
5.5 Calorimetry
5.6 Hess's Law
5.7 Enthalpies of Formation
5.8 Bond Enthalpies
5.9 Foods and Fuels

5.1 | The Nature of Chemical Energy



The study of energy and its transformations is known as **thermodynamics** (Greek: *thérme-*, "heat"; *dy'namis*, "power"). This area of study began during the Industrial Revolution in order to develop the relationships among heat, work, and fuels. These were used in steam engines, such as the beam engine pictured here. Here, we will examine the relationships between chemical reactions and energy changes that involve heat. This portion of thermodynamics is called **thermochemistry**. We will discuss additional aspects of thermodynamics in Chapter 19.

By the end of this section, you should be able to

- Understand the relationship between energy and the making or breaking of chemical bonds

As we learned in Chapter 1 (Section 1.4), energy is defined as the capacity to do work or transfer heat. Anyone who has sat by a fire or used a propane grill has witnessed chemical reactions that release heat [**Figure 5.1(a)**]. Some chemical reactions also absorb heat, such as those that occur when you cook. Chemical reactions can also do work in various ways. Recall the definition of work from Chapter 1:

$$w = F \times d \qquad [5.1]$$

For example, the combustion reaction between fuel and oxygen produces gases that expand and in the process do work that can be used to power a car. Champagne is made when yeasts use chemical reactions to ferment sugars into ethanol and carbon dioxide. By carrying out the last stages of fermentation in a corked bottle, pressure from the generated CO_2 builds up and can be used to do work when the cork is popped [Figure 5.1(**b**)]. Yet another example is a battery, where redox reactions produce electrical energy that can be used to do work.

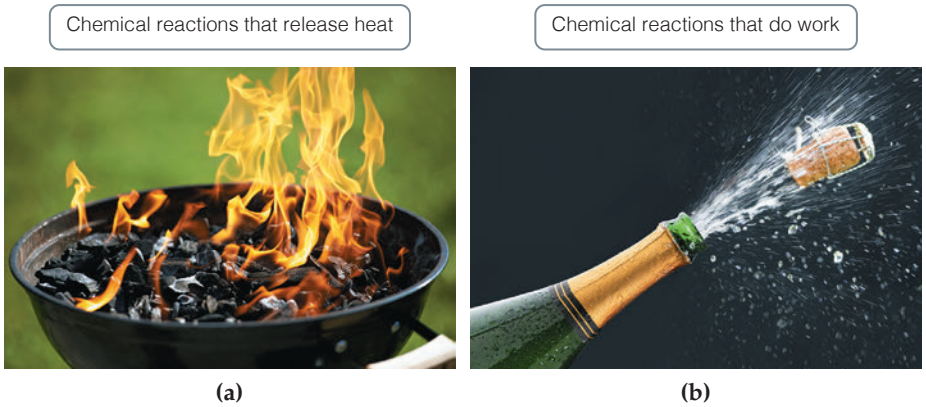
All forms of energy can be classified as either kinetic or potential energy. The energy that originates from chemical reactions is associated mainly with changes in potential energy. This energy results from electrostatic interactions at the atomic level. Thus, if we are to understand the energy associated with chemical reactions, we must first understand electrostatic potential energy, which arises from the interactions between charged particles.

The electrostatic potential energy, E_{el}, associated with two charged particles is proportional to their electrical charges, Q_1 and Q_2, and is inversely proportional to the distance, d, separating them:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \qquad [5.2]$$

where κ is a proportionality constant whose value is 8.99×10^9 J-m/C^2.* Recall from Chapter 1 that the units used to measure energy are joules, where $1\text{ J} = 1\text{ kg-m}^2/\text{s}^2$. At the atomic level, the charges Q_1 and Q_2 are typically on the order of magnitude of the charge of an electron (1.60×10^{-19} C), while distances range from tenths to tens of nanometers ($1\text{ nm} = 1 \times 10^{-9}$ m).

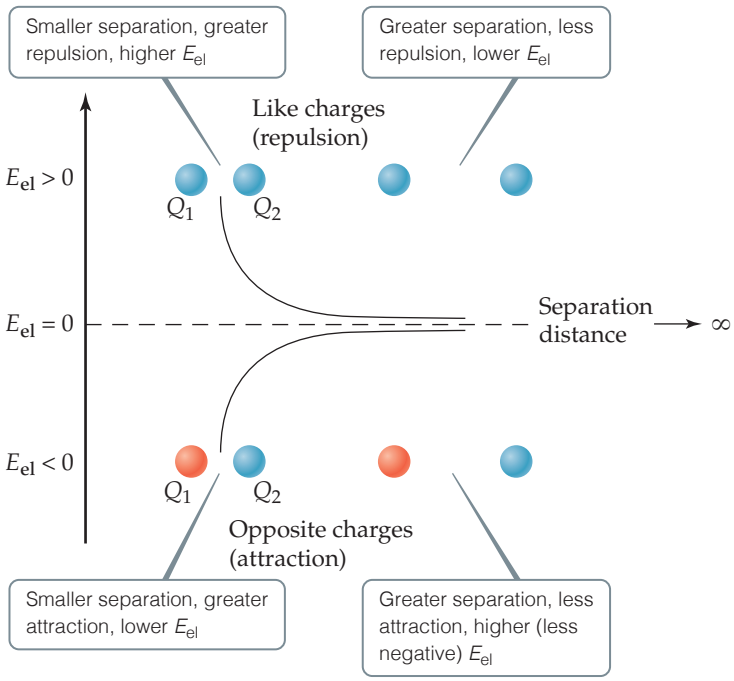
Inspection of Equation 5.2 shows that electrostatic potential energy goes to zero as d becomes infinite. Thus, zero electrostatic potential energy is defined as infinite



▲ **Figure 5.1 Chemical reactions and energy.** Energy changes in chemical reactions can be used to transfer heat or do work.

*We read the combined units J-m/C^2 as joule-meters per coulomb squared. You may see combinations of units such as J-m/C^2 expressed with dots separating units instead of short dashes, J·m/C^2, or with dashes and dots totally absent, J m/C^2.

Go Figure A positively charged particle and a negatively charged particle are initially far apart. What happens to their electrostatic potential energy as they are brought closer together?



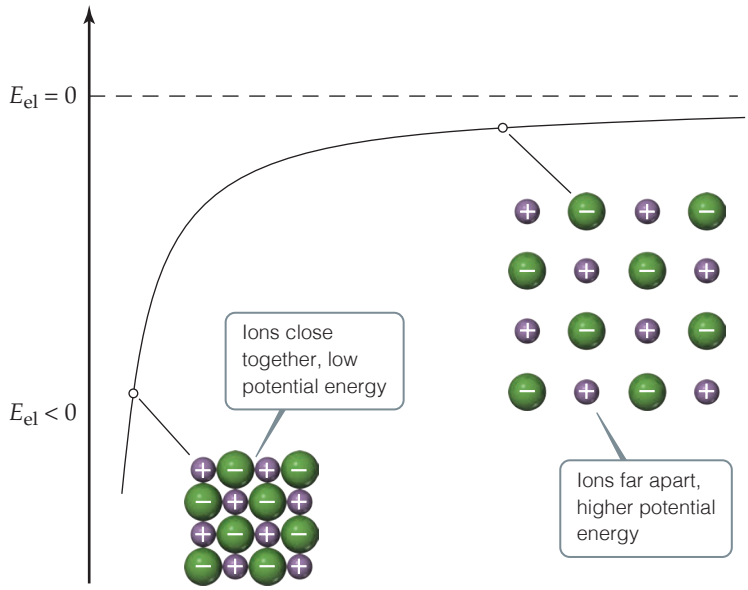
▲ **Figure 5.2 Electrostatic potential energy.** At finite separation distances the electrostatic potential energy, E_{el}, is positive for objects with like charges, and negative for objects that are oppositely charged. As the particles move farther apart, their electrostatic potential energy approaches zero.

separation of the charged particles. **Figure 5.2** illustrates how E_{el} behaves as the distance between two charges is varied. When Q_1 and Q_2 have the same sign (for example, both are positive), the two charged particles repel each other, and a repulsive force pushes them apart. In order to bring two positively charged objects close together, one would have to do work to overcome the repulsive force that exists between the two. Upon releasing them, they would move away from each other as potential energy is converted to kinetic energy. In this case, E_{el} is positive, and the potential energy decreases as the distance between particles increases. When Q_1 and Q_2 have opposite signs, the particles attract each other, and an attractive force pulls them toward each other. In this case E_{el} is negative, and the potential energy increases (becomes less negative) as the particles move apart.

To understand the relationship between electrostatic potential energy and the energy stored in chemical bonds, it is instructive to consider an ionic compound like NaCl. The Na^+ cations and Cl^- anions are held together by the electrostatic attraction between the oppositely charged ions. In chemistry we refer to this force as ionic bonding. We'll go into the details of ionic bonding in Chapter 8, but for now it is sufficient to understand that the ionic bonds that hold sodium and chloride ions together are based on the electrostatic attraction between cations and anions. To separate the ions, we must overcome, or break, the ionic bonds between Na^+ and Cl^-, increasing the potential energy, as illustrated in **Figure 5.3**. The energy to do this must come from some other source. The reverse process where ions separated by a large distance are allowed to come together to form ionic bonds lowers the potential energy and therefore releases energy. This illustrates a fundamental principle of thermochemistry:

Energy is released when chemical bonds are formed;
energy is consumed when chemical bonds are broken.

Go Figure If the ions in the figure on the right were released and allowed to move, would they move closer together or farther apart?



▲ **Figure 5.3 Electrostatic potential energy and ionic bonding.** As the separation between ions increases, the electrostatic potential energy increases (becomes less negative). As the distance separating the ions goes toward infinity, the electrostatic potential energy goes to zero. In real compounds, repulsions between core electrons place a lower limit on how closely the ions can approach each other.

You may be wondering how these same principles apply to molecular substances such as water, H_2O, and methane, CH_4, that do not contain cations and anions. As we will learn in Chapters 8 and 9, the atoms in a molecule are held together by covalent bonds. While the link to electrostatic potential energy is less obvious, the forces that underlie covalent bonds are also electrostatic in nature. Just like ionic bonds, energy must be provided to break covalent bonds and is released when they form.

Self-Assessment Exercise

5.1 Which solid would have the lower (more negative) potential energy?

(a) NaCl

(b) CaO

Exercises

5.2 (**a**) What is the electrostatic potential energy (in joules) between an electron and a proton that are separated by 230 pm? (**b**) What is the change in potential energy if the distance separating the electron and proton is increased to 1.0 nm? (**c**) Does the potential energy of the two particles increase or decrease when the distance is increased to 1.0 nm?

5.3 A sodium ion, Na^+, with a charge of 1.6×10^{-19} C and a chloride ion, Cl^-, with charge of -1.6×10^{-19} C, are separated by a distance of 0.50 nm. How much work would be required to increase the separation of the two ions to an infinite distance?

5.4 Identify the force present and explain whether work is being performed in the following cases: (**a**) You lift a book off the top of a desk. (**b**) Air is compressed in a bicycle pump.

Answers to Self-Assessment Exercise

5.1 (b)

5.2 The First Law of Thermodynamics



With the exception of the energy from the Sun, most of the energy used in our daily lives comes from chemical reactions. The combustion of fuel, the production of electricity from coal, the heating of homes by natural gas, and the use of batteries to power electronic devices are all examples of how chemical reactions are used to produce energy. But that's only the beginning. Chemical reactions provide the energy that sustains living systems. Plants use solar energy to carry out photosynthesis, allowing them to grow. In the process, they store a portion of the Sun's energy in the chemical bonds of the molecules that are produced during photosynthesis. When animals eat and digest plants, they derive the energy needed to move, maintain body temperature, and carry out all other bodily functions from that same chemical energy.

Energy comes in many different forms, including kinetic energy, which we encountered in Chapter 1, and various types of potential energy. You don't have to look far to find processes that involve conversions from one form of energy to another. Dropping a stone down a deep well converts gravitational potential energy into kinetic energy. Heating your house by reacting natural gas with oxygen converts chemical energy into heat. In both cases—and every other one you can imagine—*energy can be converted from one form to another, but it is neither created nor destroyed*. This observation, one of the most important in all of science, is known as the **first law of thermodynamics**. To apply this law quantitatively we need to divide the universe into a finite system of interest to us, and define the energy of that system more precisely. We explore these concepts next.

System and Surroundings

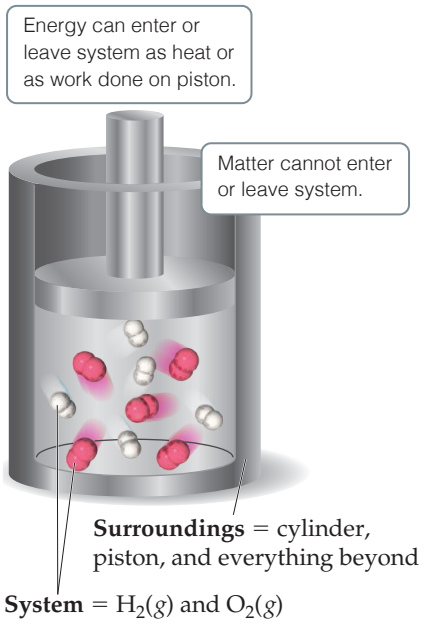
When analyzing energy changes, we need to focus on a limited and well-defined part of the universe to keep track of the energy changes that occur. The portion we single out for study is called the **system**; everything else is called the **surroundings**. When we study the energy change that accompanies a chemical reaction in a laboratory, the reactants and products constitute the system. The container and everything beyond it are considered the surroundings.

Systems may be open, closed, or isolated. An *open* system is one in which matter and energy can be exchanged with the surroundings. An uncovered pot of boiling water on a stove is an open system: Heat comes into the system from the stove, and water is released to the surroundings as steam.

The systems we can most readily study in thermochemistry are called *closed systems*—systems that can exchange energy but not matter with their surroundings. For example, consider a mixture of hydrogen gas, H_2, and oxygen gas, O_2, in a cylinder fitted

Go Figure

If the H_2 and O_2 molecules in the cylinder react to form H_2O, will the number of molecules in the cylinder change? Will the mass in the cylinder change?



▲ **Figure 5.4** **A closed system.**

with a piston (**Figure 5.4**). The system is just the hydrogen and oxygen; the cylinder, piston, and everything beyond them (including us) are the surroundings. If the gases react to form water, energy is liberated:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) + \text{energy}$$

Although the chemical form of the hydrogen and oxygen atoms in the system is changed by this reaction, the system has not lost or gained mass, which means it has not exchanged any matter with its surroundings. However, it can exchange energy with its surroundings in the form of *work* and *heat*.

An *isolated* system is one in which neither energy nor matter can be exchanged with the surroundings. An insulated thermos containing hot coffee approximates an isolated system. We know, however, that the coffee eventually cools, so it is not perfectly isolated.

Internal Energy

The **internal energy**, E, of a system is the sum of *all* the kinetic and potential energies of the components of the system. For the system in Figure 5.4, for example, the internal energy includes not only the motions and interactions of the H_2 and O_2 molecules but also the motions and interactions of their component nuclei and electrons. We generally do not know the numerical value of a system's internal energy. In thermodynamics, we are mainly concerned with the *change* in E (and, as we shall see, changes in other quantities as well) that accompanies a change in the system.

Imagine that we start with a system with an initial internal energy $E_{initial}$. The system then undergoes a change, which might involve work being done or heat being transferred. After the change, the final internal energy of the system is E_{final}. We define the *change* in internal energy, denoted ΔE (read "delta E"),* as the difference between E_{final} and $E_{initial}$:

$$\Delta E = E_{final} - E_{initial} \qquad [5.3]$$

We generally cannot determine the actual values of E_{final} and $E_{initial}$ for any system of practical interest. Nevertheless, we can determine the value of ΔE experimentally by applying the first law of thermodynamics.

Thermodynamic quantities such as ΔE have three parts:

1. a number
2. a unit
3. a sign

(1) and (2) together give the magnitude of the change, while (3) gives the direction. A *positive* value of ΔE results when $E_{final} > E_{initial}$, indicating that the system has gained energy from its surroundings. A *negative* value of ΔE results when $E_{final} < E_{initial}$, indicating that the system has lost energy to its surroundings. Notice that we are taking the point of view of the system rather than that of the surroundings in discussing the energy changes. We need to remember, however, that any increase in the energy of the system is accompanied by a decrease in the energy of the surroundings, and vice versa. These features of energy changes are summarized in **Figure 5.5**.

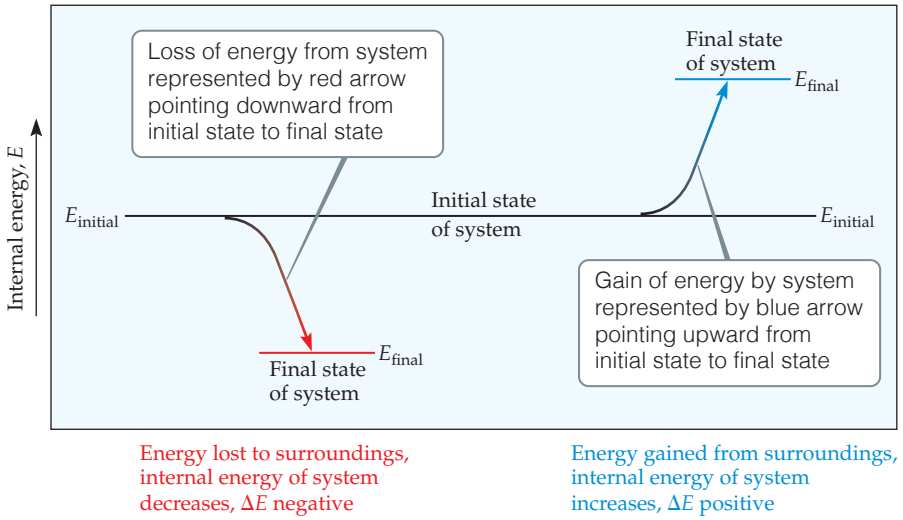
In a chemical reaction, the initial state of the system refers to the reactants and the final state refers to the products. In the reaction

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

for instance, the initial state is $2\,H_2(g) + O_2(g)$ and the final state is $2\,H_2O(l)$. When hydrogen and oxygen form water at a given temperature, the system loses energy to the surroundings. Because energy is lost from the system, the internal energy of the products (final state) is less than that of the reactants (initial state), and ΔE for the process is negative. Thus, the *energy diagram* in **Figure 5.6** shows that the internal energy of the mixture of H_2 and O_2 is greater than that of the H_2O produced in the reaction.

*The symbol Δ is commonly used to denote *change*. For example, a change in height, h, can be represented by Δh.

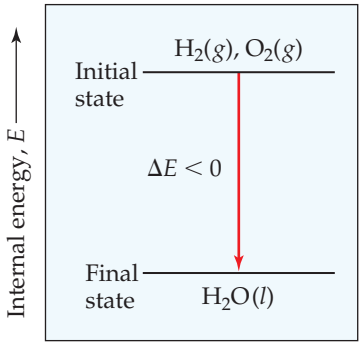
Go Figure What is the value of ΔE if E_{final} equals $E_{initial}$?



▲ **Figure 5.5** **Changes in internal energy.**

Go Figure

Sketch the energy diagram representing the reaction $MgCl_2(s) \longrightarrow Mg(s) + Cl_2(g)$ knowing that the internal energy for a mixture of $Mg(s)$ and $Cl_2(g)$ is larger than that of $MgCl_2(s)$.



$E_{initial}$ greater than E_{final}; therefore, energy is released from system to surroundings during reaction and $\Delta E < 0$.

▲ **Figure 5.6** **Energy diagram for the reaction $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$.**

Relating ΔE to Heat and Work

As we noted in Section 5.1, a system may exchange energy with its surroundings in two general ways: as heat or as work. The internal energy of a system changes in magnitude as heat is added to or removed from the system or as work is done on or by the system. If we think of internal energy as the system's bank account of energy, we see that deposits or withdrawals can be made in the form of either heat or work. Deposits increase the energy of the system (positive ΔE), whereas withdrawals decrease the energy of the system (negative ΔE).

We can use these ideas to write a useful algebraic expression of the first law of thermodynamics. When a system undergoes any chemical or physical change, the accompanying change in internal energy, ΔE, is the sum of the heat added to or liberated from the system, q, and the work done on or by the system, w:

$$\Delta E = q + w \qquad [5.4]$$

When heat is added to a system or work is done on a system, its internal energy increases. Therefore, when heat is transferred to the system from the surroundings, q has a positive value. Adding heat to the system is like making a deposit to the energy account—the energy of the system increases (**Figure 5.7**). Likewise, when work is done on the system by the surroundings, w has a positive value. Conversely, both the heat lost by the system to the surroundings and the work done by the system on the surroundings have negative values; that is, they lower the internal energy of the system. They are energy withdrawals and lower the amount of energy in the system's account.

The sign conventions for q, w, and ΔE are summarized in **Table 5.1**. Notice that any energy entering the system as either heat or work carries a positive sign.

Sample Exercise 5.1

Relating Heat and Work to Changes of Internal Energy

Gases A(g) and B(g) are confined in a cylinder-and-piston arrangement like that in Figure 5.4 and react to form a solid product C(s): $A(g) + B(g) \longrightarrow C(s)$. As the reaction occurs, the system loses 1150 J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480 J of work on the system. What is the change in the internal energy of the system?

Continued

SOLUTION

Analyze The question asks us to determine ΔE, given information about q and w.

Plan We first determine the signs of q and w (Table 5.1) and then use Equation 5.4, $\Delta E = q + w$, to calculate ΔE.

Solve Heat is transferred from the system to the surroundings, and work is done on the system by the surroundings, so q is negative and w is positive: $q = -1150\,\text{J}$ and $w = 480\,\text{J}$. Thus,

$$\Delta E = q + w = (-1150\,\text{J}) + (480\,\text{J}) = -670\,\text{J}$$

The negative value of ΔE tells us that a net quantity of 670 J of energy has been transferred from the system to the surroundings.

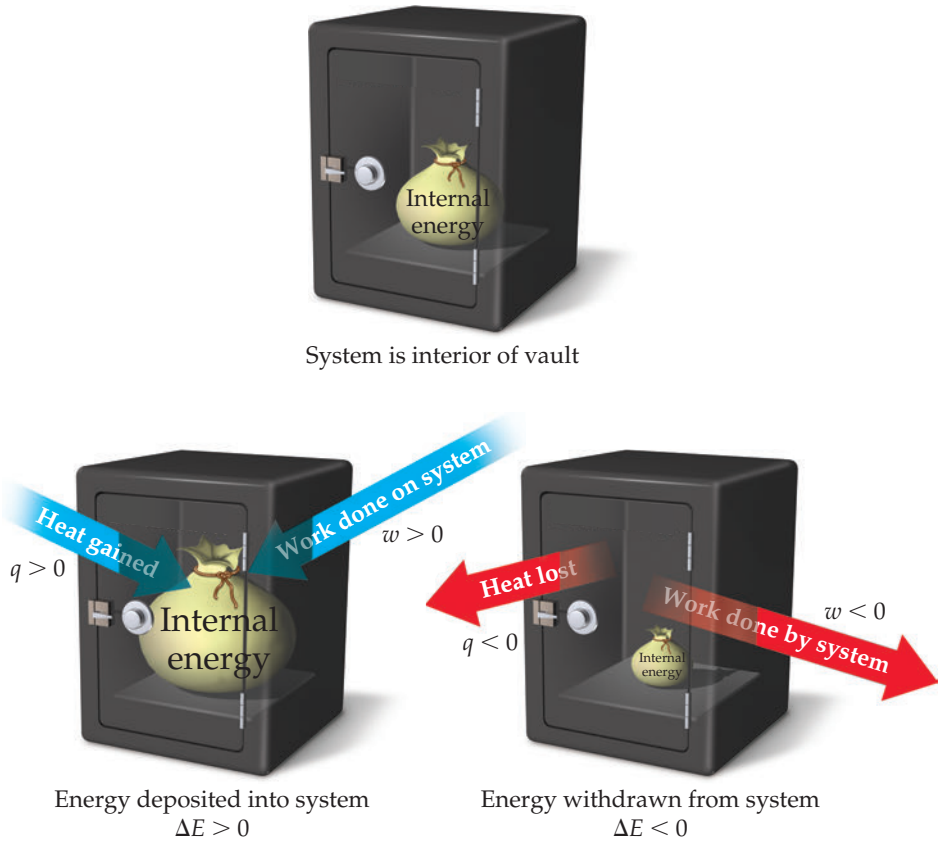
Comment You can think of this change as a decrease of 670 J in the net value of the system's energy bank account (hence, the negative sign); 1150 J is withdrawn in the form of heat, while 480 J is deposited in the form of work. Notice that as the volume of the gases decreases, work is being done *on* the system *by* the surroundings, resulting in a deposit of energy.

▶ Practice Exercise

A mixture of gases A_2 and B_2 are introduced to a slender metal cylinder that has one end closed and the other fitted with a piston that makes a gas-tight seal so that the gases are a closed system. The cylinder is submerged in a large beaker of water whose temperature is 25 °C, and a spark is used to trigger a reaction in the cylinder. At the completion of the reaction, the piston has moved downward, and the temperature of the water bath has increased to 28 °C. If we define the system as the gases inside the cylinder, which of the following best describes the signs of q, w, and ΔE for this reaction?

(**a**) $q < 0, w < 0, \Delta E < 0$
(**b**) $q < 0, w > 0, \Delta E < 0$
(**c**) $q < 0, w > 0,$ the sign of ΔE cannot be determined from the information given
(**d**) $q > 0, w > 0, \Delta E > 0$
(**e**) $q > 0, w < 0,$ the sign of ΔE cannot be determined from the information given

Go Figure Suppose a system receives a "deposit" of 50 J of work from the surroundings and loses a "withdrawal" of 85 J of heat to the surroundings. What is the magnitude and the sign of ΔE for this process?



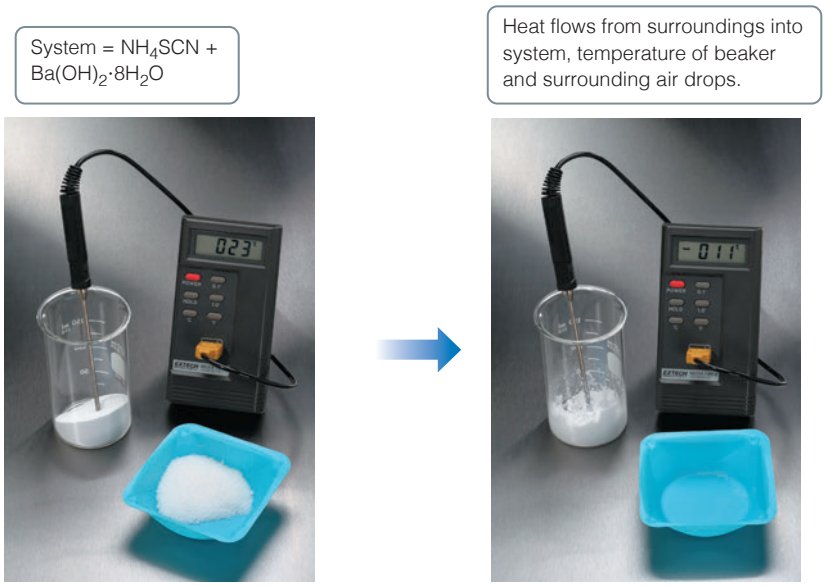
▲ **Figure 5.7** **Sign conventions for heat and work.** Heat, q, transferred into a system and work, w, done on a system are both positive quantities, corresponding to "deposits" of internal energy into the system. Conversely, heat transferred out of a system to the surroundings and work done by the system on the surroundings are both "withdrawals" of internal energy from the system.

TABLE 5.1 Sign Conventions for q, w, and ΔE

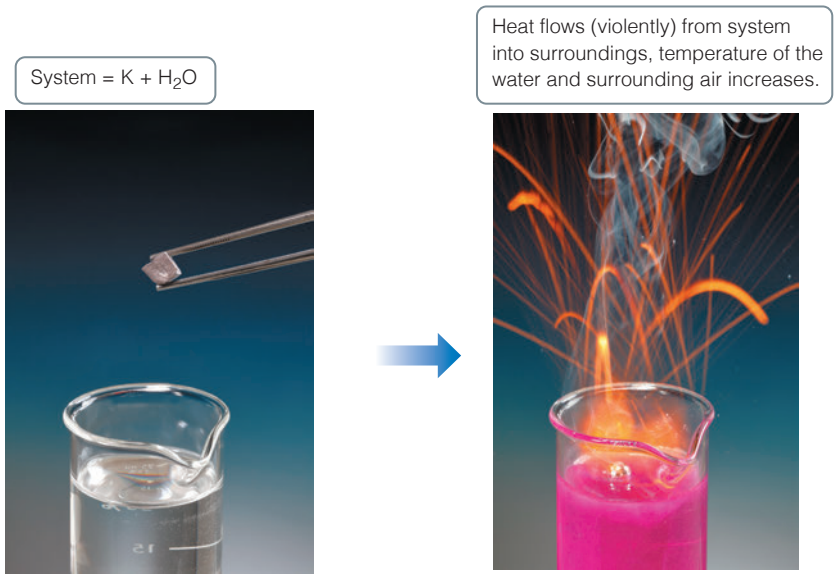
For q	+ means system *gains* heat	− means system *loses* heat
For w	+ means work done *on* system	− means work done *by* system
For ΔE	+ means *net gain* of energy by system	− means *net loss* of energy by system

Endothermic and Exothermic Processes

Because transfer of heat to and from the system is central to our discussion in this chapter, we have some special terminology to indicate the direction of transfer. When a process occurs in which the system absorbs heat, the process is called **endothermic** (*endo-* means "into"). During an endothermic process, such as the melting of ice, heat flows *into* the system from its surroundings [Figure 5.8**(a)**]. If we, as part of the surroundings, touch a container in which ice is melting, the container feels cold to us because heat has passed from our hand to the container.

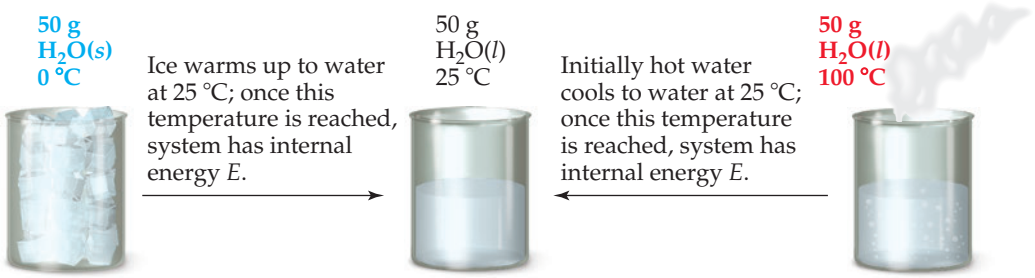


(a) $Ba(OH)_2 \cdot 8H_2O + 2\ NH_4SCN \longrightarrow Ba(SCN)_2 + 2\ NH_3 + 10\ H_2O$
An endothermic reaction



(b) $2\ K + 2\ H_2O \longrightarrow 2\ KOH + H_2$
An exothermic reaction

◀ **Figure 5.8 Endothermic and exothermic reactions.** In both instances, the system is defined as the reactants and products, while surroundings are the containers and everything else in the universe.



▲ **Figure 5.9 Internal energy, *E*, a state function.** Any state function depends only on the present state of the system and not on the path by which the system arrived at that state.

A process in which the system loses heat is called **exothermic** (*exo-* means "out of"). During an exothermic process, such as the combustion of gas, heat *exits* or flows *out* of the system into the surroundings [Figure 5.8(**b**)].

State Functions

Although we usually have no way of knowing the precise value of the internal energy of a system, E, it does have a fixed value for a given set of conditions. The conditions that influence internal energy include the temperature and pressure. Furthermore, the internal energy of a system is proportional to the total quantity of matter in the system because energy is an extensive property.

Suppose we define our system as 50 g of water at 25 °C (**Figure 5.9**). The system could have reached this state by cooling 50 g of water from 100 to 25 °C or by melting 50 g of ice and subsequently warming the water to 25 °C. The internal energy of the water at 25 °C is the same in either case. Internal energy is an example of a **state function**, a property of a system that is determined by specifying the system's condition, or state (in terms of temperature, pressure, and so forth). *The value of a state function depends only on the present state of the system, not on the path the system took to reach that state.* Because E is a state function, ΔE depends only on the initial and final states of the system, not on how the change occurs.

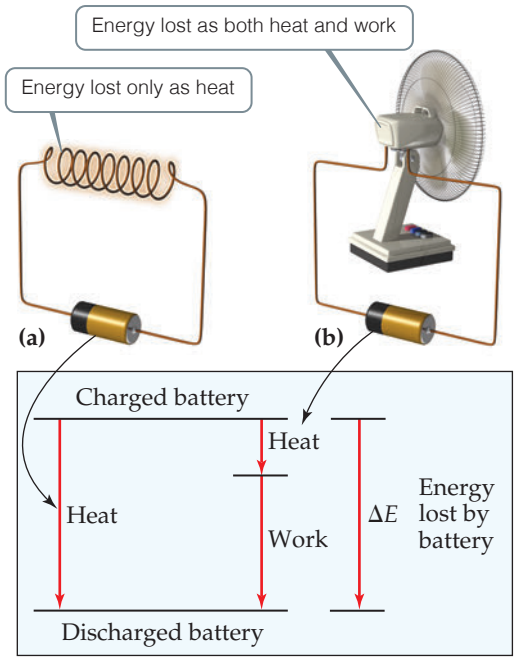
An analogy may help you understand the difference between quantities that are state functions and those that are not. Suppose you drive from one city, which is 180 m above sea level, to another city, which is 1610 m above sea level. No matter which route you take, the altitude change is 1430 m. The distance you travel, however, depends on your route. Altitude is analogous to a state function because the change in altitude is independent of the path taken. Distance traveled is not a state function.

Some thermodynamic quantities, such as E, are state functions. Other quantities, such as q and w, are not. This means that, although $\Delta E = q + w$ does not depend on how the change occurs, the specific amounts of heat and work depend on the way in which the change occurs. Thus, if changing the path by which a system goes from an initial state to a final state increases the value of q, that path change will also decrease the value of w by exactly the same amount. The result is that ΔE is the same for the two paths.

We can illustrate this principle using a battery as our system. As the battery is discharged, its internal energy decreases as the energy stored in the battery is released to the surroundings. In **Figure 5.10**, we consider two possible ways of discharging the battery at constant temperature. In Figure 5.10(a), a wire shorts out the battery and no work is accomplished because nothing is moved against a force. All the energy lost from the battery is in the form of heat. (The wire gets warmer and releases heat to the surroundings.) In Figure 5.10(b), the battery is used to make a motor turn and the discharge produces work. Some heat is released, but not as much as when the battery is shorted out. We see that the magnitudes of q and w must be different for these two cases. If the initial and final states of the battery are identical in the two cases, however, then $\Delta E = q + w$ must be the same in both cases because E is a state function. *Remember: ΔE depends only on the initial and final states of the system, not on the specific path taken from the initial to the final state.*

Go Figure

If the battery is defined as the system, what is the sign of w in part (b)?



▲ **Figure 5.10** **Internal energy is a state function, but heat and work are not.** (**a**) A battery shorted out by a wire loses energy to the surroundings only as heat; no work is performed. (**b**) A battery discharged through a motor loses energy as work (to make the fan turn) and also loses some energy as heat. The value of ΔE is the same for both processes even though the values of q and w in (a) are different from those in (b).

Self-Assessment Exercise

5.5 An aluminum can of a soft drink is placed in a freezer. Later, you find that the can is split open and its contents have frozen. Work was done on the can in splitting it open. Where did the energy for this work come from?

(a) Freezing of water releases energy

(b) The cold temperature in the freezer provided the energy

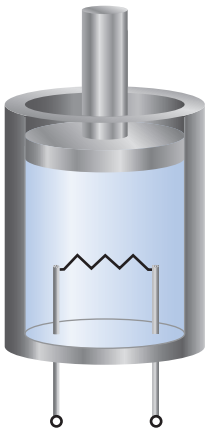
Exercises

5.6 (**a**) Which of the following cannot leave or enter a closed system: heat, work, or matter? (**b**) Which cannot leave or enter an isolated system? (**c**) What do we call the part of the universe that is not part of the system?

5.7 (**a**) According to the first law of thermodynamics, what quantity is conserved? (**b**) What is meant by the *internal energy* of a system? (**c**) By what means can the internal energy of a closed system increase?

5.8 Calculate ΔE and determine whether the process is endothermic or exothermic for the following cases: (**a**) $q = 0.763$ kJ and $w = -840$ J. (**b**) A system releases 66.1 kJ of heat to its surroundings while the surroundings do 44.0 kJ of work on the system.

5.9 A gas is confined to a cylinder fitted with a piston and an electrical heater, as shown here:



Suppose that current is supplied to the heater so that 100 J of energy is added. Consider two different situations. In case (1) the piston is allowed to move as the energy is added. In case (2) the piston is fixed so that it cannot move. (**a**) In which case does the gas have the higher temperature after addition of the electrical energy? (**b**) Identify the sign (positive, negative, or zero) of q and w in each case? (**c**) In which case is ΔE for the system (the gas in the cylinder) larger?

5.10 (**a**) What is meant by the term *state function*? (**b**) Give an example of a quantity that is a state function and one that is not. (**c**) Is the volume of a system a state function? Why or why not?

Answers to Self-Assessment Exercise

5.4 (a)

5.3 | Enthalpy



The reaction between aluminum metal and iron oxide produces aluminum oxide and iron metal. It also generates enough heat to melt the iron metal formed in the reaction. It can be used for welding railway lines and provides a convenient method of generating molten iron without the need of high temperature blow torches. The thermite reaction is a dramatic illustration of how potential energy stored in chemical bonds can be converted to heat.

By the end of this section, you should be able to

- Understand the relationship between enthalpy and heat in a chemical reaction.

The chemical and physical changes that occur around us, such as photosynthesis in the leaves of a plant, evaporation of water from a lake, or a reaction in an open beaker in a laboratory, occur under the essentially constant pressure of Earth's atmosphere.* These changes can result in the release or absorption of heat and can be accompanied by work done by or on the system. In exploring these changes, it is useful to have a thermodynamic function that is a state function and relates mainly to heat flow. Under conditions of constant pressure, a thermodynamic quantity called *enthalpy* (from the Greek *enthalpein*, "to warm") provides such a function.

Enthalpy, which we denote by the symbol H, is defined as the internal energy plus the product of the *pressure, P*, and *volume, V,* of the system:

$$H = E + PV \qquad [5.5]$$

*You are probably familiar with the notion of atmospheric pressure from a previous course in chemistry. We will discuss it in detail in Chapter 10. Here we need realize only that the atmosphere exerts a pressure on the surface of Earth that is nearly constant.

Like internal energy E, both P and V are state functions—they depend only on the current state of the system and not on the path taken to that state. Because energy, pressure, and volume are all state functions, enthalpy is also a state function.

Pressure–Volume Work

To better understand the significance of enthalpy, recall from Equation 5.4 that ΔE involves not only the heat q added to or removed from the system but also the work w done by or on the system. Most commonly, the only kind of work produced by chemical or physical changes open to the atmosphere is the mechanical work associated with a change in volume. For example, when the reaction of zinc metal with hydrochloric acid solution

$$Zn(s) + 2\,H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad [5.6]$$

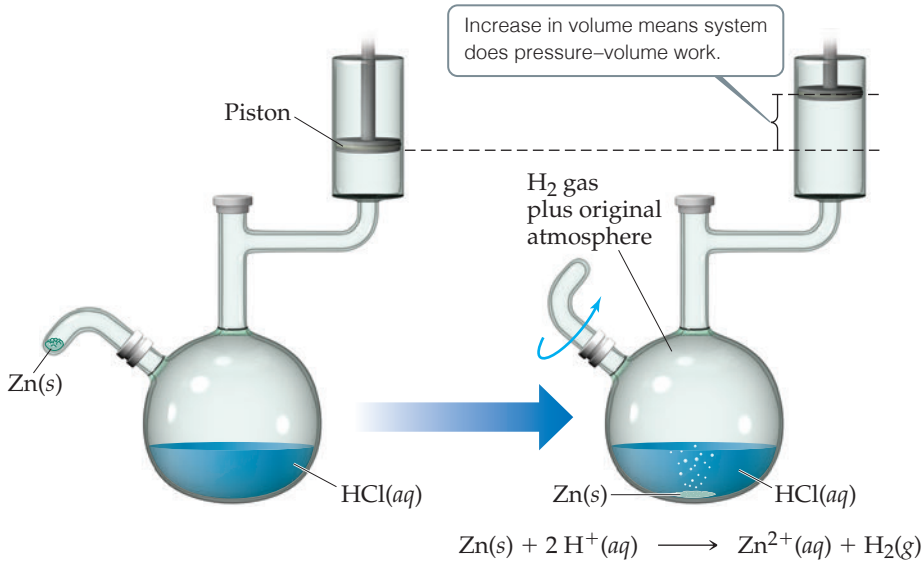
is run at constant pressure in the apparatus illustrated in **Figure 5.11**, the piston moves up or down to maintain a constant pressure in the vessel. If we assume for simplicity that the piston has no mass, the pressure in the apparatus is the same as atmospheric pressure. As the reaction proceeds, H_2 gas forms, and the piston rises. The gas within the flask is thus doing work on the surroundings by lifting the piston against the force of atmospheric pressure.

The work involved in the expansion or compression of gases is called **pressure–volume work** (P–V work). When pressure is constant in a process, as in our preceding example, the sign and magnitude of the pressure–volume work are given by

$$w = -P\,\Delta V \qquad [5.7]$$

where P is pressure and $\Delta V = V_{final} - V_{initial}$ is the change in volume of the system. The pressure P is always either a positive number or zero. If the volume of the system expands, then ΔV is positive as well. The negative sign in Equation 5.7 is necessary to conform to the sign convention for w (Table 5.1). When a gas expands, the system does work on the surroundings, as indicated by a negative value of w. (The negative sign $\times$ positive $P \times$ positive ΔV results in a negative number for w.) On the other hand, if the gas is compressed, ΔV is negative (the volume decreases), and Equation 5.7 indicates that w is therefore positive, meaning work is done on the system by the surroundings. The box "A Closer Look: Energy, Enthalpy, and P–V Work" discusses pressure–volume work in detail, but all you need to keep in mind for now is Equation 5.7, which applies to processes occurring at constant pressure.

Go Figure If we define the system as the reactants and products, what is the sign of work in this process, positive or negative?



▲ **Figure 5.11** **A system that does work on its surroundings.**

The units of work obtained by using Equation 5.7 will be those of pressure (usually kPa) multiplied by those of volume (usually L). To express the work in the more familiar unit of joules, we use the conversion factor 1 L-kPa = 1 J.

Sample Exercise 5.2

Calculating Pressure-Volume Work

A fuel is burned in a cylinder equipped with a piston. The initial volume of the cylinder is 0.250 L, and the final volume is 0.980 L. If the piston expands against a constant pressure of 136.8 kPa, how much work (in J) is done?

SOLUTION

Analyze We are given an initial volume and a final volume from which we can calculate ΔV. We are also given the pressure, P. We are asked to calculate work, w.

Plan The equation $w = -P\,\Delta V$ allows us to calculate the work done by the system from the given information.

Solve The volume change is

$$\Delta V = V_{final} - V_{initial} = 0.980\,\text{L} - 0.250\,\text{L} = 0.730\,\text{L}$$

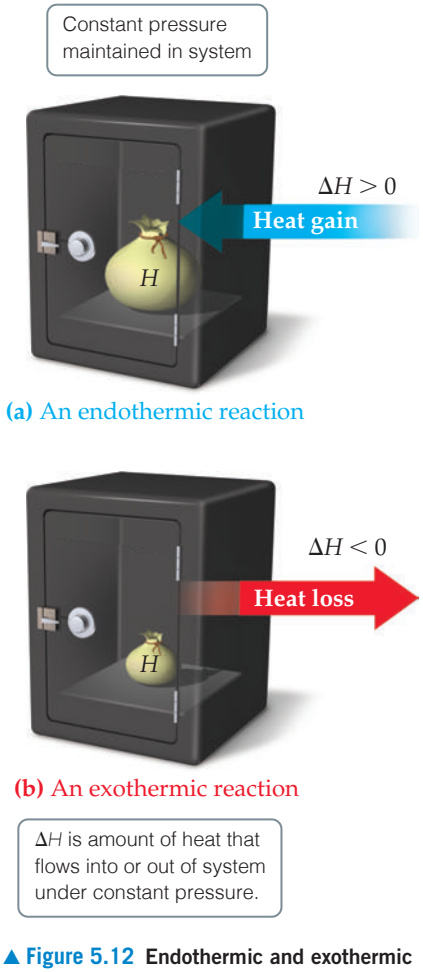
Thus, the quantity of work is

$$w = -P\Delta V = -(136.8\,\text{kPa})(0.730\,\text{L}) = 99.8\,\text{L-kPa}$$
$$= -99.8\,\text{J}$$

Check The significant figures are correct (3), and the units are the requested ones for energy (J). The negative sign is consistent with an expanding gas doing work on its surroundings.

Practice Exercise

Calculate the work, in J, if the volume of a system contracts from 1.55 to 0.85 L at a constant pressure of 99.8 kPa.



▲ **Figure 5.12 Endothermic and exothermic processes.** (**a**) An endothermic process ($\Delta H > 0$) deposits heat into the system. (**b**) An exothermic process ($\Delta H < 0$) withdraws heat from the system.

Enthalpy Change

Let's now return to our discussion of enthalpy. When a change occurs at constant pressure, the change in enthalpy, ΔH, is given by the relationship

$$\Delta H = \Delta(E + PV)$$
$$= \Delta E + P\Delta V \quad \text{(constant pressure)} \qquad [5.8]$$

That is, the change in enthalpy equals the change in internal energy plus the product of the constant pressure and the change in volume.

Recall that $\Delta E = q + w$ (Equation 5.4) and that the work involved in the expansion or compression of a gas is $w = -P\Delta V$ (at constant pressure). Substituting $-w$ for $P\Delta V$ and $q + w$ for ΔE into Equation 5.8, we have

$$\Delta H = \Delta E + P\Delta V = (q_P + w) - w = q_P \qquad [5.9]$$

The subscript P on q indicates that the process occurs at constant pressure. Thus, the equations show:

The change in enthalpy equals the heat q_P gained or lost at constant pressure.

Because q_P is something we can either measure or calculate and because so many physical and chemical changes of interest to us occur at constant pressure, enthalpy is a more useful function for most reactions than is internal energy. In addition, for most reactions the difference in ΔH and ΔE is small because $P\Delta V$ is small.

When ΔH is positive (that is, when q_P is positive), the system has gained heat from the surroundings (Table 5.1), which means the process is endothermic. When ΔH is negative, the system has released heat to the surroundings, which means the process is exothermic. To continue the bank analogy of Figure 5.7, under constant pressure, an endothermic process deposits energy in the system in the form of heat and an exothermic process withdraws energy in the form of heat (**Figure 5.12**).

Because H is a state function, ΔH (which equals q_P) depends only on the initial and final states of the system, not on how the change occurs. At first glance this statement might seem to contradict our discussion in Section 5.2, in which we said that q is *not* a state function. There is no contradiction, however, because the relationship between ΔH and q_P has special limitations that only P–V work is involved and that the pressure is constant.

Sample Exercise 5.3

Determining the Sign of ΔH

Indicate the sign of the enthalpy change, ΔH, in the following processes carried out under atmospheric pressure and indicate whether each process is endothermic or exothermic: (**a**) An ice cube melts; (**b**) 1 g of butane (C_4H_{10}) is combusted in sufficient oxygen to give complete combustion to CO_2 and H_2O.

SOLUTION

Analyze Our goal is to determine whether ΔH is positive or negative for each process. Because each process occurs at constant pressure, the enthalpy change equals the quantity of heat absorbed or released, $\Delta H = q_P$.

Plan We must predict whether heat is absorbed or released by the system in each process. Processes in which heat is absorbed are endothermic and have a positive sign for ΔH; those in which heat is released are exothermic and have a negative sign for ΔH.

Solve In (a) the water that makes up the ice cube is the system. The ice cube absorbs heat from the surroundings as it melts, so ΔH is positive and the process is endothermic. In (b) the system is the 1 g of butane and the oxygen required to combust it. The combustion of butane in oxygen gives off heat, so ΔH is negative and the process is exothermic.

Practice Exercise

A chemical reaction that gives off heat to its surroundings is said to be _____ and has a _____ value of ΔH.
(**a**) endothermic, positive (**b**) endothermic, negative
(**c**) exothermic, positive (**d**) exothermic, negative

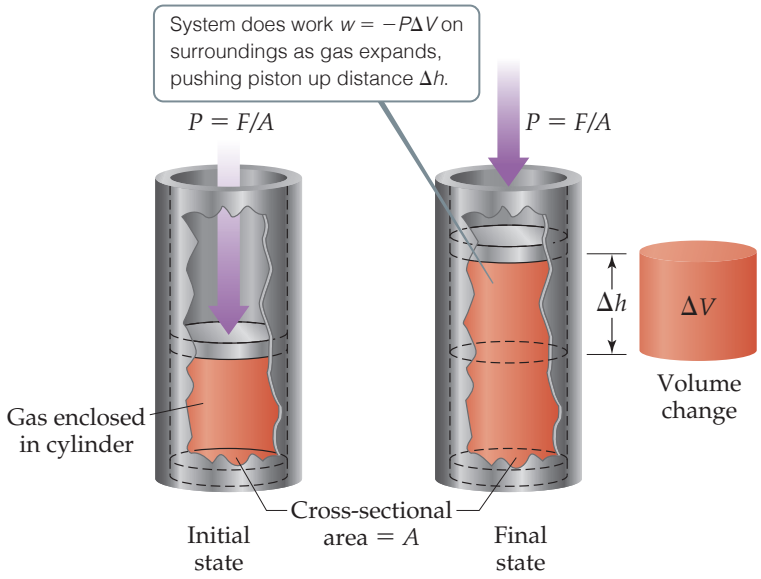
A CLOSER LOOK Energy, Enthalpy, and *P-V* Work

In chemistry we are interested mainly in two types of work: electrical work and mechanical work done by expanding gases. We focus here on the latter, called pressure–volume, or *P–V*, work. Expanding gases in the cylinder of an automobile engine do *P–V* work on the piston; this work eventually turns the wheels. Expanding gases from an open reaction vessel do *P–V* work on the atmosphere. This work accomplishes nothing in a practical sense, but we must keep track of all work, useful or not, when monitoring energy changes in a system.

Let's consider a gas confined to a cylinder with a movable piston of cross-sectional area A (Figure 5.13). A downward force F acts on the piston. The pressure, P, on the gas is the force per area: $P = F/A$. We assume that the piston is massless and that the only pressure acting on it is the *atmospheric pressure* that is due to Earth's atmosphere, which we assume to be constant.

Suppose the gas expands and the piston moves a distance Δh. From Equation 5.1, the magnitude of the work done by the system is

$$\text{Magnitude of work} = \text{force} \times \text{distance} = F \times \Delta h \qquad [5.10]$$



▲ **Figure 5.13 Pressure–volume work.** The amount of work done by the system on the surroundings is $w = -P\Delta V$.

We can rearrange the definition of pressure, $P = F/A$, to $F = P \times A$. The volume change, ΔV, resulting from the movement of the piston is the product of the cross-sectional area of the piston and the distance it moves: $\Delta V = A \times \Delta h$. Substituting into Equation 5.10 gives

$$\text{Magnitude of work} = F \times \Delta h = P \times A \times \Delta h$$
$$= P \times \Delta V$$

Because the system (the confined gas) does work on the surroundings, the work is a negative quantity:

$$w = -P\Delta V \qquad [5.11]$$

Now, if *P–V* work is the only work that can be done, we can substitute Equation 5.11 into Equation 5.4 to give

$$\Delta E = q + w = q - P\Delta V \qquad [5.12]$$

When a reaction is carried out in a constant-volume container ($\Delta V = 0$), the heat transferred equals the change in internal energy:

$$\Delta E = q - P\Delta V = q - P(0) = q_V \quad \text{(constant volume)} \qquad [5.13]$$

The subscript V indicates that the volume is constant.

Most reactions are run under constant pressure, so that Equation 5.12 becomes

$$\Delta E = q_P - P\Delta V$$
$$q_P = \Delta E + P\Delta V \quad \text{(constant pressure)} \qquad [5.14]$$

We see from Equation 5.8 that the right side of Equation 5.14 is the enthalpy change under constant-pressure conditions. Thus, $\Delta H = q_P$, as we saw in Equation 5.9.

In summary, the change in internal energy is equal to the heat gained or lost at constant volume, and the change in enthalpy is equal to the heat gained or lost at constant pressure. The difference between ΔE and ΔH is the amount of *P–V* work done by the system when the process occurs at constant pressure, $-P\Delta V$. The volume change accompanying many reactions is close to zero, which makes $P\Delta V$ and, therefore, the difference between ΔE and ΔH small. Under most circumstances, it is generally satisfactory to use ΔH as the measure of energy changes during most chemical processes.

Related Exercises: 5.15, 5.73–5.75

Self-Assessment Exercise

5.11 Enthalpy can be measured from heat flow under which of the following conditions?

(a) constant pressure

(b) constant volume

Exercises

5.12 During a deep breath, our lungs expand about 2.0 L against an external pressure of 101.3 kPa. How much work is involved in this process (in J)?

5.13 (**a**) Why is the change in internal energy ΔE usually harder to measure than the change in enthalpy ΔH? (**b**) E is a state function, but q is not a state function. Explain. (**c**) For a given process at constant pressure, ΔH is negative. Is the process endothermic or exothermic?

Answers to Self-Assessment Exercise

5.11 (a)

5.4 Enthalpies of Reaction



The thermite reaction is spectacular as a lot of heat is generated from small quantities of solid reactants. In this section, we start to focus on the energy changes that accompany a chemical reaction and this provides us with an additional depth of understanding of the process under study.

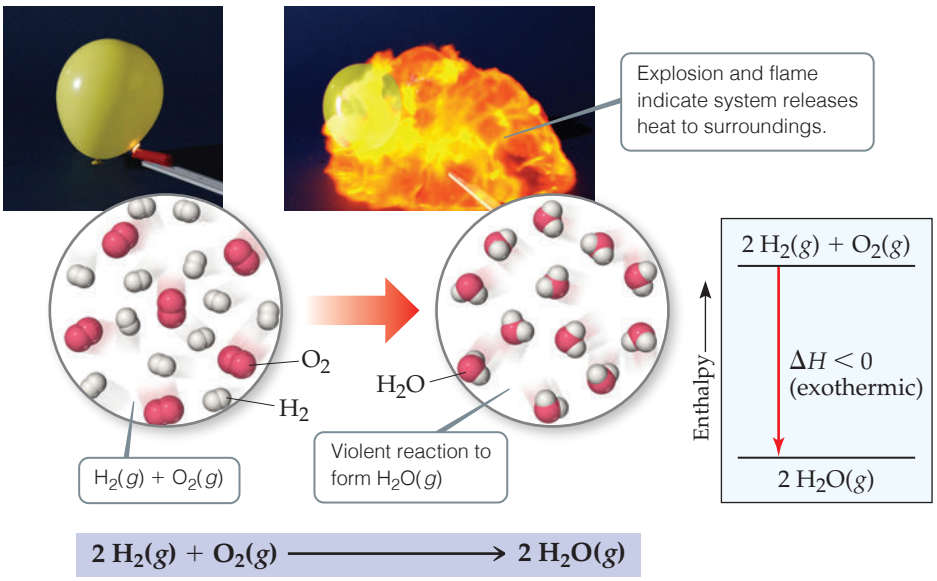
By the end of this section, you should be able to

- Use thermochemical equations to relate the amount of heat energy transferred in reactions at constant pressure ΔH to the amount of substance involved in the reaction.

Because $\Delta H = H_{\text{final}} - H_{\text{initial}}$, the enthalpy change for a chemical reaction is given by

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} \qquad [5.15]$$

The enthalpy change that accompanies a reaction is called either the **enthalpy of reaction** or the *heat of reaction* and is sometimes written ΔH_{rxn}, where "rxn" is a commonly used abbreviation for "reaction."



◀ **Figure 5.14 Exothermic reaction of hydrogen with oxygen.** When a mixture of $H_2(g)$ and $O_2(g)$ is ignited to form $H_2O(g)$, the resultant explosion produces a ball of flame. Because the system releases heat to the surroundings, the reaction is exothermic as indicated in the enthalpy diagram.

When we give a numerical value for ΔH_{rxn}, we must specify the reaction involved. For example, when 2 mol $H_2(g)$ burn to form 2 mol $H_2O(g)$ at a constant pressure, the system releases 483.6 kJ of heat. We can summarize this information as

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H = -483.6\ \text{kJ} \qquad [5.16]$$

The negative sign for ΔH tells us that this reaction is exothermic. Notice that ΔH is reported at the end of the balanced equation, without explicitly specifying the amounts of chemicals involved. In such cases the coefficients in the balanced equation represent the number of moles of reactants and products producing the associated enthalpy change. Balanced chemical equations that show the associated enthalpy change in this way are called *thermochemical equations*.

The exothermic nature of this reaction is also shown in the *enthalpy diagram* in Figure 5.14. Notice that the enthalpy of the reactants is greater (more positive) than the enthalpy of the products. Thus, $\Delta H = H_{products} - H_{reactants}$ is negative.

The following guidelines are helpful when using thermochemical equations and enthalpy diagrams:

1. **Enthalpy is an extensive property.** The magnitude of ΔH is proportional to the amount of reactant consumed in the process. For example, 890 kJ of heat is produced when 1 mol of CH_4 is burned in a constant-pressure system:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -890\ \text{kJ} \qquad [5.17]$$

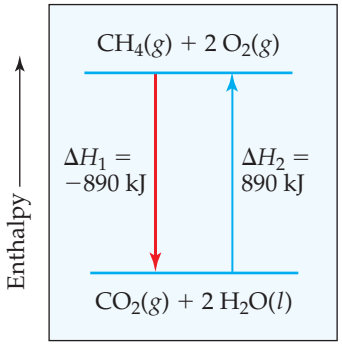
Because the combustion of 1 mol of CH_4 with 2 mol of O_2 releases 890 kJ of heat, the combustion of 2 mol of CH_4 with 4 mol of O_2 releases twice as much heat, 1780 kJ. Although chemical equations are usually written with whole-number coefficients, thermochemical equations sometimes utilize fractions, as in the preceding Give It Some Thought question.

2. **The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.** For example, ΔH for the reverse of Equation 5.17 is +890 kJ:

$$CO_2(g) + 2\,H_2O(l) \longrightarrow CH_4(g) + 2\,O_2(g) \qquad \Delta H = +890\ \text{kJ} \qquad [5.18]$$

When we reverse a reaction, we reverse the roles of the products and the reactants. From Equation 5.15, we see that reversing the products and reactants leads to the same magnitude of ΔH, but a change in sign (Figure 5.15).

3. **The enthalpy change for a reaction depends on the states of the reactants and products.** If the product in Equation 5.17 were $H_2O(g)$ instead of $H_2O(l)$, ΔH_{rxn} would be −802 kJ instead of −890 kJ. Less heat would be available for



▲ **Figure 5.15 ΔH for a reverse reaction.** Reversing a reaction changes the sign but not the magnitude of the enthalpy change: $\Delta H_2 = -\Delta H_1$.

transfer to the surroundings because the enthalpy of $H_2O(g)$ is greater than that of $H_2O(l)$. One way to see this is to imagine that the product is initially liquid water. The liquid water must be converted to water vapor, and the conversion of 2 mol $H_2O(l)$ to 2 mol $H_2O(g)$ is an endothermic process that absorbs 88 kJ:

$$2\,H_2O(l) \longrightarrow 2\,H_2O(g) \qquad \Delta H = +88\text{ kJ} \qquad [5.19]$$

Thus, it is important to specify the states of the reactants and products in thermochemical equations. In addition, we will generally assume that the reactants and products are both at the same temperature, 25 °C, unless otherwise indicated.

Sample Exercise 5.4

Relating ΔH to Quantities of Reactants and Products

How much heat is released when 4.50 g of methane gas is burned in a constant-pressure system? (Use the information given in Equation 5.17.)

SOLUTION

Analyze Our goal is to use a thermochemical equation to calculate the heat produced when a specific amount of methane gas is combusted. According to Equation 5.17, 890 kJ is released by the system when 1 mol CH_4 is burned at constant pressure.

Plan Equation 5.17 provides us with a stoichiometric conversion factor: (1 mol $CH_4 \cong -890$ kJ). Thus, we can convert moles of CH_4 to kJ of energy. First, however, we must convert grams of CH_4 to moles of CH_4.

Solve

The conversion sequence is:

Grams CH_4 (given) → Molar mass CH_4 16.0 g/mol → Moles CH_4 → ΔH = −890 kJ/mol → kJ of heat (unkown)

By adding the atomic weights of C and 4 H, we have 1 mol CH_4 = 16.0 CH_4. We can use the appropriate conversion factors to convert grams of CH_4 to moles of CH_4 to kilojoules:

$$\text{Heat} = (4.50\text{ g } \cancel{CH_4})\left(\frac{1\text{ mol } \cancel{CH_4}}{16.0\text{ g } \cancel{CH_4}}\right)\left(\frac{-890\text{ kJ}}{1\text{ mol } \cancel{CH_4}}\right) = -250\text{ kJ}$$

The negative sign indicates that the system released 250 kJ into the surroundings.

Practice Exercise

Hydrogen peroxide can decompose to water and oxygen by the reaction

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g) \qquad \Delta H = -196\text{ kJ}$$

Calculate the quantity of heat released when 5.00 g of $H_2O_2(l)$ decomposes at constant pressure.

A CLOSER LOOK Using Enthalpy as a Guide

If you hold a brick in the air and let it go, you know what happens: It falls as the force of gravity pulls it toward Earth. A process that is thermodynamically favored to happen, such as a brick falling to the ground, is called a *spontaneous* process. A spontaneous process can be either fast or slow; the rate at which processes occur is not governed by thermodynamics.

Chemical processes can be thermodynamically favored, or spontaneous, too. By spontaneous, however, we do not mean that the reaction will form products without any intervention. That can be the case, but often some energy must be imparted to get the process started. Just as it is spontaneous for a rock to roll down the side of a hill once started, so too can it be spontaneous for chemical reactions to proceed once enough energy is imparted to initiate the reaction (**Figure 5.16**). The enthalpy change in a reaction gives one indication as to whether the reaction is likely to be spontaneous. The combustion of $H_2(g)$ and $O_2(g)$, for example, is highly exothermic:

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242\text{ kJ}$$

Hydrogen gas and oxygen gas can exist together in a volume indefinitely without noticeable reaction occurring. Once the reaction is initiated, however, energy is rapidly transferred from the system (the reactants) to the surroundings as heat. The system thus loses enthalpy by transferring the heat to the surroundings. (Recall that the first law of thermodynamics tells us that the total energy of the system plus the surroundings does not change; energy is conserved.)

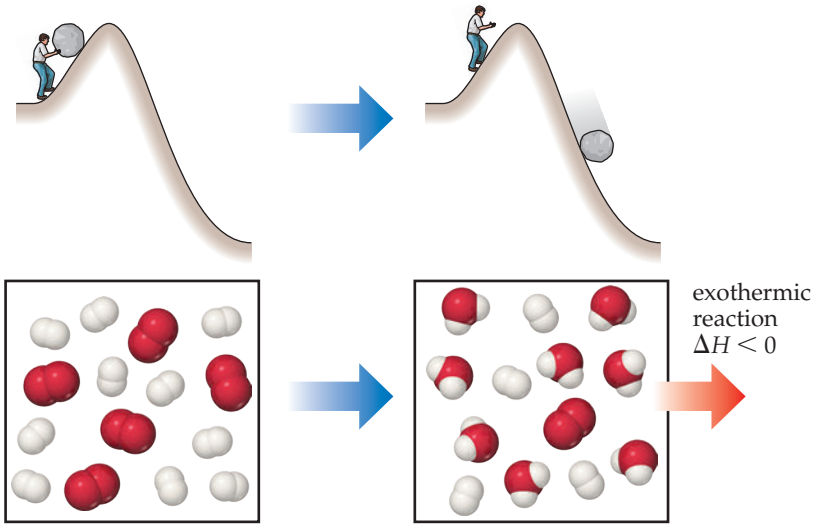
Enthalpy change is not the only consideration in the spontaneity of reactions, nor is it a foolproof guide. For example, even though ice melting is an endothermic process,

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = +6.01 \text{ kJ}$$

this process is spontaneous at temperatures above the freezing point of water (0 °C). The reverse process, water freezing, is spontaneous at temperatures below 0 °C. Thus, we know that ice at room temperature melts and water put into a freezer at −20 °C turns into ice. Both processes are spontaneous under different conditions even though they are the reverse of one another. In Chapter 19, we will address the spontaneity of processes more fully. We will see why a process can be spontaneous at one temperature but not at another, as is the case for the conversion of water to ice.

Despite these complicating factors, you should pay attention to the enthalpy changes in reactions. As a general observation, when the enthalpy change is large, it is the dominant factor in determining spontaneity. Thus, reactions for which ΔH is *large* (about 100 kJ or more) and *negative* tend to be spontaneous. Reactions for which ΔH is *large* and *positive* tend to be spontaneous only in the reverse direction.

Related Exercises: 5.20, 5.80



▲ **Figure 5.16 Exothermic reactions and spontaneity.** Chemical reactions that are highly exothermic (ΔH much less than 0) usually occur spontaneously. Such reactions often need some input of energy to get started, just like it can take a push to get a boulder rolling down a hill to a spot of lower potential energy. However, once they get started, such reactions spontaneously proceed to form the products, which have lower potential energy.

In many situations, we will find it valuable to know the sign and magnitude of the enthalpy change associated with a given chemical process. As we see in the following sections, ΔH can be either determined directly by experiment or calculated from known enthalpy changes of other reactions.

Self-Assessment Exercise

5.14 Given $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)\,\Delta H = -484$ kJ

What is the enthalpy change for the formation of hydrogen and oxygen from one mole of steam?

$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$

(a) $\Delta H = +242$ kJ

(b) $\Delta H = +484$ kJ

(c) $\Delta H = +968$ kJ

Exercises

5.15 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When the gas undergoes a particular chemical reaction, it absorbs 824 J of heat from its surroundings and has 0.65 kJ of $P\,V$ work done on it by its surroundings. What are the values of ΔH and ΔE for this process?

5.16 The complete combustion of methane, $CH_4(g)$, to form $H_2O(l)$ and $CO_2(g)$ at constant pressure releases 890 kJ of heat per mole of CH_4. (**a**) Write a balanced thermochemical equation for this reaction. (**b**) Draw an enthalpy diagram for the reaction.

5.17 Atomic hydrogen (H) is used in welding (AHW). The atoms recombine to hydrogen molecules with a large release of heat according to the following reaction:

$$2\,H(g) \longrightarrow H_2(g)$$

(**a**) Using the thermodynamic data in Appendix C, calculate the enthalpy change for this reaction per mole of H_2.

(**b**) Which has the higher enthalpy under these conditions, $2\,H(g)$ or $H_2(g)$?

5.18 Consider the following reaction:

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s) \quad \Delta H = -1204 \text{ kJ}$$

(**a**) Is this reaction exothermic or endothermic?

(**b**) Calculate the amount of heat transferred when 3.55 g of Mg(*s*) reacts at constant pressure.

(**c**) How many grams of MgO are produced during an enthalpy change of −234 kJ?

(**d**) How many kilojoules of heat are absorbed when 40.3 g of MgO(*s*) is decomposed into Mg(*s*) and $O_2(g)$ at constant pressure?

5.19 When solutions containing silver ions and chloride ions are mixed, silver chloride precipitates

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s) \qquad \Delta H = -65.5 \text{ kJ}$$

(**a**) Calculate ΔH for the production of 0.450 mol of AgCl by this reaction. (**b**) Calculate ΔH for the production of 9.00 g of AgCl. (**c**) Calculate ΔH when 9.25×10^{-4} mol of AgCl dissolves in water.

5.20 Consider the combustion of liquid methanol, $CH_3OH(l)$:

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -726.5 \text{ kJ}$$

(**a**) What is the enthalpy change for the reverse reaction? (**b**) Balance the forward reaction with whole-number coefficients. What is ΔH for the reaction represented by this equation? (**c**) Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction? (**d**) If the reaction were written to produce $H_2O(g)$ instead of $H_2O(l)$, would you expect the magnitude of ΔH to increase, decrease, or stay the same? Explain.

Answers to Self-Assessment Exercise

5.14 (a)

5.5 | Calorimetry



The word *thermometer* comes from the Greek words 'thermos' meaning hot, and 'metron' meaning measure. Early instruments that attempted to measure temperature utilized an air bubble trapped in a glass tube closed at one end and dipped into water at the other end. As the temperature changed, the volume of the trapped air changed. However, this was also subject to changes in atmospheric pressure. The first reliable thermometer was invented in 1714 by Daniel Gabriel Fahrenheit, who employed a sealed tube—to avoid the effects of changing atmospheric pressures—and the high coefficient of expansion of mercury to translate temperature changes to the visible movement of the mercury along the tube. Fahrenheit is remembered with a monument in the city of his birth, Gdansk, Poland, but lived most of his life in the Dutch Republic. He also suggested a scale for temperature, which bears his name.

Nowadays, we have many different devices that measure temperature and the use of mercury in thermometers is diminishing. While the use of the Celsius scale is widespread, it is not yet universal with some countries still recording, for example, weather temperatures in Fahrenheit.

By the end of this section, you should be able to

- Calculate the heat transferred in a process from temperature measurements together with heat capacities or specific heats

The value of ΔH can be determined experimentally by measuring the heat flow accompanying a reaction at constant pressure. Typically, we can determine the magnitude of the heat flow by measuring the magnitude of the temperature change the heat flow produces. The measurement of heat flow is **calorimetry**; a device used to measure heat flow is a **calorimeter**.

Heat Capacity and Specific Heat

The more heat an object gains, the hotter it gets. All substances change temperature when they are heated, but the magnitude of the temperature change produced by a given quantity of heat varies from substance to substance. The temperature change experienced by an object when it absorbs a certain amount of heat is determined by its **heat capacity**, denoted C. The heat capacity of an object is the amount of heat required to raise its temperature by 1 K (or 1 °C). The greater the heat capacity, the greater the heat required to produce a given increase in temperature.

For pure substances the heat capacity is usually given for a specified amount of the substance. The heat capacity of one mole of a substance is called its **molar heat capacity**, C_m. The heat capacity of one gram of a substance is called its *specific heat capacity*, or merely its **specific heat**, c. The specific heat, c, of a substance can be determined experimentally by measuring the temperature change, ΔT, that a known mass m of the substance undergoes when it gains or loses a specific quantity of heat q:

$$\text{Specific heat} = \frac{(\text{quantity of heat transferred})}{(\text{grams of substance}) \times (\text{temperature change})}$$

$$c = \frac{q}{m \times \Delta T} \qquad [5.20]$$

For example, 209 J is required to increase the temperature of 50.0 g of water by 1.00 K. Thus, the specific heat of water is

$$c = \frac{209\ \text{J}}{(50.0\ \text{g})(1.00\ \text{K})} = 4.18\ \text{J/g K}$$

Notice how the units combine in the calculation. A temperature change in kelvins is equal in magnitude to the temperature change in degrees Celsius: ΔT in $K = \Delta T$ in °C. Therefore, this specific heat for water can also be reported as 4.18 J/g °C, where the unit is pronounced "Joules per gram-degree Celsius."

Because the specific heat values for a given substance can vary slightly with temperature, the temperature is often precisely specified. The 4.18 J/g K value we use here for water, for instance, is for water initially at 14.5 °C (**Figure 5.17**). Water's specific heat at this temperature is used to define the calorie: 1 cal = 4.184 J exactly.

When a sample absorbs heat (positive q), its temperature increases (positive ΔT). Rearranging Equation 5.20, we get

$$q = C_s \times m \times \Delta T \qquad [5.21]$$

Thus, we can calculate the quantity of heat a substance gains or loses by using its specific heat together with its measured mass and temperature change.

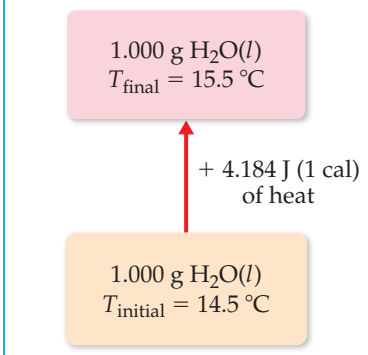
Table 5.2 lists the specific heats of several substances. Notice that the specific heat of liquid water is higher than those of the other substances listed. The high specific heat of water affects Earth's climate because it makes the temperatures of the oceans relatively resistant to change.

TABLE 5.2 Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	Specific Heat (J/g K)	Substance	Specific Heat (J/g K)
$N_2(g)$	1.04	$H_2O(l)$	4.18
$Al(s)$	0.90	$CH_4(g)$	2.20
$Fe(s)$	0.45	$CO_2(g)$	0.84
$Hg(l)$	0.14	$CaCO_3(s)$	0.82

Go Figure

Is the process shown in the figure endothermic or exothermic?



▲ **Figure 5.17** Specific heat of water.

Sample Exercise 5.5

Relating Heat, Temperature Change, and Heat Capacity

(**a**) How much heat is needed to warm 250 g of water (about 1 cup) from 22 °C (about room temperature) to 98 °C (near its boiling point)? (**b**) What is the molar heat capacity of water?

SOLUTION

Analyze In part (a) we must find the quantity of heat (q) needed to warm the water, given the mass of water (m), its temperature change (ΔT), and its specific heat (c). In part (b) we must calculate the molar heat capacity (heat capacity per mole, C_m) of water from its specific heat (heat capacity per gram).

Plan (**a**) Given c, m, and ΔT, we can calculate the quantity of heat, q, using Equation 5.21. (**b**) We can use the molar mass of water and dimensional analysis to convert from heat capacity per gram to heat capacity per mole.

Solve

(**a**) The water undergoes a temperature change of:

$$\Delta T = 98\,°C - 22\,°C = 76\,°C = 76\,K$$

Using Equation 5.21, we have:

$$q = C_s \times m \times \Delta T$$
$$= (4.18\,J/\cancel{g}\,\cancel{K})(250\,\cancel{g})(76\,\cancel{K}) = 7.9 \times 10^4\,J$$

(**b**) The molar heat capacity is the heat capacity of one mole of substance. Using the atomic weights of hydrogen and oxygen, we have:

$$1\ mol\ H_2O = 18.0\ g\ H_2O$$

From the specific heat used in part (a), we have:

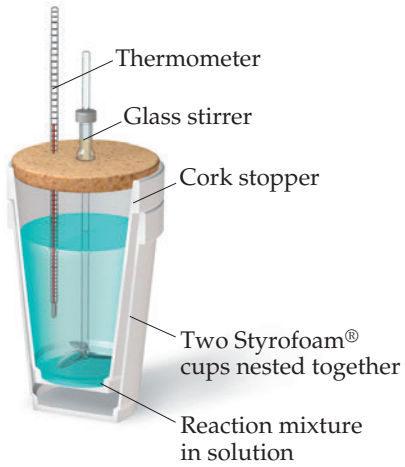
$$C_m = \left(4.18\,\frac{J}{\cancel{g}\,K}\right)\left(\frac{18.0\,\cancel{g}}{1\ mol}\right) = 75.2\,J/mol\text{-}K$$

Practice Exercise

(**a**) Large beds of rocks are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is 0.82 J/g K. Calculate the quantity of heat absorbed by 50.0 kg of rocks if their temperature increases by 12.0 °C. (**b**) What temperature change would these rocks undergo if they emitted 450 kJ of heat?

Go Figure

Why do you think two Styrofoam® cups are often used instead of just one.



▲ **Figure 5.18 Coffee-cup calorimeter.** This simple apparatus is used to measure temperature changes of reactions at constant pressure.

Constant-Pressure Calorimetry

The techniques and equipment employed in calorimetry depend on the nature of the process being studied. For many reactions, such as those occurring in solution, it is easy to control pressure so that ΔH is measured directly. Although the calorimeters used for highly accurate work are precision instruments, a simple "coffee-cup" calorimeter (**Figure 5.18**) is often used in general chemistry laboratories to illustrate the principles of calorimetry. Because the calorimeter is not sealed, the reaction occurs under the essentially constant pressure of the atmosphere.

Imagine adding two aqueous solutions, each containing a reactant, to a coffee-cup calorimeter. Once mixed, a reaction occurs. In this case, there is no physical boundary between the system and the surroundings. The reactants and products of the reaction are the system, and the water in which they are dissolved is part of the surroundings. (The calorimeter apparatus is also part of the surroundings.) If we assume that the calorimeter is perfectly insulated, then any heat released or absorbed by the reaction will raise or lower the temperature of the water in the solution. Thus, we measure the temperature change of the solution and assume that any changes are due to heat transferred from the reaction to the water (for an exothermic process) or transferred from the water to the reaction (endothermic). In other words, by monitoring the temperature of the solution, we are seeing the flow of heat between the system (the reactants and products in the solution) and the surroundings (the water that forms the bulk of the solution).

For an exothermic reaction, heat is "lost" by the reaction and "gained" by the water in the solution, so the temperature of the solution rises. The opposite occurs for an

endothermic reaction: Heat is gained by the reaction and lost by the water in the solution, and the temperature of the solution decreases. The heat gained or lost by the solution, q_{soln}, is therefore equal in magnitude but opposite in sign to the heat absorbed or released by the reaction, q_{rxn}, in mathematical terms $q_{soln} = -q_{rxn}$. The value of q_{soln} is readily calculated from the mass of the solution, its specific heat, and the temperature change:

$$q_{soln} = (\text{specific heat of solution}) \times (\text{grams of solution}) \times \Delta T = -q_{rxn} \qquad [5.22]$$

For dilute aqueous solutions we usually assume that the specific heat of the solution is the same as that of water, 4.18 J/g K.

Equation 5.22 makes it possible to calculate q_{rxn} from the temperature change of the solution in which the reaction occurs. A temperature increase ($\Delta T > 0$) means the reaction is exothermic ($q_{rxn} < 0$).

Sample Exercise 5.6

Measuring ΔH Using a Coffee-Cup Calorimeter

When a student mixes 50 mL of 1.0 *M* HCl and 50 mL of 1.0 *M* NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100 mL, that its density is 1.0 g/mL, and that its specific heat is 4.18 J/g K.

SOLUTION

Analyze Mixing solutions of HCl and NaOH results in an acid–base reaction:

$$HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq)$$

We need to calculate the heat produced per mole of HCl, given the temperature increase of the solution, the number of moles of HCl and NaOH involved, and the density and specific heat of the solution.

Plan The total heat produced can be calculated using Equation 5.22. The number of moles of HCl consumed in the reaction must be calculated from the volume and molarity of this substance, and this amount is then used to determine the heat produced per mol HCl.

Solve

Because the total volume of the solution is 100 mL, its mass is:	$(100\ \text{mL})(1.0\ \text{g/mL}) = 100\ \text{g}$
The temperature change is:	$\Delta T = 27.5\ ^\circ\text{C} - 21.0\ ^\circ\text{C} = 6.5\ ^\circ\text{C} = 6.5\ \text{K}$
Using Equation 5.22, we have:	$q_{rxn} = -c \times m \times \Delta T$ $= -(4.18\ \text{J/g}\,\cancel{\text{K}})(100\ \cancel{\text{g}})(6.5\ \cancel{\text{K}}) = -2.7 \times 10^3\ \text{J} = -2.7\ \text{kJ}$
Because the process occurs at constant pressure,	$\Delta H = q_P = -2.7\ \text{kJ}$
To express the enthalpy change on a molar basis, we use the fact that the number of moles of HCl is given by the product of the volume (50 mL = 0.050 L) and concentration (1.0 *M* = 1.0 mol/L) of the HCl solution:	$(0.050\ \cancel{\text{L}})(1.0\ \text{mol/}\cancel{\text{L}}) = 0.050\ \text{mol}$
Thus, the enthalpy change per mole of HCl is:	$\Delta H = -2.7\ \text{kJ}/0.050\ \text{mol} = -54\ \text{kJ/mol}$

Check ΔH is negative (exothermic), as evidenced by the observed increase in the temperature. The magnitude of the molar enthalpy change seems reasonable.

PPractice Exercise

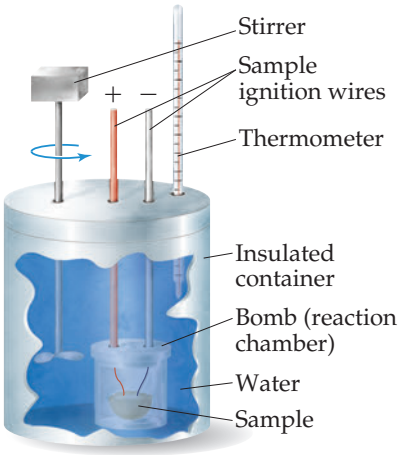
When 50.0 mL of 0.100 *M* $AgNO_3$ and 50.0 mL of 0.100 *M* HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 to 23.11 °C. The temperature increase is caused by the following reaction:

$$AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s) + HNO_3(aq)$$

Calculate ΔH for this reaction in kJ/mol $AgNO_3$, assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g-°C.

Go Figure

Is the water surrounding the reaction chamber part of the system or the surroundings?



▲ **Figure 5.19** Bomb calorimeter.

Bomb Calorimetry (Constant-Volume Calorimetry)

An important type of reaction studied using calorimetry is combustion, in which a compound reacts completely with excess oxygen. (Section 3.2) Combustion reactions are most accurately studied using a **bomb calorimeter** (Figure 5.19). The substance to be studied is placed in a small cup within an insulated sealed vessel called a *bomb*. The bomb, which is designed to withstand high pressures, has an inlet valve for adding oxygen and electrical leads for initiating the reaction. After the sample has been placed in the bomb, the bomb is sealed and pressurized with oxygen. It is then placed in the calorimeter and covered with an accurately measured quantity of water. The combustion reaction is initiated by passing an electrical current through a fine wire in contact with the sample. When the wire becomes sufficiently hot, the sample ignites.

The heat released when combustion occurs is absorbed by the water and the various components of the calorimeter (which all together make up the surroundings), causing the water temperature to rise. The change in water temperature caused by the reaction is measured very precisely.

To calculate the heat of combustion from the measured temperature increase, we must know the total heat capacity of the calorimeter, C_{cal}. This quantity is determined by combusting a sample that releases a known quantity of heat and measuring the temperature change. For example, combustion of exactly 1 g of benzoic acid, C_6H_5COOH, in a bomb calorimeter produces 26.38 kJ of heat. Suppose 1.000 g of benzoic acid is combusted in a calorimeter, leading to a temperature increase of 4.857 °C. The heat capacity of the calorimeter is then $C_{cal} = 26.38\ kJ/4.857\ °C = 5.431\ kJ/°C$. Once we know C_{cal}, we can measure temperature changes produced by other reactions, and from these we can calculate the heat evolved in the reaction, q_{rxn}:

$$q_{rxn} = -C_{cal} \times \Delta T \qquad [5.23]$$

Because reactions in a bomb calorimeter are carried out at constant volume, the heat transferred corresponds to the change in internal energy, ΔE, rather than the change in enthalpy, ΔH (Equation 5.13). For most reactions, however, the difference between ΔE and ΔH is very small. For the reaction discussed in Sample Exercise 5.7, for example, the difference between ΔE and ΔH is about 1 kJ/mol—a difference of less than 0.1%. It is possible to calculate ΔH from ΔE, but we need not concern ourselves with how these small corrections are made.

Sample Exercise 5.7

Measuring q_{rxn} Using a Bomb Calorimeter

The combustion of methylhydrazine (CH_6N_2), a liquid rocket fuel, produces $N_2(g)$, $CO_2(g)$, and $H_2O(l)$:

$$2\,CH_6N_2(l) + 5\,O_2(g) \longrightarrow 2\,N_2(g) + 2\,CO_2(g) + 6\,H_2O(l)$$

When 4.00 g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 to 39.50 °C. In a separate experiment the heat capacity of the calorimeter is measured to be 7.794 kJ/°C. Calculate the heat of reaction for the combustion of a mole of CH_6N_2.

SOLUTION

Analyze We are given a temperature change and the total heat capacity of the calorimeter. We are also given the amount of reactant combusted. Our goal is to calculate the enthalpy change per mole for combustion of the reactant.

Plan We will first calculate the heat evolved for the combustion of the 4.00 g sample. We will then convert this heat to a molar quantity.

Solve

For combustion of the 4.00 g sample of methylhydrazine, the temperature change of the calorimeter is:

$$\Delta T = (39.50\ °C - 25.00\ °C) = 14.50\ °C$$

We can use ΔT and the value for C_{cal} to calculate the heat of reaction (Equation 5.23):

$$q_{rxn} = -C_{cal} \times \Delta T = -(7.794\ kJ/\cancel{°C})(14.50\ \cancel{°C}) = -113.0\ kJ$$

We can readily convert this value to the heat of reaction for a mole of CH_6N_2:

$$\left(\frac{-113.0\text{ kJ}}{4.00\text{ g }\cancel{CH_6N_2}}\right) \times \left(\frac{46.1\text{ g }\cancel{CH_6N_2}}{1\text{ mol }CH_6N_2}\right) = -1.30 \times 10^3\text{ kJ/mol }CH_6N_2$$

Check The units cancel properly, and the sign of the answer is negative as it should be for an exothermic reaction. The magnitude of the answer seems reasonable.

▶ Practice Exercise

A 0.5865 g sample of lactic acid ($HC_3H_5O_3$) reacts with oxygen in a calorimeter whose heat capacity is 4.812 kJ/°C. The temperature increases from 23.10 to 24.95 °C. Calculate the heat of combustion of lactic acid (**a**) per gram and (**b**) per mole.

CHEMISTRY AND LIFE The Regulation of Body Temperature

For most of us, being asked the question "Are you running a fever?" was one of our first introductions to medical diagnosis. Indeed, a deviation in body temperature of only a few degrees indicates something amiss. Maintaining a near-constant temperature is one of the primary physiological functions of the human body.

To understand how the body's heating and cooling mechanisms operate, we can view the body as a thermodynamic system. The body increases its internal energy content by ingesting foods from the surroundings. The foods, such as glucose ($C_6H_{12}O_6$), are metabolized—a process that is essentially controlled oxidation to CO_2 and H_2O:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$
$$\Delta H = -2803\text{ kJ}$$

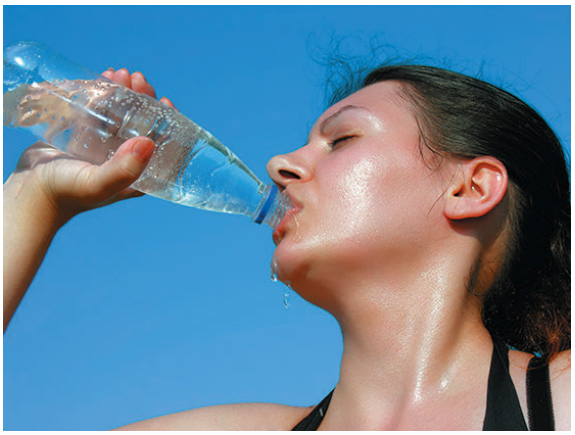
Roughly 40% of the energy produced is ultimately used to do work in the form of muscle contractions and nerve cell activities. The remainder is released as heat, part of which is used to maintain body temperature. When the body produces too much heat, as in times of heavy physical exertion, it dissipates the excess to the surroundings.

Heat is transferred from the body to its surroundings primarily by *radiation*, *convection*, and *evaporation*. Radiation is the direct loss of heat from the body to cooler surroundings, much as a hot stovetop radiates heat to its surroundings. Convection is heat loss by virtue of heating air that is in contact with the body. The heated air rises and is replaced with cooler air, and the process continues. Warm clothing decreases convective heat loss in cold weather. Evaporative cooling occurs when perspiration is generated at the skin surface by the sweat glands (**Figure 5.20**). Heat is removed from the body as the perspiration evaporates. Perspiration is predominantly water, so the process is the endothermic conversion of liquid water into water vapor:

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H = +44.0\text{ kJ}$$

The speed with which evaporative cooling occurs decreases as the atmospheric humidity increases, which is why we feel more sweaty and uncomfortable on hot, humid days.

When body temperature becomes too high, heat loss increases in two principal ways. First, blood flow near the skin surface increases,



▲ **Figure 5.20** Perspiration.

which allows for increased radiational and convective cooling. The reddish, "flushed" appearance of a hot individual is due to this increased blood flow. Second, we sweat, which increases evaporative cooling. During extreme activity, the amount of perspiration can be as high as 2 to 4 liters per hour. As a result, the body's water supply must be replenished during these periods. If the body loses too much liquid through perspiration, it will no longer be able to cool itself and blood volume decreases, which can lead to either *heat exhaustion* or the more serious *heat stroke*. However, replenishing water without replenishing the electrolytes lost during perspiration can also lead to serious problems. If the normal blood sodium level drops too low, dizziness and confusion set in, and the condition can become critical. Drinking a sport drink that contains some electrolytes helps to prevent this problem.

When body temperature drops too low, blood flow to the skin surface decreases, thereby decreasing heat loss. The lower temperature also triggers small involuntary contractions of the muscles (shivering); the biochemical reactions that generate the energy to do this work also generate heat for the body. If the body is unable to maintain a normal temperature, the very dangerous condition called *hypothermia* can result.

Self-Assessment Exercise

5.21 How much energy (heat) does it take to heat an Al saucepan (0.20 kg) containing 1.0 L of water from room temperature (20 °C) to boiling? Assume thermal equilibrium between the pan and water at all times (specific heat capacity for Al is 0.90 J/g K and H_2O is 4.18 J/g K. Assume the density of water is 1 g/mL).

(a) $q = +15$ kJ
(b) $q = +87$ kJ
(c) $q = +330$ kJ
(d) $q = +330$ kJ

Exercises

5.22 (**a**) Derive an equation to convert the specific heat of a pure substance to its molar heat capacity. (**b**) The specific heat of aluminum is 0.9 J/(g K). Calculate its molar heat capacity. (**c**) If you know the specific heat of aluminum, what additional information do you need to calculate the heat capacity of a particular piece of an aluminum component?

5.23 (**a**) What amount of heat (in joules) is required to raise the temperature of 1 g of water by 1 kelvin? (**b**) What is the heat capacity of 370 g of liquid water? (**c**) How many kJ of heat are needed to raise the temperature of 5.00 kg of liquid water from 24.6 to 46.2 °C?

5.24 The specific heat of octane, $C_8H_{18}(l)$, is 2.22 J/g K. (**a**) How many J of heat are needed to raise the temperature of 80.0 g of octane from 10.0 to 25.0 °C? (**b**) Which will require more heat, increasing the temperature of 1 mol of $C_8H_{18}(l)$ by a certain amount or increasing the temperature of 1 mol of $H_2O(l)$ by the same amount?

5.25 When an 18.6 g sample of solid potassium hydroxide dissolves in 200.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature rises from 23.7 to 44.5 °C. (**a**) Calculate the quantity of heat (in kJ) released in the reaction. (**b**) Using your result from part (a), calculate ΔH (in kJ/mol KOH) for the solution process. Assume that the specific heat of the solution is the same as that of pure water.

5.26 A 1.50 g sample of quinone ($C_6H_4O_2$) is burned in a bomb calorimeter whose total heat capacity is 8.500 kJ/°C. The temperature of the calorimeter increases from 25.00 to 29.49°C. (**a**) Write a balanced chemical equation for the bomb calorimeter reaction. (**b**) What is the heat of combustion per gram of quinone and per mole of quinone?

5.27 Under constant-volume conditions, the heat of combustion of sucrose ($C_{12}H_{22}O_{11}$) is 16.49 kJ/g. A 3.00 g sample of sucrose is burned in a bomb calorimeter. The temperature of the calorimeter increases from 21.94 to 24.62 °C. (**a**) What is the total heat capacity of the calorimeter? (**b**) If the size of the sucrose sample had been exactly twice as large, what would the temperature change of the calorimeter have been?

Answers to Self-Assessment Exercise

5.21 (d)

5.6 | Hess's Law



A fish ladder is a device that allows the movement of fish up a river when an obstruction such as a weir is built across their pathway. It provides an alternative route to get to the same end point. There are many reactions in chemistry where it may be difficult to determine the enthalpy change. Hess's Law allows us to calculate such a change from data that is easier to obtain.

By the end of this section, you should be able to

- Use Hess's law to determine enthalpy changes for reactions.

It is often possible to calculate the ΔH for a reaction from the tabulated ΔH values of other reactions. Thus, it is not necessary to make calorimetric measurements for all reactions.

Because enthalpy is a state function, the enthalpy change, ΔH, associated with any chemical process depends only on the amount of matter that undergoes change and on the nature of the initial state of the reactants and the final state of the products. This means that whether a particular reaction is carried out in one step or in a series of steps, the sum of the enthalpy changes associated with the individual steps must be the same as the enthalpy change associated with the one-step process. As an example, combustion of methane gas, $CH_4(g)$, to form $CO_2(g)$ and $H_2O(l)$ can be thought of as occurring in one step, as represented on the left in **Figure 5.21**, or in two steps, as represented on the right in Figure 5.21: (1) combustion of $CH_4(g)$ to form $CO_2(g)$ and $H_2O(g)$ and (2) condensation of $H_2O(g)$ to form $H_2O(l)$. The enthalpy change for the overall process is the sum of the enthalpy changes for these two steps:

$$\begin{array}{lll} & CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) & \Delta H = -802\text{ kJ} \\ \text{(Add)} & 2\,H_2O(g) \longrightarrow 2\,H_2O(l) & \Delta H = -88\text{ kJ} \\ \hline & CH_4(g) + 2\,O_2(g) + 2\,H_2O(g) \longrightarrow CO_2(g) + 2\,H_2O(l) + 2\,H_2O(g) & \Delta H = -890\text{ kJ} \end{array}$$

The net equation is

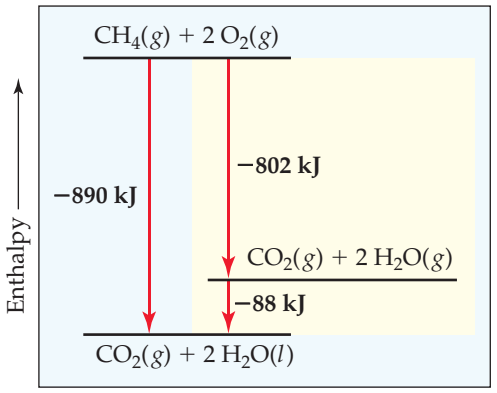
$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \quad \Delta H = -890\text{ kJ}$$

Hess's law states that *if a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps*. The overall enthalpy change for the process is independent of the number of steps and independent of the path by which the reaction is carried out. This law is a consequence of the fact that enthalpy is a state function. We can therefore calculate ΔH for any process as long as we find a route for which ΔH is known for each step. This means that a relatively small number of experimental measurements can be used to calculate ΔH for a vast number of reactions.

Hess's law provides a useful means of calculating energy changes that are difficult to measure directly. For instance, it is impossible to measure directly the enthalpy for the combustion of carbon to form carbon monoxide. Combustion of 1 mol of carbon with 0.5 mol of O_2 produces both CO and CO_2, leaving some carbon unreacted. However, solid carbon and carbon monoxide can both be completely burned in O_2 to produce CO_2. We can therefore use the enthalpy changes of these reactions to calculate the heat of combustion of carbon as illustrated in Sample Exercise 5.8.

Go Figure

What process corresponds to the −88 kJ enthalpy change?



▲ Figure 5.21 Enthalpy diagram for combustion of 1 mol of methane. The enthalpy change of the one-step reaction equals the sum of the enthalpy changes of the reaction run in two steps: $-890\text{ kJ} = -802\text{ kJ} + (-88\text{ kJ})$.

Sample Exercise 5.8

Using Hess's Law to Calculate ΔH

The enthalpy of reaction for the combustion of C to CO_2 is −393.5 kJ/mol C, and the enthalpy for the combustion of CO to CO_2 is −283.0 kJ/mol CO:

(1) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.5\text{ kJ}$

(2) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -283.0\text{ kJ}$

Using these data, calculate the enthalpy for the combustion of C to CO:

(3) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad \Delta H = ?$

Continued

SOLUTION

Analyze We are given two thermochemical equations, and our goal is to combine them in such a way as to obtain the third equation and its enthalpy change.

Plan We will use Hess's law. In doing so, we first note the number of moles of substances among the reactants and products in the target equation (3). We then manipulate equations (1) and (2) to give the same number of moles of these substances, so that when the resulting equations are added, we obtain the target equation. At the same time, we keep track of the enthalpy changes, which we add.

Solve To use equations (1) and (2), we arrange them so that C(*s*) is on the reactant side and CO(*g*) is on the product side of the arrow, as in the target reaction, equation (3). Because equation (1) has C(*s*) as a reactant, we can use that equation just as it is. We need to turn equation (2) around, however, so that CO(*g*) is a product. Remember that when reactions are turned around, the sign of ΔH is reversed. We arrange the two equations so that they can be added to give the desired equation:

$$\begin{aligned} C(s) + O_2(g) &\longrightarrow CO_2(g) && \Delta H = -393.5\ \text{kJ} \\ CO_2(g) &\longrightarrow CO(g) + \tfrac{1}{2}O_2(g) && -\Delta H = 283.0\ \text{kJ} \\ \hline C(s) + \tfrac{1}{2}O_2(g) &\longrightarrow CO(g) && \Delta H = -110.5\ \text{kJ} \end{aligned}$$

When we add the two equations, $CO_2(g)$ appears on both sides of the arrow and therefore cancels out. Likewise, $\frac{1}{2}O_2(g)$ is eliminated from each side.

Practice Exercise

Calculate ΔH for $2\,NO(g) + O_2(g) \longrightarrow N_2O_4(g)$, using the following information:

$$\begin{aligned} N_2O_4(g) &\longrightarrow 2\,NO_2(g) && \Delta H = +57.9\ \text{kJ} \\ 2\,NO(g) + O_2(g) &\longrightarrow 2\,NO_2(g) && \Delta H = -113.1\ \text{kJ} \end{aligned}$$

(a) 2.7 kJ **(b)** −55.2 kJ **(c)** −85.5 kJ **(d)** −171.0 kJ **(e)** +55.2 kJ

Sample Exercise 5.9

Using Hess's Law with Three Equations to Calculate ΔH

Calculate ΔH for the reaction

$$2\,C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

given the following chemical equations and their respective enthalpy changes:

$$\begin{aligned} C_2H_2(g) + \tfrac{5}{2}O_2(g) &\longrightarrow 2\,CO_2(g) + H_2O(l) && \Delta H = -1299.6\ \text{kJ} \\ C(s) + O_2(g) &\longrightarrow CO_2(g) && \Delta H = -393.5\ \text{kJ} \\ H_2(g) + \tfrac{1}{2}O_2(g) &\longrightarrow H_2O(l) && \Delta H = -285.8\ \text{kJ} \end{aligned}$$

SOLUTION

Analyze We are given a chemical equation and asked to calculate its ΔH using three chemical equations and their associated enthalpy changes.

Plan We will use Hess's law, summing the three equations or their reverses and multiplying each by an appropriate coefficient so that they add to give the net equation for the reaction of interest. At the same time, we keep track of the ΔH values, reversing their signs if the reactions are reversed and multiplying them by whatever coefficient is employed in the equation.

Solve Because the target equation has C_2H_2 as a product, we turn the first equation around; the sign of ΔH is therefore changed. The desired equation has 2 C(*s*) as a reactant, so we multiply the second equation and its ΔH by 2. Because the target equation has H_2 as a reactant, we keep the third equation as it is. We then add the three equations and their enthalpy changes in accordance with Hess's law:

$$\begin{aligned} 2\,\cancel{CO_2(g)} + \cancel{H_2O(l)} &\longrightarrow C_2H_2(g) + \tfrac{5}{2}\,\cancel{O_2(g)} && -\Delta H = 1299.6\ \text{kJ} \\ 2\,C(s) + 2\,\cancel{O_2(g)} &\longrightarrow 2\,\cancel{CO_2(g)} && \Delta H = -787.0\ \text{kJ} \\ H_2(g) + \tfrac{1}{2}\,\cancel{O_2(g)} &\longrightarrow \cancel{H_2O(l)} && \Delta H = -285.8\ \text{kJ} \\ \hline 2\,C(s) + H_2(g) &\longrightarrow C_2H_2(g) && \Delta H = 226.8\ \text{kJ} \end{aligned}$$

When the equations are added, there are 2 CO_2, $\frac{5}{2}$ O_2, and H_2O on both sides of the arrow. These are canceled in writing the net equation.

Check The procedure must be correct because we obtained the correct net equation. In cases like this, you should go back over the numerical manipulations of the ΔH values to ensure that you did not make an inadvertent error with signs.

Practice Exercise

Calculate ΔH for the reaction

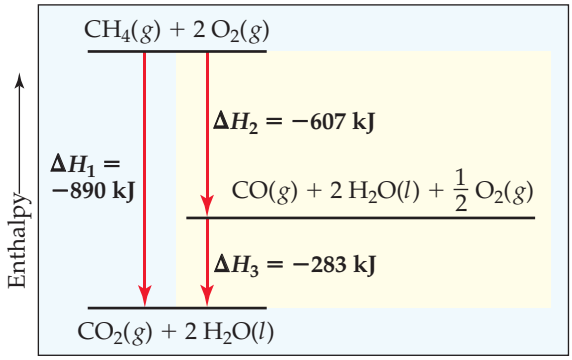
$$NO(g) + O(g) \longrightarrow NO_2(g)$$

given the following information:

$$\begin{aligned} NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) && \Delta H = -198.9\ \text{kJ} \\ O_3(g) &\longrightarrow \tfrac{3}{2}O_2(g) && \Delta H = -142.3\ \text{kJ} \\ O_2(g) &\longrightarrow 2\,O(g) && \Delta H = 495.0\ \text{kJ} \end{aligned}$$

Go Figure

Suppose the overall reaction were modified to produce 2 $H_2O(g)$ rather than 2 $H_2O(l)$. Would any of the values of ΔH in the diagram stay the same?



▲ **Figure 5.22 Enthalpy diagram illustrating Hess's law.** The net reaction is the same as in Figure 5.21, but here we imagine different reactions in our two-step version. As long as we can write a series of equations, each with a known value of ΔH, that add up to the equation we need, we can calculate the overall ΔH.

The key point of these examples is that H is a state function.

Because H is a state function, for a particular set of reactants and products, ΔH is the same whether the reaction takes place in one step or in a series of steps.

We reinforce this point by giving one more example of an enthalpy diagram and Hess's law. Again we use combustion of methane to form CO_2 and H_2O, our reaction from Figure 5.21. This time we envision a different two-step path, with the initial formation of CO, which is then combusted to CO_2 (**Figure 5.22**). Even though the two-step path is different from that in Figure 5.21, the overall reaction again has $\Delta H_1 = -890$ kJ. Because H is a state function, both paths *must* produce the same value of ΔH. In Figure 5.22, that means $\Delta H_1 = \Delta H_2 + \Delta H_3$. We will soon see that breaking up reactions in this way allows us to derive the enthalpy changes for reactions that are hard to carry out in the laboratory.

Self-Assessment Exercise

5.28 Calculate the enthalpy change for the reaction:

$$CO(g) + NO(g) \longrightarrow CO_2(g) + \tfrac{1}{2}N_2(g)$$

Given: $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -283$ kJ/mol

$NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \quad \Delta H = -90.3$ kJ/mol

(a) $\Delta H = +373$ kJ/mol
(b) $\Delta H = +193$ kJ/mol
(c) $\Delta H = -193$ kJ/mol
(d) $\Delta H = -373$ kJ/mol

Exercises

5.29 Consider the following hypothetical reactions:

$$A \longrightarrow B \quad \Delta H_I = +60\text{ kJ}$$
$$B \longrightarrow C \quad \Delta H_{II} = -90\text{ kJ}$$

(a) Use Hess's law to calculate the enthalpy change for the reaction A ⟶ C.

(b) Construct an enthalpy diagram for substances A, B, and C, and show how Hess's law applies.

5.30 Calculate the enthalpy change for the reaction

$$P_4O_6(s) + 2\,O_2(g) \longrightarrow P_4O_{10}(s)$$

given the following enthalpies of reaction:

$$P_4(s) + 3\,O_2(g) \longrightarrow P_4O_6(s) \quad \Delta H = -1640.1\text{ kJ}$$
$$P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s) \quad \Delta H = -2940.1\text{ kJ}$$

5.31 From the enthalpies of reaction

$$H_2(g) + F_2(g) \longrightarrow 2\,HF(g) \qquad \Delta H = -537\ kJ$$
$$C(s) + 2\,F_2(g) \longrightarrow CF_4(g) \qquad \Delta H = -680\ kJ$$
$$2\,C(s) + 2\,H_2(g) \longrightarrow C_2H_4(g) \qquad \Delta H = +52.3\ kJ$$

calculate ΔH for the reaction of ethylene with F_2:

$$C_2H_4(g) + 6\,F_2(g) \longrightarrow 2\,CF_4(g) + 4\,HF(g)$$

Answers to Self-Assessment Exercise

5.28 (d)

5.7 | Enthalpies of Formation



Data banks play an important part in modern society, empowering decisions that have been informed by ready access to relevant data. In the area of thermochemistry, the compilation of standard enthalpies of formation is the most important. We examine how to use this wealth of knowledge in this section, by the end of which you should be able to

- Use standard enthalpies of formation to calculate heats of reaction.

We can use the methods just discussed to calculate enthalpy changes for a great many reactions from tabulated ΔH values. For example, extensive tables exist of *enthalpies of vaporization* (ΔH for converting liquids to gases), *enthalpies of fusion* (ΔH for melting solids), *enthalpies of combustion* (ΔH for combusting a substance in oxygen), and so forth. A particularly important process used for tabulating thermochemical data is the formation of a compound from its constituent elements. The enthalpy change associated with this process is called the **enthalpy of formation** (or *heat of formation*), ΔH_f, where the subscript *f* indicates that the substance has been *formed* from its constituent elements.

The magnitude of any enthalpy change depends on the temperature, pressure, and state (gas, liquid, or solid crystalline form) of the reactants and products. To compare enthalpies of different reactions, we must define a set of conditions, called a *standard state*, at which most enthalpies are tabulated. The standard state of a substance is its pure form at atmospheric pressure (100 kPa) and the temperature of interest, which we usually choose to be 298 K (25 °C). The **standard enthalpy change** of a reaction is defined as the enthalpy change when all reactants and products are in their standard states. We denote a standard enthalpy change as $\Delta H°$, where the superscript ° indicates standard-state conditions.

TABLE 5.3 Standard Enthalpies of Formation, ΔH°_f, at 298 K

Substance	Formula	ΔH°_f (kJ/mol)	Substance	Formula	ΔH°_f (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	−92.30
Ammonia	$NH_3(g)$	−46.19	Hydrogen fluoride	$HF(g)$	−268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	−1207.1	Methane	$CH_4(g)$	−74.80
Calcium oxide	$CaO(s)$	−635.5	Methanol	$CH_3OH(l)$	−238.6
Carbon dioxide	$CO_2(g)$	−393.5	Propane	$C_3H_8(g)$	−103.85
Carbon monoxide	$CO(g)$	−110.5	Silver chloride	$AgCl(s)$	−127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	−947.7
Ethane	$C_2H_6(g)$	−84.68	Sodium carbonate	$Na_2CO_3(s)$	−1130.9
Ethanol	$C_2H_5OH(l)$	−277.7	Sodium chloride	$NaCl(s)$	−410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	−2221
Glucose	$C_6H_{12}O_6(s)$	−1273	Water	$H_2O(l)$	−285.8
Hydrogen bromide	$HBr(g)$	−36.23	Water vapor	$H_2O(g)$	−241.8

The **standard enthalpy of formation** of a compound, ΔH_f°, is the change in enthalpy for the reaction that forms one mole of the compound from its elements with all substances in their standard states:

$$\underset{\text{(in standard state)}}{\text{elements}} \longrightarrow \underset{\text{(1 mol in standard state)}}{\text{compound}} \qquad \Delta H_{rxn} = \Delta H_f^\circ \qquad [5.24]$$

We usually report ΔH_f° values at 298 K. If an element exists in more than one form under standard conditions, the most stable form of the element is usually used for the formation reaction. For example, the standard enthalpy of formation for ethanol, C_2H_5OH, is the enthalpy change for the reaction

$$2\,C(\textit{graphite}) + 3\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H_f^\circ = -277.7\ \text{kJ} \qquad [5.25]$$

The elemental source of oxygen is O_2, not O or O_3, because O_2 is the stable form of oxygen at 298 K and atmospheric pressure. Similarly, the elemental source of carbon is graphite and not diamond because graphite is the more stable (lower-energy) form at 298 K and atmospheric pressure. Likewise, the most stable form of hydrogen under standard conditions is $H_2(g)$, so this is used as the source of hydrogen in Equation 5.25.

The stoichiometry of formation reactions always indicates that one mole of the desired substance is produced, as in Equation 5.25. As a result, standard enthalpies of formation are reported in kJ/mol of the substance being formed. Some values are given in Table 5.3, and a more extensive table is provided in Appendix C.

By definition, *the standard enthalpy of formation of the most stable form of any element is zero* because there is no formation reaction needed when the element is already in its standard state. Thus, the values of ΔH_f° for $C(\textit{graphite})$, $H_2(g)$, $O_2(g)$, and the standard states of other elements are zero by definition.

Sample Exercise 5.10



Equations Associated with Enthalpies of Formation

For which of these reactions at 25 °C does the enthalpy change represent a standard enthalpy of formation? For each that does not, what changes are needed to make it an equation whose ΔH is an enthalpy of formation?

(a) $2\,Na(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow Na_2O(s)$

(b) $2\,K(l) + Cl_2(g) \longrightarrow 2\,KCl(s)$

(c) $C_6H_{12}O_6(s) \longrightarrow 6\,C(\textit{diamond}) + 6\,H_2(g) + 3\,O_2(g)$

Continued

SOLUTION

Analyze The standard enthalpy of formation is represented by a reaction in which each reactant is an element in its standard state and the product is one mole of the compound.

Plan We need to examine each equation to determine (1) whether the reaction is one in which one mole of substance is formed from the elements, and (2) whether the reactant elements are in their standard states.

Solve In (a) 1 mol Na_2O is formed from the elements sodium and oxygen in their proper states, solid Na and O_2 gas, respectively. Therefore, the enthalpy change for reaction (a) corresponds to a standard enthalpy of formation.

In (b) potassium is given as a liquid. It must be changed to the solid form, its standard state at room temperature. Furthermore, 2 mol KCl are formed, so the enthalpy change for the reaction as written is twice the standard enthalpy of formation of KCl(*s*). The equation for the formation reaction of 1 mol of KCl(*s*) is

$$K(s) + \tfrac{1}{2}\,Cl_2(g) \longrightarrow KCl(s)$$

Reaction (c) does not form a substance from its elements. Instead, a substance decomposes to its elements, so this reaction must be reversed. Next, the element carbon is given as diamond, whereas graphite is the standard state of carbon at room temperature and 101.3 kPa pressure. The equation that correctly represents the enthalpy of formation of glucose from its elements is

$$6\,C(\textit{graphite}) + 6\,H_2(g) + 3\,O_2(g) \longrightarrow C_6H_{12}O_6(s)$$

Practice Exercise
Write the equation corresponding to the standard enthalpy of formation of liquid carbon tetrachloride (CCl_4) and look up ΔH_f° for this compound in Appendix C.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

We can use Hess's law and tabulations of ΔH_f° values, such as those in Table 5.3 and Appendix C, to calculate the standard enthalpy change for any reaction for which we know the ΔH_f° values for all reactants and products. For example, consider the combustion of propane under standard conditions:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

We can write this equation as the sum of three equations associated with standard enthalpies of formation:

$$C_3H_8(g) \longrightarrow 3\,C(s) + 4\,H_2(g) \qquad \Delta H_1 = -\Delta H_f^\circ[C_3H_8(g)] \qquad [5.26]$$

$$3\,C(s) + 3\,O_2(g) \longrightarrow 3\,CO_2(g) \qquad \Delta H_2 = 3\Delta H_f^\circ[CO_2(g)] \qquad [5.27]$$

$$4\,H_2(g) + 2\,O_2(g) \longrightarrow 4\,H_2O(l) \qquad \Delta H_3 = 4\Delta H_f^\circ[H_2O(l)] \qquad [5.28]$$

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H_{rxn}^\circ = \Delta H_1 + \Delta H_2 + \Delta H_3 \qquad [5.29]$$

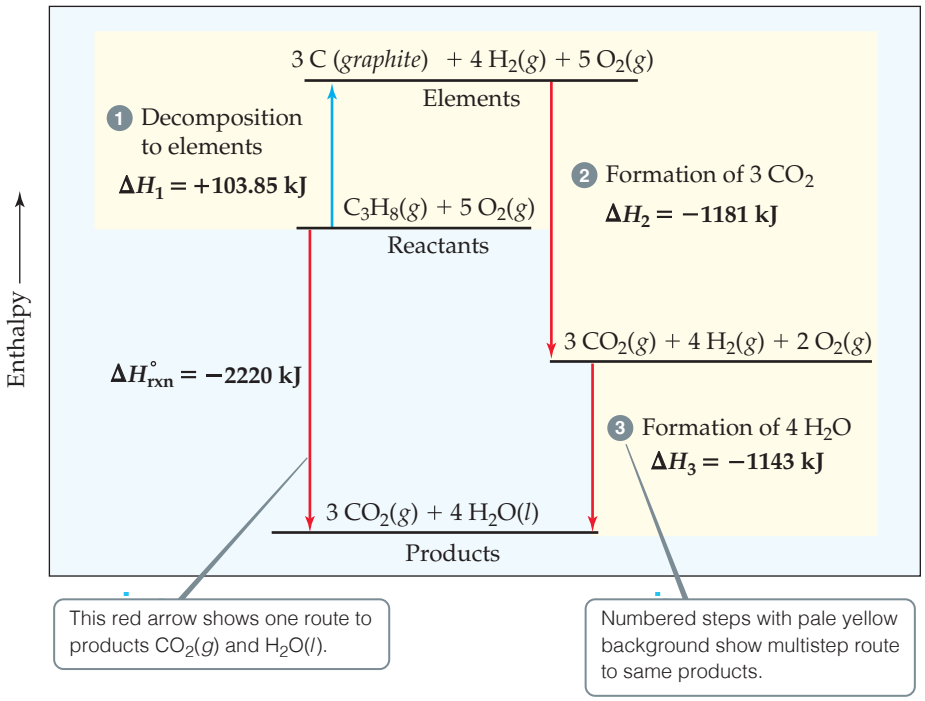
(Note that it is sometimes useful to add subscripts to the enthalpy changes, as we have done here, to keep track of the associations between reactions and their ΔH values.)

Notice that we have used Hess's law to write the standard enthalpy change for Equation 5.29 as the sum of the enthalpy changes for Equations 5.26 through 5.28. We can use values from Table 5.3 to calculate ΔH_{rxn}°:

$$\begin{aligned}\Delta H_{rxn}^\circ &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= -\Delta H_f^\circ[C_3H_8(g)] + 3\Delta H_f^\circ[CO_2(g)] + 4\Delta H_f^\circ[H_2O(l)] \\ &= -(-103.85\ \text{kJ}) + 3(-393.5\ \text{kJ}) + 4(-285.8\ \text{kJ}) = -2220\ \text{kJ}\end{aligned} \qquad [5.30]$$

The enthalpy diagram in **Figure 5.23** shows the components of this calculation. In Step ❶ the reactants are decomposed into their constituent elements in their standard states. In Steps ❷ and ❸ the products are formed from the elements. Several aspects of how we use enthalpy changes in this process depend on the guidelines we discussed in Section 5.4.

❶ **Decomposition.** Equation 5.26 is the reverse of the formation reaction for $C_3H_8(g)$, so the enthalpy change for this decomposition reaction is the negative of the ΔH_f° value for the propane formation reaction: $-\Delta H_f^\circ[C_3H_8(g)]$.



◀ **Figure 5.23** Enthalpy diagram for propane combustion.

2 **Formation of CO_2.** Equation 5.27 is the formation reaction for 3 mol of $CO_2(g)$. Because enthalpy is an extensive property, the enthalpy change for this step is $3\Delta H_f^\circ[CO_2(g)]$.

3 **Formation of H_2O.** The enthalpy change for Equation 5.28, formation of 4 mol of H_2O, is $4\Delta H_f^\circ[H_2O(l)]$. The reaction specifies that $H_2O(l)$ is produced, so be careful to use the value of ΔH_f° for $H_2O(l)$ and not the value for $H_2O(g)$.

Note that in this analysis we assume that the stoichiometric coefficients in the balanced equation represent the number of moles of each substance. For Equation 5.29, therefore, $\Delta H_{rxn}^\circ = -2220$ kJ represents the enthalpy change for the reaction of 1 mol C_3H_8 and 5 mol O_2 to form 3 mol CO_2 and 4 mol H_2O.

We can break down any reaction into formation reactions as we have done here. When we do, we obtain the general result that the standard enthalpy change of a reaction is the sum of the standard enthalpies of formation of the products minus the standard enthalpies of formation of the reactants:

$$\Delta H_{rxn}^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) \qquad [5.31]$$

The symbol Σ (sigma) means "the sum of," and n and m are the stoichiometric coefficients of the relevant chemical equation. The first term on the right in Equation 5.31 represents the formation reactions of the products, which are written in the "forward" direction in the chemical equation, that is, elements reacting to form products. This term is analogous to Equations 5.27 and 5.28. The second term on the right in Equation 5.31 represents the reverse of the formation reactions of the reactants, analogous to Equation 5.26, which is why this term is preceded by a minus sign.

Sample Exercise 5.11

Calculating an Enthalpy of Reaction from Enthalpies of Formation

(**a**) Calculate the standard enthalpy change for the combustion of 1 mol of benzene, $C_6H_6(l)$, to $CO_2(g)$ and $H_2O(l)$.
(**b**) Compare the quantity of heat produced by combustion of 1.00 g propane with that produced by 1.00 g benzene.

Continued

SOLUTION

Analyze (**a**) We are given a reaction (combustion of $C_6H_6(l)$ to form $CO_2(g)$ and $H_2O(l)$) and asked to calculate its standard enthalpy change, ΔH°. (**b**) We then need to compare the quantity of heat produced by combustion of 1.00 g C_6H_6 with that produced by 1.00 g C_3H_8, whose combustion was treated previously in the text. (See Equations 5.29 and 5.30.)

Plan (**a**) We first write the balanced equation for the combustion of C_6H_6. We then look up ΔH_f° values in Appendix C or in Table 5.3 and apply Equation 5.31 to calculate the enthalpy change for the reaction. (**b**) We use the molar mass of C_6H_6 to change the enthalpy change per mole to that per gram. We similarly use the molar mass of C_3H_8 and the enthalpy change per mole calculated in the text previously to calculate the enthalpy change per gram of that substance.

Solve

(**a**) We know that a combustion reaction involves $O_2(g)$ as a reactant. Thus, the balanced equation for the combustion reaction of 1 mol $C_6H_6(l)$ is:

$$C_6H_6(l) + \tfrac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(l)$$

We can calculate ΔH° for this reaction by using Equation 5.31 and data in Table 5.3. Remember to multiply the ΔH_f° value for each substance in the reaction by that substance's stoichiometric coefficient. Recall also that $\Delta H_f^\circ = 0$ for any element in its most stable form under standard conditions, so $\Delta H_f^\circ[O_2(g)] = 0$.

$$\begin{aligned}\Delta H^\circ_{rxn} &= [6\Delta H_f^\circ(CO_2) + 3\Delta H_f^\circ(H_2O)] - [\Delta H_f^\circ(C_6H_6) + \tfrac{15}{2}\Delta H_f^\circ(O_2)]\\ &= [6(-393.5\text{ kJ}) + 3(-285.8\text{ kJ})] - [(49.0\text{ kJ}) + \tfrac{15}{2}(0\text{ kJ})]\\ &= (-2361 - 857.4 - 49.0)\text{ kJ}\\ &= -3267\text{ kJ}\end{aligned}$$

(**b**) From the example worked in the text, $\Delta H^\circ = -2220$ kJ for the combustion of 1 mol of propane. In part (a) of this exercise we determined that $\Delta H^\circ = -3267$ kJ for the combustion of 1 mol benzene. To determine the heat of combustion per gram of each substance, we use the molar masses to convert moles to grams:

$$C_3H_8(g):\quad (-2220\text{ kJ/mol})(1\text{ mol}/44.1\text{ g}) = -50.3\text{ kJ/g}$$
$$C_6H_6(l):\quad (-3267\text{ kJ/mol})(1\text{ mol}/78.1\text{ g}) = -41.8\text{ kJ/g}$$

Comment Both propane and benzene are hydrocarbons. As a rule, the energy obtained from the combustion of a gram of hydrocarbon is between 40 and 50 kJ.

Practice Exercise

Calculate the enthalpy change for the reaction

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g)$$

using enthalpies of formation:

$\Delta H_f^\circ[H_2O_2(l)] = -187.8$ kJ/mol $\quad \Delta H_f^\circ[H_2O(l)] = -285.8$ kJ/mol

(**a**) −88.0 kJ
(**b**) −196.0 kJ
(**c**) +88.0 kJ
(**d**) +196.0 kJ
(**e**) more information needed

Sample Exercise 5.12

Calculating an Enthalpy of Formation Using an Enthalpy of Reaction

The standard enthalpy change for the reaction $CaCO_3[s] \longrightarrow CaO[s] + CO_2[g]$ is 178.1 kJ. Use Table 5.3 to calculate the standard enthalpy of formation of $CaCO_3[s]$.

SOLUTION

Analyze Our goal is to obtain $\Delta H_f^\circ[CaCO_3]$.

Plan We begin by writing the expression for the standard enthalpy change for the reaction:

$$\Delta H^\circ_{rxn} = \Delta H_f^\circ[CaO] + \Delta H_f^\circ[CO_2] - \Delta H_f^\circ[CaCO_3]$$

Solve

Inserting the given ΔH°_{rxn} and the known ΔH_f° values from Table 5.3 or Appendix C, we have:

$$178.1\text{ kJ} = -635.5\text{ kJ} - 393.5\text{ kJ} - \Delta H_f^\circ[CaCO_3]$$

Solving for $\Delta H_f^\circ[CaCO_3]$ gives:

$$\Delta H_f^\circ[CaCO_3] = -1207.1\text{ kJ/mol}$$

Check We expect the enthalpy of formation of a stable solid such as calcium carbonate to be negative, as obtained.

Practice Exercise

Given $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$, which of the following equations is correct?

(a) $\Delta H_f^\circ[SO_3] = \Delta H_{rxn}^\circ - \Delta H_f^\circ[SO_2]$

(b) $\Delta H_f^\circ[SO_3] = \Delta H_{rxn}^\circ + \Delta H_f^\circ[SO_2]$

(c) $2\Delta H_f^\circ[SO_3] = \Delta H_{rxn}^\circ + 2\Delta H_f^\circ[SO_2]$

(d) $2\Delta H_f^\circ[SO_3] = \Delta H_{rxn}^\circ - 2\Delta H_f^\circ[SO_2]$

(e) $2\Delta H_f^\circ[SO_3] = 2\Delta H_f^\circ[SO_2] - \Delta H_{rxn}^\circ$

Self-Assessment Exercise

5.32 The equation for the combustion of urea is: $(NH_2)_2CO(s) + 1\frac{1}{2}\,O_2(g) \longrightarrow CO_2(g) + N_2(g) + 2\,H_2O(l)$

Use ΔH_f° (urea) $= -333$ kJ and the values in Table 5.3 to calculate the enthalpy of combustion of urea.

(a) $\Delta H = -346$ kJ

(b) $\Delta H = -632$ kJ

(c) $\Delta H = -1300$ kJ

Exercises

5.33 (**a**) What is meant by the term *standard conditions* with reference to enthalpy changes? (**b**) What is meant by the term *enthalpy of formation*? (**c**) What is meant by the term *standard enthalpy of formation*?

5.34 For each of the following compounds, write a balanced thermochemical equation depicting the formation of one mole of the compound from its elements in their standard states and then look up ΔH°_f for each substance in Appendix C. (**a**) $NO_2(g)$, (**b**) $SO_3(g)$, (**c**) $NaBr(s)$, (**d**) $Pb(NO_3)_2(s)$.

5.35 The following is known as the thermite reaction:

$$2\,Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2\,Fe(s)$$

This highly exothermic reaction is used for welding massive units, such as propellers for large ships. Using standard enthalpies of formation in Appendix C, calculate ΔH° for this reaction.

5.36 Using values from Appendix C, calculate the standard enthalpy change for each of the following reactions:

(a) $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

(b) $Mg(OH)_2(s) \longrightarrow MgO(s) + H_2O(l)$

(c) $N_2O_4(g) + 4\,H_2(g) \longrightarrow N_2(g) + 4\,H_2O(g)$

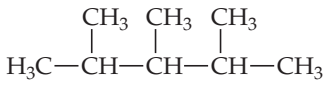
(d) $SiCl_4(l) + 2\,H_2O(l) \longrightarrow SiO_2(s) + 4\,HCl(g)$

5.37 Complete combustion of 1 mol of acetone (C_3H_6O) liberates 1790 kJ:

$$C_3H_6O(l) + 4\,O_2(g) \longrightarrow 3\,CO_2(g) + 3\,H_2O(l) \qquad \Delta H^\circ = -1790\text{ kJ}$$

Using this information together with the standard enthalpies of formation of $O_2(g)$, $CO_2(g)$, and $H_2O(l)$ from Appendix C, calculate the standard enthalpy of formation of acetone.

5.38 Petrol is composed primarily of hydrocarbons, including many with eight carbon atoms, called *octanes*. One of the cleanest-burning octanes is a compound called 2,3,4-trimethylpentane, which has the following structural formula:



The complete combustion of one mole of this compound to $CO_2(g)$ and $H_2O(g)$ leads to $\Delta H^\circ = -5064.9$ kJ. (**a**) Write a balanced equation for the combustion of 1 mol of $C_8H_{18}(l)$. (**b**) By using the information in this problem and data in Table 5.3, calculate ΔH_f° for 2,3,4-trimethylpentane.

5.39 Ethanol (C_2H_5OH) is blended with petrol as a vehicle fuel. (**a**) Write a balanced equation for the combustion of liquid ethanol in air. (**b**) Calculate the standard enthalpy change for the reaction, assuming $H_2O(g)$ as a product. (**c**) Calculate the heat produced per liter of ethanol by combustion of ethanol under constant pressure. Ethanol has a density of 0.789 g/mL. (**d**) Calculate the mass of CO_2 produced per kJ of heat emitted.

Answers to Self-Assessment Exercise

5.32 (b)

5.8 | Bond Enthalpies

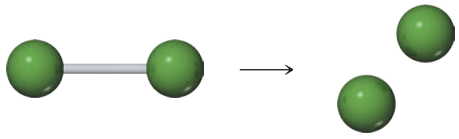


Knowing the limitations of the data that you are using is an important part of estimating errors. As we shall see with bond enthalpies, the data is compiled from reactions involving gases. While this is useful in estimating enthalpy changes for some reactions—principally gas phase ones—it may be less accurate for reactions in liquid or solid states. Nevertheless, it can still give us useful approximations of energy changes. By the end of this section, you should be able to

- Use average bond enthalpies to estimate the reaction enthalpies of reactions where all reactants and products are in the gas phase.

The energy changes that accompany chemical reactions are closely related to the changes associated with forming and breaking chemical bonds—breaking bonds requires energy and forming bonds releases energy. It follows that if we measure the enthalpy of a reaction and keep track of the bonds that are broken and formed, we can assign an enthalpy value to specific bonds. The **bond enthalpy** is the enthalpy change, ΔH, for the breaking of a particular bond in one mole of a gaseous substance. It is easiest to determine bond enthalpies from simple reactions where only one bond is broken, such as the dissociation of $Cl_2(g)$. A Cl_2 molecule is held together by a single covalent bond, which is represented as Cl—Cl. The dissociation of $Cl_2(g)$ into chlorine atoms results when the Cl—Cl bond is broken:

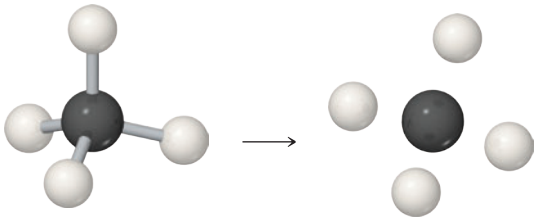
$$Cl_2(g) \longrightarrow 2Cl(g)$$



The bond enthalpy for a Cl—Cl bond is equal to the enthalpy of this reaction, 242 kJ/mol. The bond enthalpy is a positive number because energy must be supplied from the surroundings to break the Cl—Cl bond. We use the letter D followed by the bond in question to represent bond enthalpies. For example, D(Cl—Cl) is the bond enthalpy for the Cl_2 bond, and D(H—Br) is the bond enthalpy for the HBr bond.

It is straightforward to assign bond enthalpies for a reaction involving the breaking of a bond in a diatomic molecule: the bond enthalpy is simply equal to the enthalpy of the reaction. However, many important bonds, such as the C—H bond, exist only in polyatomic molecules. For these bonds, we usually use average bond enthalpies. For example, the enthalpy change for the following process in which a methane molecule is decomposed into its five constituent atoms can be used to define an average bond enthalpy for the C—H bond:

$$CH_4(g) \longrightarrow C(g) + 4\,H(g) \qquad \Delta H = 1660\ \text{kJ}$$



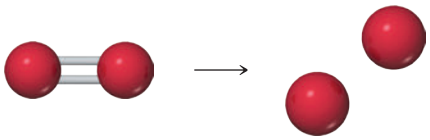
Because there are four equivalent C—H bonds in methane, the enthalpy of this reaction is four times the enthalpy needed to break a single C—H bond. Therefore, the average C—H bond enthalpy in CH_4 is $D(C—H) = (1660/4)$ kJ/mol = 415 kJ/mol.

The exact bond enthalpy for a given pair of atoms, say C—H, depends on the rest of the molecule containing the atom pair. However, the variation from one molecule to another is generally small. If we consider C—H bond enthalpies in many different compounds, we find that the average bond enthalpy is 413 kJ/mol, close to the 415 kJ/mol value we just calculated from for the dissociation of CH_4.

The bond enthalpy is always a positive quantity because energy is required to break chemical bonds. Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments. The greater the bond enthalpy, the stronger the bond.

Table 5.4 lists average bond enthalpies for a number of atom pairs. Further, a molecule with strong chemical bonds is generally less likely to undergo chemical change than one with weak bonds. As we will learn in later chapters, atom pairs are sometimes held together by multiple bonds. For example, the oxygen atoms in an O_2 molecule are held together by a double bond, O═O, rather than a single bond, O—O.

$$O{=}O(g) \longrightarrow 2\,O(g) \qquad \Delta H = 495 \text{ kJ}$$



Inspection of Table 5.4 shows that $D(O{=}O) = 495$ kJ/mol, which is larger but not exactly twice the enthalpy of an oxygen–oxygen single bond, $D(O—O) = 146$ kJ/mol. We will consider the variations in bond enthalpy for double and triple bonds in more detail in Chapter 8.

Bond Enthalpies and the Enthalpies of Reactions

Because enthalpy is a state function, we can use average bond enthalpies to estimate the enthalpies of reactions in which bonds are broken and new bonds are formed. This procedure allows us to estimate quickly whether a given reaction will be endothermic

TABLE 5.4 Average Bond Enthalpies (kJ/mol)

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C═C	614	N—O	201	O═O	495	Cl—F	253
C—N	293	N—F	272	O—F	190	Cl—Cl	242
C—O	358	N—Cl	200	O—Cl	203		
C═O	799	N—Br	243	O—I	234	Br—F	237
C—F	485					Br—Cl	218
C—Cl	328	H—H	436			Br—Br	193
C—Br	276	H—F	567				
C—I	240	H—Cl	431			I—Cl	208
		H—Br	366			I—Br	175
		H—I	299			I—I	151

($\Delta H > 0$) or exothermic ($\Delta H < 0$), even if we do not know ΔH_f° for all of the species involved.

Our strategy for estimating reaction enthalpies is a straightforward application of Hess's law. We use the fact that breaking bonds is always endothermic and forming bonds is always exothermic. We therefore imagine that the reaction occurs in two steps:

1. We supply enough energy to break those bonds in the reactants that are not present in the products. The enthalpy of the system is increased by the sum of the bond enthalpies of the bonds that are broken.
2. We form the bonds in the products that were not present in the reactants. This step releases energy and therefore lowers the enthalpy of the system by the sum of the bond enthalpies of the bonds that are formed.

The enthalpy of the reaction, ΔH_{rxn}, is estimated as the sum of the bond enthalpies of the bonds broken minus the sum of the bond enthalpies of the bonds formed:

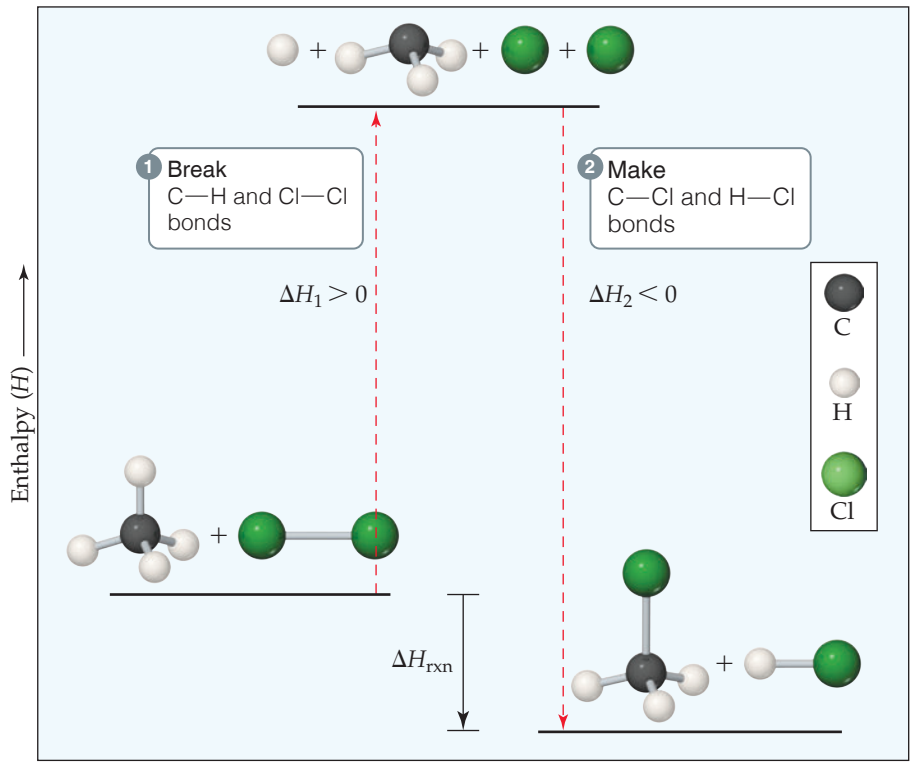
$$\Delta H_{rxn} = \sum \text{(bond enthalpies of bonds broken)} - \sum \text{(bond enthalpies of bonds formed)} \quad [5.32]$$

If the total enthalpy of the broken bonds is larger, the reaction is endothermic ($\Delta H_{rxn} > 0$); if the total enthalpy of the newly formed bonds is larger, the reaction is exothermic ($\Delta H_{rxn} < 0$).

Consider for example, the gas-phase reaction between methane, CH_4, and chlorine to produce chloromethane, CH_3Cl, and hydrogen chloride, HCl:

$$H{-}CH_3(g) + Cl{-}Cl(g) \longrightarrow Cl{-}CH_3(g) + H{-}Cl(g) \qquad \Delta H_{rxn} = ? \quad [5.33]$$

Go Figure Is this reaction exothermic or endothermic?



▲ **Figure 5.24 Using bond enthalpies to estimate ΔH_{rxn}.** Average bond enthalpies are used to estimate ΔH_{rxn} for the reaction of methane with chlorine to make methyl chloride and hydrogen chloride.

Our two-step procedure is outlined in **Figure 5.24**. We note that the following bonds are broken and formed:

Bonds broken: 1 mol C—H, 1 mol Cl—Cl

Bonds formed: 1 mole C—Cl, 1 mol H—Cl

We first supply enough energy to break the C—H and Cl—Cl bonds, which raises the enthalpy of the system (indicated as $\Delta H_1 > 0$ in Figure 5.24). We then form the C—Cl and H—Cl bonds, which release energy and lower the enthalpy of the system ($\Delta H_2 < 0$ in Figure 5.24). We then use Equation 5.32 to estimate the enthalpy of the reaction:

$$\Delta H_{rxn} = [D(\text{C—H}) + D(\text{Cl—Cl})] - [D(\text{C—Cl}) + D(\text{H—Cl})]$$

$$\Delta H_{rxn} = (413\ \text{kJ} + 242\ \text{kJ}) - (328\ \text{kJ} + 431\ \text{kJ}) = -104\ \text{kJ}$$

The reaction is exothermic because the bonds in the products are stronger than the bond in the reactants.

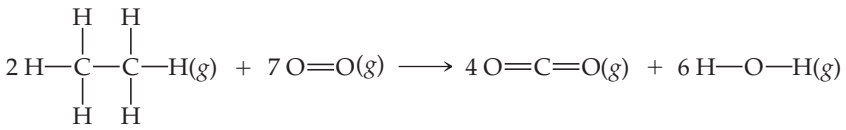
Typically, bond enthalpies are used to estimate ΔH_{rxn} only if the needed ΔH_f° values are not readily available. For the preceding reaction, we cannot calculate ΔH_{rxn} from ΔH_f° values and Hess's law because ΔH_f° for $CH_3Cl(g)$ is not given in Appendix C. If we obtain the value of ΔH_f° for $CH_3Cl(g)$ from another source and use Equation 5.31, we find that $\Delta H_{rxn} = -99.8$ kJ for the reaction in Equation 5.33. The two values are slightly different because bond enthalpies are averaged over many compounds, but the use of average bond enthalpies provides a reasonably accurate estimate of the actual reaction enthalpy change.

It is important to remember that bond enthalpies are derived for gaseous molecules. In solids, liquids, and solutions, intermolecular forces between different molecules must also be taken into account. We will examine the strengths of those forces in detail in Chapter 11, but for now it is sufficient to remember that bond enthalpies cannot be used to accurately estimate the enthalpies of reactions containing solids, liquids, or solutions.

Sample Exercise 5.13

Estimating Reaction Enthalpies from Bond Enthalpies

Use Table 5.4 to estimate ΔH for the following combustion reaction.



SOLUTION

Analyze We are asked to use average bond enthalpies to estimate the enthalpy change for a chemical reaction.

Plan Energy is required to break twelve C—H bonds and two C—C bonds in the two molecules of C_2H_6, and seven O=O bonds in the seven O_2 molecules. Energy is released by forming eight C=O bonds, two per molecule of CO_2, and twelve O—H bonds, two per H_2O molecule.

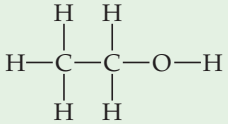
Solve Using Equation 5.32 and data from Table 5.4, we have

$$\begin{aligned}\Delta H &= [12D(\text{C—H}) + 2D(\text{C—C}) + 7D(\text{O=O})] \\ &\quad - [8D(\text{C=O}) + 12D(\text{O—H})] \\ &= [12(413\ \text{kJ}) + 2(348\ \text{kJ}) + 7(495\ \text{kJ})] \\ &\quad - [8(799\ \text{kJ}) + 12(463\ \text{kJ})] \\ &= 9117\ \text{kJ} - 11948\ \text{kJ} \\ &= -2831\ \text{kJ}\end{aligned}$$

Check This estimate can be compared with the value of −2856 kJ calculated from more accurate thermochemical data; the agreement is good.

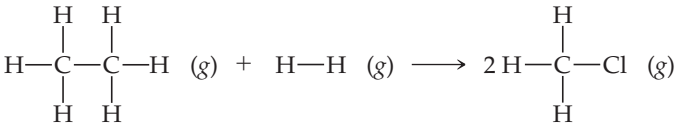
Practice Exercise

Use the average bond enthalpies in Table 5.4 to estimate ΔH for the combustion of ethanol.



Self-Assessment Exercise

5.40 Use average bond enthalpies from Table 5.4 to estimate the enthalpy change in the reaction:

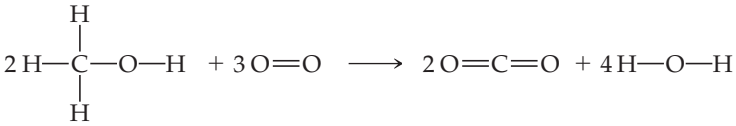


(a) $\Delta H = -42$ kJ
(b) $\Delta H = +42$ kJ
(c) $\Delta H = +371$ kJ

Exercises

5.41 Without doing any calculations, predict the sign of ΔH for each of the following reactions:
(a) $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$
(b) $2\,H(g) \longrightarrow H_2(g)$
(c) $Na(g) \longrightarrow Na^+(g) + e^-$
(d) $I_2(s) \longrightarrow I_2(l)$

5.42 Use bond enthalpies in Table 5.4 to estimate ΔH for each of the following reactions:
(a) $H{-}H(g) + Br{-}Br(g) \longrightarrow 2\,H{-}Br(g)$
(b)



5.43 (**a**) Use enthalpies of formation given in Appendix C to calculate ΔH for the reaction $Br_2(g) \longrightarrow 2\,Br(g)$, and use this value to estimate the bond enthalpy $D(Br{-}Br)$. (**b**) How large is the difference between the value calculated in part (a) and the value given in Table 5.4?

5.44 Consider the reaction $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$. (**a**) Use the bond enthalpies in Table 5.4 to estimate ΔH for this reaction, ignoring the fact that water is in the liquid state. (**b**) Without doing a calculation, predict whether your estimate in part (a) is more negative or less negative than the true reaction enthalpy. (**c**) Use the enthalpies of formation in Appendix C to determine the true reaction enthalpy.

Answers to Self-Assessment Exercise

5.40 (a)

5.9 | Foods and Fuels



Everything we do is connected in one way or another with energy. Without energy, modern society could not function and life itself would not exist. The issues surrounding energy—its sources, production, distribution, consumption, and environmental impact—pervade conversations in science, politics, economics, and public policy.

At the end of this section, you should have

- An insight into global energy issues

Most chemical reactions used for the production of heat are combustion reactions. The energy released when one gram of any substance is combusted is the **fuel value** of the substance. The fuel value of any food or fuel can be measured by calorimetry.

Foods

Most of the energy our bodies need comes from carbohydrates and fats. The carbohydrates known as starches are decomposed in the intestines into glucose, $C_6H_{12}O_6$. Glucose is soluble in blood, and in the human body it is known as blood sugar. It is transported by the blood to cells where it reacts with O_2 in a series of steps, eventually producing $CO_2(g)$, $H_2O(l)$, and energy:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H^\circ = -2803\ \text{kJ}$$

Because carbohydrates break down rapidly, their energy is quickly supplied to the body. However, the body stores only a very small amount of carbohydrates. The average fuel value of carbohydrates is 17 kJ/g. Although fuel values represent the heat released in a combustion reaction, by convention fuel values are reported as positive numbers.

Like carbohydrates, fats produce CO_2 and H_2O when metabolized. The reaction of tristearin, $C_{57}H_{110}O_6$, a typical fat, is

$$2\,C_{57}H_{110}O_6(s) + 163\,O_2(g) \longrightarrow 114\,CO_2(g) + 110\,H_2O(l) \qquad \Delta H^\circ = -71{,}609\ \text{kJ}$$

The body uses the chemical energy from foods to maintain body temperature (see the "Chemistry and Life" box in Section 5.5), to contract muscles, and to construct and repair tissues. Any excess energy is stored as fats. Fats are well suited to serve as the body's energy reserve for at least two reasons: (1) They are insoluble in water, which facilitates storage in the body, and (2) they produce more energy per gram than either proteins or carbohydrates, which makes them efficient energy sources on a mass basis. The average fuel value of fats is 38 kJ/g.

The combustion of carbohydrates and fats in a bomb calorimeter gives the same products as when they are metabolized in the body. The metabolism of proteins produces less energy than combustion in a calorimeter because the products are different. Proteins contain nitrogen, which is released in the bomb calorimeter as N_2. In the body this nitrogen ends up mainly as urea, $(NH_2)_2CO$. Proteins are used by the body mainly as building materials for organ walls, skin, hair, muscle, and so forth. On average, the metabolism of proteins produces 17 kJ/g, the same as for carbohydrates.

Fuel values for some common foods are shown in **Table 5.5**. Labels on packaged foods show the amounts of carbohydrate, fat, and protein contained in an average serving, as well as the amount of energy supplied by a serving (**Figure 5.25**).

The amount of energy our bodies require varies considerably, depending on such factors as weight, age, and muscular activity. About 100 kJ per kilogram of body mass per day is required to keep the body functioning at a minimal level. An average 70 kg person expends about 800 kJ/h when doing light work, and strenuous activity often requires 2000 kJ/h or more. When the fuel value, or caloric content, of the food we ingest exceeds the energy we expend, our body stores the surplus as fat.

Go Figure

Which value would change most if this label were for skim milk instead of whole milk: grams of fat, grams of total carbohydrate, or grams of protein?

Vitamin D Milk

Nutrition Facts

Serving Size 1 cup (236mL)

Amount Per Serving	
Calories 150	Calories from Fat 70
	% Daily Value*
Total Fat 8g	12%
Saturated Fat 5g	25%
Trans Fat 0g	
Cholesterol 35mg	11%
Sodium 125mg	5%
Total Carbohydrate 12g	4%
Dietary Fiber 0g	0%
Sugars 12g	
Protein 8g	
Vitamin A 6% •	Vitamin C 4%
Calcium 30% •	Iron 0%
Vitamin D 25%	

* Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.

	Calories:	2,000	2,500
Total fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2,400g	2,400g
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

Ingredients: Grade A Pasteurized Milk, Vitamin D3.



▲ **Figure 5.25** Nutrition label for whole milk.

TABLE 5.5 Compositions and Fuel Values of Some Common Foods

	Approximate Composition (% by Mass)			Fuel Value
	Carbohydrate	Fat	Protein	kJ/g
Carbohydrate	100	—	—	17
Fat	—	100	—	38
Protein	—	—	100	17
Apples	13	0.5	0.4	2.5
Beer[a]	1.2	—	0.3	1.8
Bread	52	3	9	12
Cheese	4	37	28	20
Eggs	0.7	10	13	6.0
Fudge	81	11	2	18
Green beans	7.0	—	1.9	1.5
Hamburger	—	30	22	15
Milk (whole)	5.0	4.0	3.3	3.0
Peanuts	22	39	26	23

[a] Beer typically contains 3.5% ethanol, which has fuel value.

Sample Exercise 5.14

Estimating the Fuel Value of a Food from Its Composition

(**a**) A 28 g serving of a popular breakfast cereal served with 120 mL of skim milk provides 8 g protein, 26 g carbohydrates, and 2 g fat. Using the average fuel values of these substances, estimate the fuel value of this serving. (**b**) A person of average weight uses about 420 KJ/km when running or jogging. How many servings of this cereal provide the fuel value requirements to run 3 km?

SOLUTION

Analyze (**a**) The fuel value of the serving will be the sum of the fuel values of the protein, carbohydrates, and fat. (**b**) Here we are faced with the reverse problem, calculating the quantity of food that provides a specific fuel value.

Plan (**a**) We are given the masses of the protein, carbohydrates, and fat contained in a serving. We can use the data in Table 5.4 to convert these masses to their fuel values, which we can sum to get the total fuel value. (**b**) The problem statement provides a conversion factor between Calories and kilometers. The answer to part (a) provides us with a conversion factor between servings and Calories.

Solve

(**a**)

$$(8\ \text{g}\ \cancel{\text{protein}})\left(\frac{17\ \text{kJ}}{1\ \text{g}\ \cancel{\text{protein}}}\right) + (26\ \text{g}\ \cancel{\text{carbohydrate}})\left(\frac{17\ \text{kJ}}{1\ \text{g}\ \cancel{\text{carbohydrate}}}\right) + (2\ \text{g}\ \cancel{\text{fat}})\left(\frac{38\ \text{kJ}}{1\ \text{g}\ \cancel{\text{fat}}}\right) = 650\ \text{kJ (to two significant figures)}$$

(**b**) We can use these factors in a straightforward dimensional analysis to determine the number of servings needed, rounded to the nearest whole number:

$$\text{Servings} = (3\ \cancel{\text{km}})\left(\frac{420\ \cancel{\text{kJ}}}{1\ \cancel{\text{km}}}\right)\left(\frac{1\ \text{serving}}{650\ \cancel{\text{kJ}}}\right) = 2\ \text{servings}$$

Practice Exercise

(**a**) Dry red beans contain 62% carbohydrate, 22% protein, and 1.5% fat. Estimate the fuel value of these beans. (**b**) During a very light activity, such as reading or watching television, the average adult expends about 7 kJ/min. How many minutes of such activity can be sustained by the energy provided by a serving of chicken noodle soup containing 13 g protein, 15 g carbohydrate, and 5 g fat?

TABLE 5.6 Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (Mass %)			
	C	H	O	Fuel Value (kJ/g)
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142

Fuels

During the complete combustion of fuels, carbon is converted to CO_2 and hydrogen is converted to H_2O, both of which have large negative enthalpies of formation. Consequently, the greater the percentage of carbon and hydrogen in a fuel, the higher its fuel value. In Table 5.6, for example, compare the compositions and fuel values of bituminous coal and wood. The coal has a higher fuel value because of its greater carbon content.

Coal, petroleum, and natural gas, which are the world's major sources of energy, are known as **fossil fuels**. All have formed over millions of years from the decomposition of plants and animals and are being depleted far more rapidly than they are being formed.

Natural gas consists of gaseous hydrocarbons, compounds of hydrogen and carbon. It contains primarily methane (CH_4), with small amounts of ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). We determined the fuel value of propane in Sample Exercise 5.10. Natural gas burns with far fewer by-products and produces less CO_2 than either petroleum or coal. **Petroleum** is a liquid composed of hundreds of compounds, most of which are hydrocarbons, with the remainder being chiefly organic compounds containing sulfur, nitrogen, or oxygen. **Coal**, which is solid, contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, or nitrogen. Coal is the most abundant fossil fuel; current reserves are projected to last for well over 100 years at current consumption rates. However, the use of coal presents a number of problems.

Coal is a complex mixture of substances, and it contains components that cause air pollution. When coal is combusted, the sulfur it contains is converted mainly to sulfur dioxide, SO_2, a troublesome air pollutant. Because coal is a solid, recovery from its underground deposits is expensive and often dangerous. Furthermore, coal deposits are not always close to locations of high-energy use, so there are often substantial shipping costs.

Fossil fuels release energy in combustion reactions, which ideally produce only CO_2 and H_2O. The production of CO_2 has become a major issue that involves science and public policy because of concerns that increasing concentrations of atmospheric CO_2 are causing global climate changes. We will discuss the environmental aspects of atmospheric CO_2 in Chapter 18.

Other Energy Sources

Nuclear energy is the energy released in either the fission (splitting) or the fusion (combining) of atomic nuclei. Nuclear energy is, in principle, free of the polluting emissions that are a major problem with fossil fuels. However, nuclear power plants produce radioactive waste products, and their use has therefore been controversial. We will discuss issues related to the production of nuclear energy in Chapter 21.

Fossil fuels and nuclear energy are *nonrenewable* sources of energy—they are limited resources that we are consuming at a much greater rate than they can be regenerated. Eventually these fuels will be expended, although estimates vary greatly as to when this will occur. Because nonrenewable energy sources will eventually be used up, a great deal of research is being conducted on **renewable energy sources**, sources that are essentially

inexhaustible. Renewable energy sources include *solar energy* from the Sun, *wind energy* harnessed by windmills, *geothermal energy* from the heat stored inside Earth, *hydroelectric energy* from flowing rivers, and *biomass energy* from crops and biological waste matter.

Fulfilling our future energy needs will depend on developing technology to harness solar energy with greater efficiency. Solar energy is the world's largest energy source. On a clear day about 1 kJ of solar energy reaches each square meter of Earth's surface every second. Harnessing this energy is difficult because it is dilute (that is, distributed over a wide area) and varies with time of day and weather conditions. The effective use of solar energy will depend on the development of some means of storing and distributing it. One practical way to do this is to use the Sun's energy to drive an endothermic chemical process that can be later reversed to release heat. One such reaction is

$$CH_4(g) + H_2O(g) + \text{heat} \longrightarrow CO(g) + 3\,H_2(g)$$

This reaction proceeds in the forward direction at high temperatures, which can be obtained in a solar furnace. The CO and H_2 formed in the reaction could then be stored and allowed to react later, with the heat released being put to useful work.

CHEMISTRY PUT TO WORK The Scientific and Political Challenges of Biofuels*

One of the biggest challenges facing us in the twenty-first century is production of abundant sources of energy, both food and fuels. At the end of 2020, the global population was estimated to be 7.8 billion people, and growing at a rate of about 750 million per decade. A growing world population puts greater demands on the global food supply, especially in Asia and Africa, which together make up more than 75% of the world population.

A growing population also increases demands on the production of fuels for transportation, industry, electricity, heating, and cooling. As populous countries such as China and India have modernized, their per capita consumption of energy has increased significantly. In China, for instance, per capita energy consumption roughly doubled between 1990 and 2010.

Global fuel energy consumption in 2012 was more than 5×10^{17} kJ, a staggeringly large number. More than 80% of current energy requirements comes from combustion of nonrenewable fossil fuels, especially coal and petroleum. The exploration of new fossil fuel sources often involves environmentally sensitive regions, making the search for new supplies of fossil fuels a major political and economic issue.

The global importance of petroleum is in large part because it provides liquid fuels, such as gasoline, that are critical to supplying transportation needs. One of the most promising—but controversial—alternatives to petroleum-based fuels is *biofuels*, liquid fuels derived from biological matter. The most common approach to producing biofuels is to transform plant sugars and other carbohydrates into combustible liquids.

The most commonly produced biofuel is *bioethanol*, which is ethanol (C_2H_5OH) made from fermentation of plant carbohydrates. The fuel value of ethanol is about two-thirds that of gasoline and is therefore comparable to that of coal (Table 5.6). The United States and Brazil dominate bioethanol production, together supplying 85% of the world's total.

In the United States, nearly all the bioethanol currently produced is made from yellow feed corn. Glucose ($C_6H_{12}O_6$) in the corn is converted to ethanol and CO_2:

$$C_6H_{12}O_6(s) \longrightarrow 2\,C_2H_5OH(l) + 2\,CO_2(g) \qquad \Delta H = 15.8\ \text{kJ}$$

Notice that this reaction is *anaerobic*—it does not involve $O_2(g)$—and that the enthalpy change is positive and much smaller in magnitude than for most combustion reactions. Other carbohydrates can be converted to ethanol in similar fashion.

Producing bioethanol from corn is controversial for two main reasons. First, growing and transporting corn are both energy-intensive processes, and growing it requires the use of fertilizers. It is estimated that the *energy return* on corn-based bioethanol is only 34%—that is, for each 1.00 J of energy expended to produce the corn, 1.34 J of energy is produced in the form of bioethanol. Second, the use of corn as a starting material for making bioethanol competes with its use as an important component of the food chain (the so-called food versus fuel debate).

Much current research focuses on the formation of bioethanol from *cellulosic* plants, plants that contain the complex carbohydrate cellulose. Cellulose is not readily metabolized and so does not compete with the food supply. However, the chemistry for converting cellulose to ethanol is much more complex than that for converting corn. Cellulosic bioethanol could be produced from very fast-growing nonfood plants, such as prairie grasses and switchgrass, which readily renew themselves without the use of fertilizers.

The Brazilian bioethanol industry uses sugarcane as its feedstock (**Figure 5.26**). Sugarcane grows much faster than corn and without the need for fertilizers or tending. Because of these differences, the energy



▲ **Figure 5.26** **Sugarcane can be converted to a sustainable bioethanol product.**

* Data from the *Annual Energy Outlook 2012*, U.S. Energy Information Administration.

return for sugarcane is much higher than the energy return for corn. It is estimated that for each 1.0 J of energy expended in growing and processing sugarcane, 8.0 J of energy is produced as bioethanol.

Other biofuels that are also becoming a major part of the world economy include *biodiesel*, a substitute for petroleum-derived diesel fuel. Biodiesel is typically produced from crops that have a high oil content, such as soybeans and canola. It can also be produced from animal fats and waste vegetable oil from the food and restaurant industry.

Related Exercise: 5.122

Plants utilize solar energy in *photosynthesis*, the reaction in which the energy of sunlight is used to convert CO_2 and H_2O into carbohydrates and O_2:

$$6\,CO_2(g) + 6\,H_2O(l) + \text{sunlight} \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g) \qquad [5.34]$$

Photosynthesis is an important part of Earth's ecosystem because it replenishes atmospheric O_2, produces an energy-rich molecule that can be used as fuel, and consumes some atmospheric CO_2.

Perhaps the most direct way to use the Sun's energy is to convert it directly into electricity in photovoltaic devices, or *solar cells*, which we mentioned at the beginning of this chapter. The efficiencies of such devices have increased dramatically during the past few years. Technological advances have led to solar panels that last longer and produce electricity with greater efficiency at steadily decreasing unit cost. Indeed, the future of solar energy is, like the Sun itself, very bright.

SAMPLE INTEGRATIVE EXERCISE

Putting Concepts Together

Trinitroglycerin, $C_3H_5N_3O_9$ (usually referred to simply as nitroglycerin), has been widely used as an explosive. Alfred Nobel used it to make dynamite in 1866. Rather surprisingly, it also is used as a medication, to relieve angina (chest pains resulting from partially blocked arteries to the heart) by dilating the blood vessels. At 100 kPa pressure and 25 °C, the enthalpy of decomposition of trinitroglycerin to form nitrogen gas, carbon dioxide gas, liquid water, and oxygen gas is −1541.4 kJ/mol.

(**a**) Write a balanced chemical equation for the decomposition of trinitroglycerin.

(**b**) Calculate the standard heat of formation of trinitroglycerin.

(**c**) A standard dose of trinitroglycerin for relief of angina is 0.60 mg. If the sample is eventually oxidized in the body (not explosively, though!) to nitrogen gas, carbon dioxide gas, and liquid water, what energy is released?

(**d**) One common form of trinitroglycerin melts at about 3 °C. From this information and the formula for the substance, would you expect it to be a molecular or ionic compound? Explain.

(**e**) Describe the various conversions of forms of energy when trinitroglycerin is used as an explosive to break rockfaces in highway construction.

SOLUTION

(**a**) The general form of the equation we must balance is

$$C_3H_5N_3O_9(l) \longrightarrow N_2(g) + CO_2(g) + H_2O(l) + O_2(g)$$

We go about balancing in the usual way. To obtain an even number of nitrogen atoms on the left, we multiply the formula for $C_3H_5N_3O_9$ by 2, which gives us 3 mol of N_2, 6 mol of CO_2 and 5 mol of H_2O. Everything is then balanced except for oxygen. We have an odd number of oxygen atoms on the right. We can balance the oxygen by using the coefficient $\frac{1}{2}$ for O_2 on the right:

$$2\,C_3H_5N_3O_9(l) \longrightarrow 3\,N_2(g) + 6\,CO_2(g) + 5\,H_2O(l) + \tfrac{1}{2}\,O_2(g)$$

We multiply through by 2 to convert all coefficients to whole numbers:

$$4\,C_3H_5N_3O_9(l) \longrightarrow 6\,N_2(g) + 12\,CO_2(g) + 10\,H_2O(l) + O_2(g)$$

(At the temperature of the explosion, water is a gas rather than a liquid. The rapid expansion of the gaseous products creates the force of an explosion.)

(**b**) We can obtain the standard enthalpy of formation of nitroglycerin by using the heat of decomposition of trinitroglycerin together with the standard enthalpies of formation of the other substances in the decomposition equation:

$$4\,C_3H_5N_3O_9(l) \longrightarrow 6\,N_2(g) + 12\,CO_2(g) + 10\,H_2O(l) + O_2(g)$$

The enthalpy change for this decomposition is $4(-1541.4\text{ kJ}) = -6165.6$ kJ. [We need to multiply by 4 because there are 4 mol of $C_3H_5N_3O_9(l)$ in the balanced equation.]

This enthalpy change equals the sum of the heats of formation of the products minus the heats of formation of the reactants, each multiplied by its coefficient in the balanced equation:

$$-6165.6\text{ kJ} = 6\Delta H_f^\circ[N_2(g)] + 12\Delta H_f^\circ[CO_2(g)] + 10\Delta H_f^\circ[H_2O(l)] + \Delta H_f^\circ[O_2(g)] - 4\Delta H_f^\circ[C_3H_5N_3O_9(l)]$$

The ΔH_f° values for $N_2(g)$ and $O_2(g)$ are zero, by definition. Using the values for $H_2O(l)$ and $CO_2(g)$ from Table 5.3 or Appendix C, we have

$$-6165.6\text{ kJ} = 12(-393.5\text{ kJ}) + 10(-285.8\text{ kJ}) - 4\Delta H_f^\circ[C_3H_5N_3O_9(l)]$$

$$\Delta H_f^\circ[C_3H_5N_3O_9(l)] = -353.6\text{ kJ/mol}$$

(**c**) Converting 0.60 mg $C_3H_5N_3O_9(l)$ to moles and using the fact that the decomposition of 1 mol of $C_3H_5N_3O_9(l)$ yields 1541.4 kJ we have:

$$(0.60 \times 10^{-3}\text{ g } C_3H_5N_3O_9)\left(\frac{1\text{ mol } C_3H_5N_3O_9}{227\text{ g } C_3H_5N_3O_9}\right)\left(\frac{1541.4\text{ kJ}}{1\text{ mol } C_3H_5N_3O_9}\right) = 4.1 \times 10^{-3}\text{ kJ} = 4.1\text{ J}$$

Continued

(**d**) Because trinitroglycerin melts below room temperature, we expect that it is a molecular compound. With few exceptions, ionic substances are generally hard, crystalline materials that melt at high temperatures. Also, the molecular formula suggests that it is a molecular substance because all of its constituent elements are nonmetals.

(**e**) The energy stored in trinitroglycerin is chemical potential energy. When the substance reacts explosively, it forms carbon dioxide, water, and nitrogen gas, which are of lower potential energy. In the course of the chemical transformation, energy is released in the form of heat; the gaseous reaction products are very hot. This high heat energy is transferred to the surroundings. Work is done as the gases expand against the surroundings, moving the solid materials and imparting kinetic energy to them. For example, a chunk of rock might be impelled upward. It has been given kinetic energy by transfer of energy from the hot, expanding gases. As the rock rises, its kinetic energy is transformed into potential energy. Eventually, it again acquires kinetic energy as it falls to Earth. When it strikes Earth, its kinetic energy is converted largely to thermal energy, though some work may be done on the surroundings as well.

Exercises

5.45 (**a**) What is meant by the term *fuel value*? (**b**) Which is a greater source of energy as food, 5 g of fat or 9 g of carbohydrate? (**c**) The metabolism of glucose produces $CO_2(g)$ and $H_2O(l)$. How does the human body expel these reaction products?

5.46 (**a**) A serving of a particular ready-to-serve brown & wild rice meal contains 4.5 g fat, 42 g carbohydrate, and 4.0 g protein. Estimate the number of calories in a serving. (**b**) According to its nutrition label, the same meal also contains 140 mg of potassium ions. Do you think the potassium contributes to the caloric content of the food?

5.47 The heat of combustion of fructose, $C_6H_{12}O_6$, is -2812 kJ/mol. If a fresh golden delicious apple weighing 120 g contains 16.0 g of fructose, what caloric content does the fructose contribute to the apple?

5.48 The standard enthalpies of formation of gaseous propyne (C_3H_4), propene (C_3H_6), and propane (C_3H_8) are $+185.4$, $+20.4$, and -103.8 kJ/mol, respectively. (**a**) Calculate the heat evolved per mole on combustion of each substance to yield $CO_2(g)$ and $H_2O(g)$. (**b**) Calculate the heat evolved on combustion of 1 kg of each substance. (**c**) Which is the most efficient fuel in terms of heat evolved per unit mass?

Chapter Summary and Key Terms

CHEMICAL ENERGY (INTRODUCTION AND SECTION 5.1) **Thermodynamics** is the study of energy and its transformations. In this chapter we have focused on **thermochemistry**, the transformations of energy—especially heat—during chemical reactions.

An object can possess energy in two forms: (1) **kinetic energy**, which is the energy due to the motion of the object, and (2) **potential energy**, which is the energy that an object possesses by virtue of its position relative to other objects. An electron in motion near a proton has kinetic energy because of its motion and potential energy because of its electrostatic attraction to the proton.

Chemical energy originates largely from electrostatic interactions at the atomic level. Energy must be supplied to break chemical bonds leading to an increase in potential energy. Conversely, energy is released when chemical bonds form as the potential energy decreases.

THE FIRST LAW OF THERMODYNAMICS (SECTION 5.2) When we study thermodynamic properties, we define a specific amount of matter as the **system**. Everything outside the system is the **surroundings**. When we study a chemical reaction, the system is generally the reactants and products. A closed system can exchange energy, but not matter, with the surroundings. The **internal energy** of a system is the sum of all the kinetic and potential energies of its component parts. The internal energy of a system can change because of energy transferred between the system and the surroundings.

According to the **first law of thermodynamics**, the change in the internal energy of a system, ΔE, is the sum of the heat, q, transferred into or out of the system and the work, w, done on or by the system: $\Delta E = q + w$. Both q and w have a sign that indicates the direction of energy transfer. When heat is transferred from the surroundings to the system, $q > 0$. Likewise, when the surroundings do work on the system, $w > 0$. In an **endothermic** process the system absorbs heat from the surroundings; in an **exothermic** process the system releases heat to the surroundings.

The internal energy, E, is a **state function**. The value of any state function depends only on the state or condition of the system and not on the details of how it came to be in that state. Heat, q, and work, w, are not state functions; their values depend on the particular way by which a system changes its state.

ENTHALPY (SECTIONS 5.3 AND 5.4) When a gas is produced or consumed in a chemical reaction occurring at constant pressure, the system may perform **pressure–volume (P–V) work** against the prevailing pressure of the surroundings. For this reason, we define a new state function called **enthalpy**, H, which is related to energy: $H = E + PV$. In systems where only pressure–volume work is involved, the change in the enthalpy of a system, ΔH, equals the heat gained or lost by the system at constant pressure: $\Delta H = q_p$ (the subscript P denotes constant pressure). For an endothermic process, $\Delta H > 0$; for an exothermic process, $\Delta H < 0$.

In a chemical process, the **enthalpy of reaction** is the enthalpy of the products minus the enthalpy of the reactants: $\Delta H_{rxn} = H(\text{products}) - H(\text{reactants})$. Enthalpies of reaction follow some simple rules: (1) The enthalpy of reaction is proportional to the amount of reactant that reacts. (2) Reversing a reaction changes the sign of ΔH. (3) The enthalpy of reaction depends on the physical states of the reactants and products.

CALORIMETRY (SECTION 5.5) The amount of heat transferred between the system and the surroundings is measured experimentally by **calorimetry**. A **calorimeter** measures the temperature change accompanying a process. The temperature change of a calorimeter depends on its **heat capacity**, the amount of heat required to raise its temperature by 1 K. The heat capacity for one mole of a pure substance is called its **molar heat capacity**; for one gram of the substance, we use the term **specific heat**. Water has a very high specific heat, 4.18 J/g K. The amount of heat, q, absorbed by a substance is the product of its specific heat (c), its mass, and its temperature change: $q = c \times m \times \Delta T$.

If a calorimetry experiment is carried out under a constant pressure, the heat transferred provides a direct measure of the enthalpy change of the reaction. Constant-volume calorimetry is carried out in a vessel of fixed volume called a **bomb calorimeter**. The heat transferred under constant-volume conditions is equal to ΔE. Corrections can be applied to ΔE values to yield ΔH.

HESS'S LAW (SECTION 5.6) Because enthalpy is a state function, ΔH depends only on the initial and final states of the system. Thus, the enthalpy change of a process is the same whether the process is carried out in one step or in a series of steps. **Hess's law** states that if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the steps. We can therefore calculate ΔH for any process, as long as we can write the process as a series of steps for which ΔH is known.

ENTHALPIES OF FORMATION (SECTION 5.7) The **enthalpy of formation**, ΔH_f, of a substance is the enthalpy change for the reaction in which the substance is formed from its constituent elements. Usually, enthalpies are tabulated for reactions where reactants and products are in their *standard states*. The standard state of a substance is its pure, most stable form at 100 kPa and the temperature of interest (usually 298 K). Thus, the **standard enthalpy change** of a reaction, ΔH°, is the enthalpy change when all reactants and products are in their standard states. The **standard enthalpy of formation**, ΔH_f°, of a substance is the change in enthalpy for the reaction that forms one mole of the substance from its elements in their standard states. For any element in its standard state, $\Delta H_f^\circ = 0$.

The standard enthalpy change for any reaction can be readily calculated from the standard enthalpies of formation of the reactants and products in the reaction:

$$\Delta H^\circ_{\text{rxn}} = \Sigma n \Delta H_f^\circ(\text{products}) - \Sigma m \Delta H_f^\circ(\text{reactants})$$

BOND ENTHALPIES (SECTION 5.8) The strength of a covalent bond is measured by its bond enthalpy, which is the molar enthalpy change required to break a particular bond. Average bond enthalpies can be determined for a wide variety of covalent bonds. We can estimate the enthalpy changes during chemical reactions involving gaseous substances by adding the average bond enthalpies of the bonds that are broken and subtracting the average bond enthalpies of the bonds that are formed. When the energy needed to break bonds is larger than the energy released by forming bonds the reaction enthalpy is positive; when the opposite situation holds the reaction enthalpy is negative.

FOODS AND FUELS (SECTION 5.9) The **fuel value** of a substance is the heat released when one gram of the substance is combusted. Different types of foods have different fuel values and differing abilities to be stored in the body. The most common fuels are hydrocarbons that are found as **fossil fuels**, such as **natural gas**, **petroleum**, and **coal**. **Renewable energy sources** include solar energy, wind energy, biomass, and hydroelectric energy. Nuclear power does not utilize fossil fuels but does create controversial waste-disposal problems.

Learning Outcomes After studying this chapter, you should be able to:

- Describe the changes in potential energy that accompany the formation and breaking of chemical bonds. (Section 5.1) *Related Exercises: 5.3, 5.64*
- Distinguish between the system and the surroundings in thermodynamics. (Section 5.2) *Related Exercises: 5.6, 5.66*
- Calculate internal energy from heat and work and state the sign conventions of these quantities. (Section 5.2) *Related Exercises: 5.8, 5.9, 5.68, 5.69*
- Explain the concept of a state function and give examples. (Section 5.2) *Related Exercises: 5.10, 5.70*
- Calculate ΔH from ΔE and $P\Delta V$ (Section 5.3) *Related Exercises: 5.15, 5.74, 5.75*
- Relate q_p to ΔH and indicate how the signs of q and ΔH relate to whether a process is exothermic or endothermic. (Sections 5.2 and 5.3) *Related Exercises: 5.18, 5.78*
- Use thermochemical equations to relate the amount of heat energy transferred in reactions at constant pressure (ΔH) to the amount of substance involved in the reaction. (Section 5.4) *Related Exercises: 5.19, 5.20, 5.79, 5.80*
- Calculate the heat transferred in a process from temperature measurements together with heat capacities or specific heats (calorimetry). (Section 5.5) *Related Exercises: 5.24, 5.81–5.83*
- Use Hess's law to determine enthalpy changes for reactions. (Section 5.6) *Related Exercises: 5.30, 5.31, 5.88, 5.89*
- Use standard enthalpies of formation to calculate ΔH° for reactions. (Section 5.7) *Related Exercises: 5.34–5.37*
- Use average bond enthalpies to estimate the reaction enthalpies of reactions where all reactants and products are in the gas phase. (Section 5.8) *Related Exercises: 5.41–5.44*

Key Equations

• $w = F \times d$	[5.1]	Relates work to force and distance
• $E_{\text{el}} = \kappa Q_1 Q_2 / d$	[5.2]	Electrostatic potential energy.
• $\Delta E = E_{\text{final}} - E_{\text{initial}}$	[5.3]	The change in internal energy
• $\Delta E = q + w$	[5.4]	Relates the change in internal energy to heat and work (the first law of thermodynamics)
• $H = E + PV$	[5.5]	Defines enthalpy
• $w = -P\Delta V$	[5.7]	The work done by an expanding gas at constant pressure
• $\Delta H = \Delta E + P\Delta V = q_P$	[5.9]	Enthalpy change at constant pressure
• $q = C_s \times m \times \Delta T$	[5.21]	Heat gained or lost based on specific heat, mass, and temperature change

- $q_{rxn} = -C_{cal} \times \Delta T$ [5.23] Heat exchanged between a reaction and calorimeter
- $\Delta H^\circ_{rxn} = \Sigma n \Delta H^\circ_f(\text{products}) - \Sigma m \Delta H^\circ_f(\text{reactants})$ [5.31] Standard enthalpy change of a reaction
- $\Delta H_{rxn} =$ (bond enthalpies of bonds broken) − (bond enthalpies of bonds formed) [5.32] The reaction enthalpy as a function of average bond enthalpies for reactions involving gas-phase molecules.

Exercises

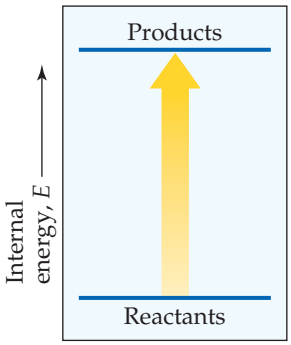
Visualizing Concepts

5.49 Two positively charged spheres, each with a charge of 2.0×10^{-5} C, a mass of 1.0 kg, and separated by a distance of 1.0 cm, are held in place on a frictionless track. (**a**) What is the electrostatic potential energy of this system? (**b**) If the spheres are released, will they move toward or away from each other? (**c**) What speed will each sphere attain as the distance between the spheres approaches infinity? [Section 5.1]

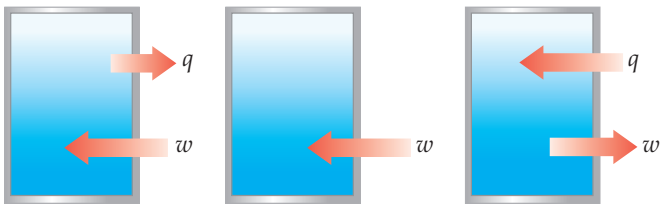
5.50 The accompanying photo shows a pipevine swallowtail caterpillar climbing up a twig. (**a**) As the caterpillar climbs, its potential energy is increasing. What source of energy has been used to effect this change in potential energy? (**b**) If the caterpillar is the system, can you predict the sign of q as the caterpillar climbs? (**c**) Does the caterpillar do work in climbing the twig? Explain. (**d**) Does the amount of work done in climbing a 30-cm section of the twig depend on the speed of the caterpillar's climb? (**e**) Does the change in potential energy depend on the caterpillar's speed of climb? [Section 5.1]



5.51 Consider the accompanying energy diagram. (**a**) Does this diagram represent an increase or decrease in the internal energy of the system? (**b**) What sign is given to ΔE for this process? (**c**) If there is no work associated with the process, is it exothermic or endothermic? [Section 5.2]

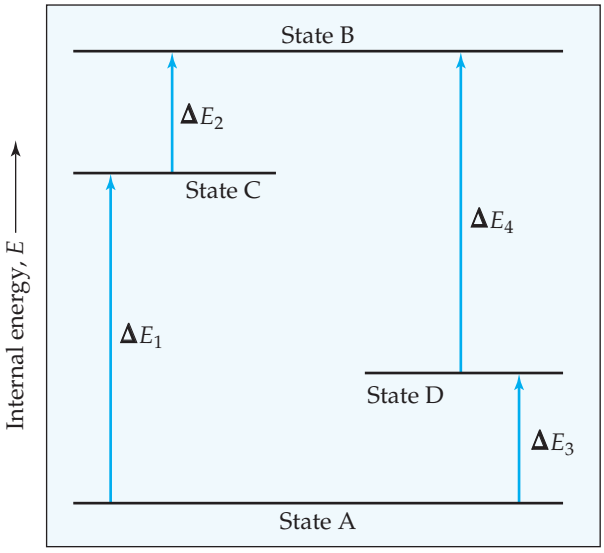


5.52 The contents of the closed box in each of the following illustrations represent a system, and the arrows show the changes to the system during some process. The lengths of the arrows represent the relative magnitudes of q and w. (**a**) Which of these processes is endothermic? (**b**) For which of these processes, if any, is $\Delta E < 0$? (**c**) For which process, if any, does the system experience a net gain in internal energy? [Section 5.2]



5.53 Imagine that you are climbing a mountain. (**a**) Is the distance you travel to the top a state function? (**b**) Is the change in elevation between your base camp and the peak a state function? [Section 5.2]

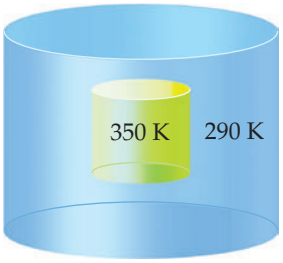
5.54 The diagram shows four states of a system, each with different internal energy, E. (**a**) Which of the states of the system has the greatest internal energy? (**b**) In terms of the ΔE values, write two expressions for the difference in internal energy between State A and State B. (**c**) Write an expression for the difference in energy between State C and State D. (**d**) Suppose there is another state of the system, State E, and its energy relative to State A is $\Delta E = \Delta E_1 + \Delta E_4$. Where would State E be on the diagram? [Section 5.2]



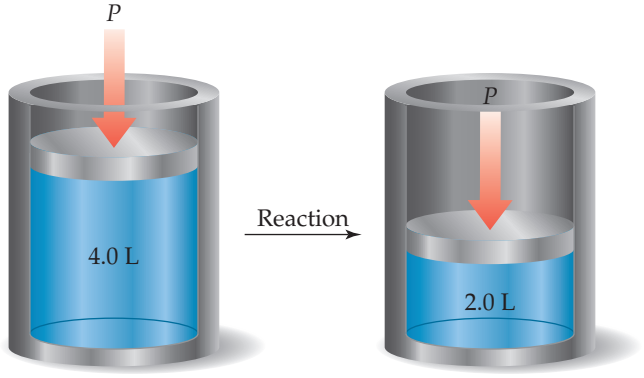
5.55 You may have noticed that when you compress the air in a bicycle pump, the body of the pump gets warmer. (**a**) Assuming the pump and the air in it comprise the system, what is the sign of w when you compress the air? (**b**) What is the sign

of q for this process? (**c**) Based on your answers to parts (a) and (b), can you determine the sign of ΔE for compressing the air in the pump? If not, what would you expect for the sign of ΔE? What is your reasoning? [Section 5.2]

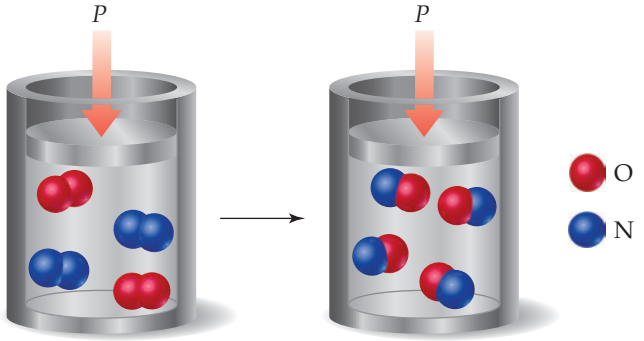
5.56 Imagine a container placed in a tub of water, as depicted in the accompanying diagram. (**a**) If the contents of the container are the system and heat is able to flow through the container walls, what qualitative changes will occur in the temperatures of the system and in its surroundings? From the system's perspective, is the process exothermic or endothermic? (**b**) If neither the volume nor the pressure of the system changes during the process, how is the change in internal energy related to the change in enthalpy? [Sections 5.2 and 5.3]



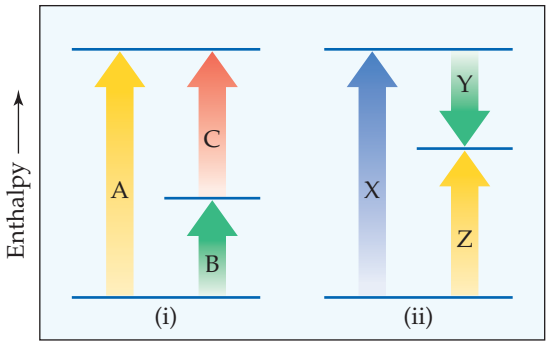
5.57 In the accompanying cylinder diagram, a chemical process occurs at constant temperature and pressure. (**a**) Is the sign of w indicated by this change positive or negative? (**b**) If the process is endothermic, does the internal energy of the system within the cylinder increase or decrease during the change and is ΔE positive or negative? [Sections 5.2 and 5.3]



5.58 The gas-phase reaction shown, between N_2 and O_2, was run in an apparatus designed to maintain a constant pressure. (**a**) Write a balanced chemical equation for the reaction depicted and predict whether w is positive, negative, or zero. (**b**) Using data from Appendix C, determine ΔH for the formation of one mole of the product. [Sections 5.3 and 5.7]



5.59 Consider the two diagrams that follow. (**a**) Based on (**i**), write an equation showing how ΔH_A is related to ΔH_B and ΔH_C. (**b**) Based on (ii), write an equation relating ΔH_Z to the other enthalpy changes in the diagram. (**c**) The equations you obtained in parts (a) and (b) are based on what law? (**d**) Would similar relationships hold for the work involved in each process? [Section 5.6]



5.60 Consider the conversion of compound A into compound B: A $\longrightarrow$ B. For both compounds A and B, $\Delta H_f^\circ > 0$. (**a**) Sketch an enthalpy diagram for the reaction that is analogous to Figure 5.23. (**b**) Suppose the overall reaction is exothermic. What can you conclude? [Section 5.7]

The Nature of Chemical Energy (Section 5.1)

5.61 (**a**) What is the electrostatic potential energy (in joules) between two electrons that are separated by 460 pm? (**b**) What is the change in potential energy if the distance separating the two electrons is increased to 1.0 nm? (**c**) Does the potential energy of the two particles increase or decrease when the distance is increased to 1.0 nm?

5.62 (**a**) The electrostatic force (not energy) of attraction between two oppositely charged objects is given by the equation $F = \kappa(Q_1Q_2/d^2)$ where $\kappa = 8.99 \times 10^9\ \text{N-m}^2/\text{C}^2$, Q_1 and Q_2 are the charges of the two objects in Coulombs, and d is the distance separating the two objects in meters. What is the electrostatic force of attraction (in Newtons) between an electron and a proton that are separated by 0.23 nm? (**b**) The force of gravity acting between two objects is given by the equation $F = G(m_1m_2/d^2)$ where G is the gravitational constant, $G = 6.674 \times 10^{-11}\ \text{N-m}^2/\text{kg}^2$, m_1 and m_2 are the masses of the two objects, and d is the distance separating them. What is the gravitational force of attraction (in Newtons) between the electron and proton? (**c**) How many times larger is the electrostatic force of attraction?

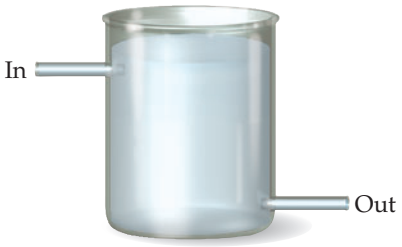
5.63 Use the equations given in Exercise 5.62 to calculate: (**a**) The electrostatic force of repulsion for two electrons separated by 75 pm. (**b**) The gravitational force of attraction for two electrons separated by 75 pm. (**c**) If allowed to move, will the electrons be repelled or attracted to one another?

5.64 A magnesium ion, Mg^{2+}, with a charge of 3.2×10^{-19} C and an oxide ion, O^{2-}, with a charge of -3.2×10^{-19} C, are separated by a distance of 0.35 nm. How much work would be required to increase the separation of the two ions to an infinite distance?

5.65 Identify the force present and explain whether work is done when (**a**) an electron moves in a circle at a fixed distance from a proton, (**b**) an iron nail is attracted by and pulled onto a magnet.

The First Law of Thermodynamics (Section 5.2)

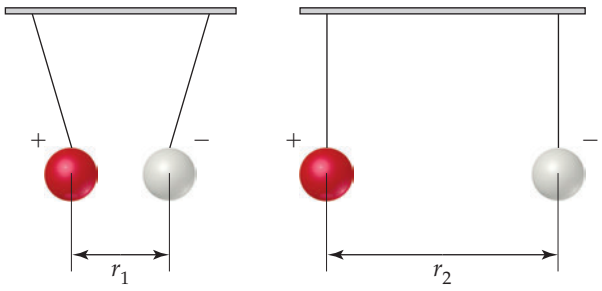
5.66 In a thermodynamic study, a scientist focuses on the properties of a solution in an apparatus as illustrated. A solution is continuously flowing into the apparatus at the top and out at the bottom, such that the amount of solution in the apparatus is constant with time. (**a**) Is the solution in the apparatus a closed system, open system, or isolated system? (**b**) If the inlet and outlet were closed, what type of system would it be?



5.67 (**a**) Write an equation that expresses the first law of thermodynamics in terms of heat and work. (**b**) Under what conditions will the quantities q and w be negative numbers?

5.68 For the following processes, calculate the change in internal energy of the system and determine whether the process is endothermic or exothermic: (**a**) A balloon is cooled by removing 0.655 kJ of heat. It shrinks on cooling, and the atmosphere does 382 J of work on the balloon. (**b**) A 100.0 g bar of gold is heated from 25 °C to 50 °C during which it absorbs 322 J of heat. Assume the volume of the gold bar remains constant.

5.69 Consider a system consisting of two oppositely charged spheres hanging by strings and separated by a distance r_1, as shown in the accompanying illustration. Suppose they are separated to a larger distance r_2, by moving them apart. (**a**) What change, if any, has occurred in the potential energy of the system? (**b**) What effect, if any, does this process have on the value of ΔE? (**c**) What can you say about q and w for this process?



5.70 Indicate which of the following is independent of the path by which a change occurs: (**a**) the change in potential energy when a book is transferred from table to shelf, (**b**) the heat evolved when a cube of sugar is oxidized to $CO_2(g)$ and $H_2O(g)$, (**c**) the work accomplished in burning a gallon of gasoline.

Enthalpy (Section 5.3 and 5.4)

5.71 How much work (in J) is involved in a chemical reaction if the volume decreases from 33.6 L to 11.2 L against a constant pressure of 90.5 kPa?

5.72 (**a**) Under what condition will the enthalpy change of a process equal the amount of heat transferred into or out of the system? (**b**) During a constant-pressure process, the system releases heat to the surroundings. Does the enthalpy of the system increase or decrease during the process? (**c**) In a constant-pressure process, $\Delta H = 0$. What can you conclude about ΔE, q, and w?

5.73 Assume that 2 moles of water are formed according to the following reaction at constant pressure (100 kPa) and constant temperature (298 K):

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

(**a**) Calculate the pressure-volume work for this reaction.

(**b**) Calculate ΔE for the reaction using your answer to (a).

5.74 Suppose that the gas-phase reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ were carried out in a constant-volume container at constant temperature. (**a**) Would the measured heat change represent ΔH or ΔE? (**b**) If there is a difference, which quantity is larger for this reaction? (**c**) Explain your answer to part (b).

5.75 A gas is confined to a cylinder under constant atmospheric pressure, as illustrated in Figure 5.4. When 0.49 kJ of heat is added to the gas, it expands and does 214 J of work on the surroundings. What are the values of ΔH and ΔE for this process?

5.76 The decomposition of sodium hydrogen carbonate (baking soda), $NaHCO_3(s)$, into $Na_2CO_3(s)$, $H_2O(l)$, and $CO_2(g)$ at constant pressure requires the addition of 85 kJ of heat per two moles of $NaHCO_3$. (**a**) Write a balanced thermochemical equation for the reaction. (**b**) Draw an enthalpy diagram for the reaction.

5.77 Without referring to tables, predict which of the following has the higher enthalpy in each case: (**a**) 1 mol $I_2(s)$ or 1 mol $I_2(g)$ at the same temperature, (**b**) 2 mol of iodine atoms or 1 mol of I_2, (**c**) 1 mol $I_2(g)$ and 1 mol $H_2(g)$ at 25 °C or 2 mol $HI(g)$ at 25 °C, (**d**) 1 mol $H_2(g)$ at 100 °C or 1 mol $H_2(g)$ at 300 °C.

5.78 Consider the following reaction:

$$2\,CH_3OH(g) \longrightarrow 2\,CH_4(g) + O_2(g) \quad \Delta H = +252.8\ \text{kJ}$$

(**a**) Is this reaction exothermic or endothermic? (**b**) Calculate the amount of heat transferred when 24.0 g of $CH_3OH(g)$ is decomposed by this reaction at constant pressure. (**c**) For a given sample of CH_3OH, the enthalpy change during the reaction is 82.1 kJ. How many grams of methane gas are produced? (**d**) How many kilojoules of heat are released when 38.5 g of $CH_4(g)$ reacts completely with $O_2(g)$ to form $CH_3OH(g)$ at constant pressure?

5.79 At one time, a common means of forming small quantities of oxygen gas in the laboratory was to heat $KClO_3$:

$$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g) \quad \Delta H = -89.4\ \text{kJ}$$

For this reaction, calculate ΔH for the formation of (**a**) 1.36 mol of O_2 and (**b**) 10.4 g of KCl. (**c**) The decomposition of $KClO_3$ proceeds spontaneously when it is heated. Do you think that the reverse reaction, the formation of $KClO_3$ from KCl and O_2, is likely to be feasible under ordinary conditions? Explain your answer.

5.80 Consider the decomposition of liquid benzene, $C_6H_6(l)$, to gaseous acetylene, $C_2H_2(g)$:

$$C_6H_6(l) \longrightarrow 3\,C_2H_2(g) \quad \Delta H = +630\ \text{kJ}$$

(**a**) What is the enthalpy change for the reverse reaction?

(**b**) What is ΔH for the formation of 1 mol of acetylene?

(**c**) Which is more likely to be thermodynamically favored, the forward reaction or the reverse reaction?

(**d**) If $C_6H_6(g)$ were consumed instead of $C_6H_6(l)$, would you expect the magnitude of ΔH to increase, decrease, or stay the same? Explain.

Calorimetry (Section 5.5)

5.81 Two solid objects, A and B, are placed in boiling water and allowed to come to the temperature of the water. Each is then lifted out and placed in separate beakers containing 1000 g of water at 10.0 °C. Object A increases the water temperature by 3.50 °C; B increases the water temperature by 2.60 °C. (**a**) Which object has the larger heat capacity? (**b**) What can you say about the specific heats of A and B?

5.82 (**a**) Which substance in Table 5.2 requires the smallest amount of energy to increase the temperature of 50.0 g of that substance by 10 K? (**b**) Calculate the energy needed for this temperature change.

5.83 Consider the data about gold metal in Exercise 5.68(b). (**a**) Based on the data, calculate the specific heat of Au(*s*). (**b**) Suppose that the same amount of heat is added to two 10.0 g blocks of metal, both initially at the same temperature. One block is gold metal, and one is iron metal. Which block will have the greater rise in temperature after the addition of the heat? (**c**) What is the molar heat capacity of Au(*s*)?

5.84 (**a**) When an 8.50 g sample of solid ammonium nitrate ($NH_4NO_3(s)$) dissolves in 120.0 g of water in a coffee-cup calorimeter (Figure 5.18), the temperature drops from 24.0 to 18.9 °C. Calculate ΔH (in kJ/mol NH_4NO_3) for the solution process:

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

Assume that the specific heat of the solution is the same as that of pure water. (**b**) Is this process endothermic or exothermic?

5.85 A 2.20 g sample of phenol (C_6H_5OH) was burned in a bomb calorimeter whose total heat capacity is 11.90 kJ/°C. The temperature of the calorimeter plus contents increased from 21.50 to 27.50 °C. (**a**) Write a balanced chemical equation for the bomb calorimeter reaction. (**b**) What is the heat of combustion per gram of phenol and per mole of phenol?

5.86 Under constant-volume conditions, the heat of combustion of naphthalene ($C_{10}H_8$) is 40.18 kJ/g. A 2.50 g sample of naphthalene is burned in a bomb calorimeter. The temperature of the calorimeter increases from 21.50 to 28.83 °C. (**a**) What is the total heat capacity of the calorimeter? (**b**) A 1.50 g sample of a new organic substance is combusted in the same calorimeter. The temperature of the calorimeter increases from 21.14 to 25.08 °C. What is the heat of combustion per gram of the new substance? (**c**) Suppose that in changing samples, a portion of the water in the calorimeter were lost. In what way, if any, would this change the heat capacity of the calorimeter?

Hess's Law (Section 5.6)

5.87 Can you use an approach similar to Hess's law to calculate the change in internal energy, ΔE, for an overall reaction by summing the ΔE values of individual reactions that add up to give the desired overall reaction?

5.88 From the enthalpies of reaction

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \qquad \Delta H = -221.0\text{ kJ}$$
$$2\,C(s) + O_2(g) + 4\,H_2(g) \longrightarrow 2\,CH_3OH(g) \qquad \Delta H = -402.4\text{ kJ}$$

calculate ΔH for the reaction

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$$

5.89 Given the data

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \qquad \Delta H = +180.7\text{ kJ}$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \qquad \Delta H = -113.1\text{ kJ}$$
$$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g) \qquad \Delta H = -163.2\text{ kJ}$$

use Hess's law to calculate ΔH for the reaction

$$N_2O(g) + NO_2(g) \longrightarrow 3\,NO(g)$$

Enthalpies of Formation (Section 5.7)

5.90 (**a**) Why does the standard enthalpy of formation of both the very reactive fluorine (F_2) and the almost inert gas nitrogen (N_2) both read zero? (**b**) Write the chemical equation for the reaction whose enthalpy change is the standard enthalpy of formation of naphthalene ($C_{10}H_8$).

5.91 Write balanced equations that describe the formation of the following compounds from elements in their standard states, and then look up the standard enthalpy of formation for each substance in Appendix C: (**a**) $CH_3OH(l)$, (**b**) $CaSO_4(s)$, (**c**) $NO(g)$, (**d**) $P_4O_6(s)$.

5.92 Acetylene ($C_2H_2(g)$) is used for welding because oxyacetylene is the hottest burning common fuel gas. Using standard enthalpies of formation, calculate the quantity of heat produced when 10 g of acetylene is completely combusted in air under standard conditions.

5.93 Using values from Appendix C, calculate the value of ΔH for each of the following reactions:

(**a**) $CaO(s) + 2HF(g) \longrightarrow CaF_2(s) + H_2O(g)$

(**b**) $Fe_2O_3(s) + 3C(s) \longrightarrow 2Fe(s) + 3CO(g)$

(**c**) $2\,CO(g) + 2\,NO(g) \longrightarrow N_2(s) + 2\,CO_2(g)$

(**d**) $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$

5.94 Calcium carbide (CaC_2) reacts with water to form acetylene (C_2H_2) and $Ca(OH)_2$. From the following enthalpy of reaction data and data in Appendix C, calculate ΔH_f° for $CaC_2(s)$:

$$CaC_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \qquad \Delta H^\circ = -127.2\text{ kJ}$$

5.95 Diethyl ether, $C_4H_{10}O(l)$, a flammable compound that was once used as a surgical anesthetic, has the structure

$$H_3C{-}CH_2{-}O{-}CH_2{-}CH_3$$

The complete combustion of 1 mol of $C_4H_{10}O(l)$ to $CO_2(g)$ and $H_2O(l)$ yields $\Delta H^\circ = -2723.7$ kJ. (**a**) Write a balanced equation for the combustion of 1 mol of $C_4H_{10}O(l)$. (**b**) By using the information in this problem and data in Table 5.3, calculate ΔH_f° for diethyl ether.

5.96 Methanol (CH_3OH) is used as a fuel in race cars. (**a**) Write a balanced equation for the combustion of liquid methanol in air. (**b**) Calculate the standard enthalpy change for the reaction, assuming $H_2O(g)$ as a product. (**c**) Calculate the heat produced by combustion per liter of methanol. Methanol has a density of 0.791 g/mL. (**d**) Calculate the mass of CO_2 produced per kJ of heat emitted.

Bond Enthalpies (Section 5.8)

5.97 Without doing any calculations, predict the sign of ΔH for each of the following reactions:

(**a**) $2\,NO_2(g) \longrightarrow N_2O_4(g)$

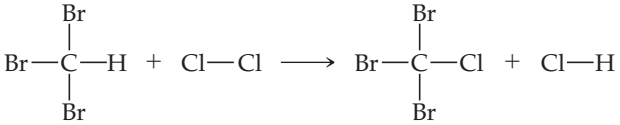
(**b**) $2\,F(g) \longrightarrow F_2(g)$

(**c**) $Mg^{2+}(g) + 2\,Cl^-(g) \longrightarrow MgCl_2(s)$

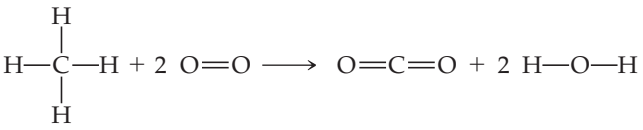
(**d**) $HBr(g) \longrightarrow H(g) + Br(g)$

5.98 Use bond enthalpies in Table 5.4 to estimate ΔH for each of the following reactions:

(**a**)



(**b**)



5.99 (**a**) The nitrogen atoms in an N_2 molecule are held together by a triple bond; use enthalpies of formation in Appendix C to estimate the enthalpy of this bond, $D(N{\equiv}N)$. (**b**) Consider the reaction between hydrazine and hydrogen to produce ammonia, $N_2H_4(g) + H_2(g) \longrightarrow 2\,NH_3(g)$. Use enthalpies of formation and bond enthalpies to estimate the enthalpy of the nitrogen– nitrogen bond in N_2H_4. (**c**) Based on your answers to parts (a) and (b), would you predict that the nitrogen–nitrogen bond in hydrazine is weaker than, similar to, or stronger than the bond in N_2?

5.100 Consider the reaction $H_2(g) + Br_2(l) \longrightarrow 2\,HBr(g)$. (**a**) Use the bond enthalpies in Table 5.4 to estimate ΔH for this reaction, ignoring the fact that bromine is in the liquid state. (**b**) Without doing a calculation, predict whether your estimate in part (a) is more negative or less negative than the true reaction enthalpy. (**c**) Use the enthalpies of formation in Appendix C to determine the true reaction enthalpy.

Foods and Fuels (Section 5.9)

5.101 (**a**) Which releases the most energy when metabolized, 1 g of carbohydrates or 1 g of fat? (**b**) A particular chip snack food is composed of 12% protein, 14% fat, and the rest carbohydrate. What percentage of the calorie content of this food is fat? (**c**) How many grams of protein provide the same fuel value as 25 g of fat?

5.102 A hamburger contains 28 g fat, 46 g carbohydrate, and 25 g protein. What is the fuel value in kJ in one hamburger? How many calories does it provide?

5.103 The heat of combustion of ethanol, $C_2H_5OH(l)$, is -1367 kJ/mol. A bottle of stout (dark beer) contains up to 6.0% ethanol by mass. Assuming the density of the beer to be 1.0 g/mL, what is the caloric content due to the alcohol (ethanol) in a bottle of beer (500 mL)?

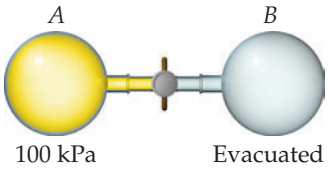
5.104 It is interesting to compare the "fuel value" of a hydrocarbon in a hypothetical world where oxygen is not the combustion agent. The enthalpy of formation of $CF_4(g)$ is -679.9 kJ/mol. Which of the following two reactions is the more exothermic?

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$
$$CH_4(g) + 4\,F_2(g) \longrightarrow CF_4(g) + 4\,HF(g)$$

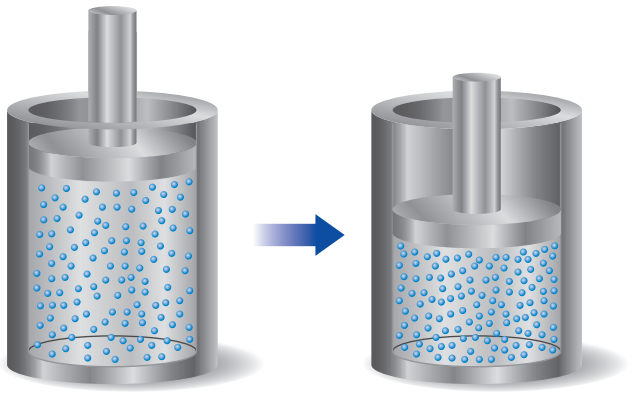
Additional Exercises

5.105 The air bags that provide protection in automobiles in the event of an accident expand because of a rapid chemical reaction. From the viewpoint of the chemical reactants as the system, what do you expect for the signs of q and w in this process?

5.106 Consider a system consisting of the following apparatus, in which gas is confined in one flask and there is a vacuum in the other flask. The flasks are separated by a valve. Assume that the flasks are perfectly insulated and will not allow the flow of heat into or out of the flasks to the surroundings. When the valve is opened, gas flows from the filled flask to the evacuated one. (**a**) Is work performed during the expansion of the gas? (**b**) Why or why not? (**c**) Can you determine the value of ΔE for the process?



5.107 A sample of gas is contained in a cylinder-and-piston arrangement. There is an external pressure of 100 kPa. The gas undergoes the change in state shown in the drawing. (**a**) Assume first that the cylinder and piston are perfect thermal insulators that do not allow heat to be transferred. What is the value of q for the state change? What is the sign of w for the state change? What can be said about ΔE for the state change? (**b**) Now assume that the cylinder and piston are made up of a thermal conductor such as a metal. During the state change, the cylinder gets colder to the touch. What is the sign of q for the state change in this case? Describe the difference in the state of the system at the end of the process in the two cases. What can you say about the relative values of ΔE?



5.108 The corrosion (rusting) of iron in oxygen-free water includes the formation of iron(II) hydroxide from iron by the following reaction:

$$Fe(s) + 2\,H_2O(l) \longrightarrow Fe(OH)_2(s) + H_2(g).$$

If 1 mol of iron reacts at 298 K under 101.3 kPa pressure, the reaction performs 2.48 kJ of P-V work, pushing back the atmosphere as the gaseous H_2 forms. At the same time, 11.73 kJ of heat is released to the environment. What are the values of ΔH and of ΔE for this reaction?

5.109 Both oxyhydrogen torches and fuel cells use the following reaction to produce energy:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

Both processes occur at constant pressure. In both cases the change in state of the system is the same: the reactant is

oxyhydrogen and the product is water. Yet, with an oxyhydrogen torch, the heat evolved is large and with a fuel cell it is small. If heat at constant pressure is considered to be a state function, why does it depend on path?

5.110 A house is designed to have passive solar energy features. Brickwork incorporated into the interior of the house acts as a heat absorber. Each brick weighs approximately 1.8 kg. The specific heat of the brick is 0.85 J/g K. How many bricks must be incorporated into the interior of the house to provide the same total heat capacity as 1.7×10^3 gal of water?

5.111 A coffee-cup calorimeter of the type shown in Figure 5.18 contains 150.0 g of water at 25.2 °C. A 200 g block of silver metal is heated to 100.5 °C by putting it in a beaker of boiling water. The specific heat of Ag(*s*) is 0.233J/(g K). The Ag is added to the calorimeter, and after some time the contents of the cup reach a constant temperature of 30.2 °C. (**a**) Determine the amount of heat, in J, lost by the silver block. (**b**) Determine the amount of heat gained by the water. The specific heat of water is 4.184 J/(g K). (**c**) The difference between your answers for (a) and (b) is due to heat loss through the Styrofoam® cups and the heat necessary to raise the temperature of the inner wall of the apparatus. The heat capacity of the calorimeter is the amount of heat necessary to raise the temperature of the apparatus (the cups and the stopper) by 1 K. Calculate the heat capacity of the calorimeter in J/K. (**d**) What would be the final temperature of the system if all the heat lost by the silver block were absorbed by the water in the calorimeter?

5.112 (**a**) When a 0.47 g sample of benzoic acid is combusted in a bomb calorimeter (Figure 5.19), the temperature rises by 3.284 °C. When a 0.53 g sample of caffeine, $C_8H_{10}N_4O_2$, is burned, the temperature rises by 3.05 °C. Using the value of 26.38 kJ/g for the heat of combustion of benzoic acid, calculate the heat of combustion per mole of caffeine at constant volume. (**b**) Assuming that there is an uncertainty of 0.002 °C in each temperature reading and that the masses of samples are measured to 0.001 g, what is the estimated uncertainty in the value calculated for the heat of combustion per mole of caffeine?

5.113 The corrosion (rusting) of iron in oxygen-free water includes the formation of iron(II) hyrdroxide from iron by the following reaction:

$$Fe(s) + 2\,H_2O(l) \longrightarrow Fe(OH)_2(s) + H_2(g)$$

(**a**) Calculate the standard enthalpy change for this reaction (the molar enthalpy of formation of $Fe(OH)_2$ is −583.39 kJ/mol).

(**b**) Calculate the number of grams of Fe needed to release enough energy to increase the temperature of 250 mL of water from 22 to 30 °C.

5.114 Burning acetylene in oxygen can produce three different carbon-containing products: soot (very fine particles of graphite), CO(*g*), and $CO_2(g)$. (**a**) Write three balanced equations for the reaction of acetylene gas with oxygen to produce these three products. In each case assume that $H_2O(l)$ is the only other product. (**b**) Determine the standard enthalpies for the reactions in part (a). (**c**) Why, when the oxygen supply is adequate, is $CO_2(g)$ the predominant carbon-containing product of the combustion of acetylene?

5.115 We can use Hess's law to calculate enthalpy changes that cannot be measured. One such reaction is the conversion of methane to ethane:

$$2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

Calculate the $\Delta H°$ for this reaction using the following thermochemical data:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H° = -890.3\text{ kJ}$$
$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \qquad \Delta H° = -571.6\text{ kJ}$$
$$2\,C_2H_6(g) + 7\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(l) \qquad \Delta H° = -3120.8\text{ kJ}$$

5.116 From the following data for three prospective fuels, calculate which could provide the most energy per unit mass and per unit volume:

Fuel	Density at 101.3 kPa (g/cm^3)	Molar Enthalpy of Combustion (MJ/mol)
Octane, $C_8H_{18}(l)$	0.70 at 20 °C	−5.53
Liquid Butane, $C_4H_{10}(l)$	0.60 at −1 °C	−2.88
Liquid hydrogen, $H_2(l)$	0.07 at −253 °C	−0.29

5.117 The hydrocarbons cyclohexane ($C_6H_{12}(l)$, $\Delta H_f° = -156$ kJ/mol) and 1-hexene ($C_6H_{12}(l)$, $\Delta H_f° = -74$ kJ/mol) have the same empirical formula. (**a**) Calculate the standard enthalpy change for the transformation of cyclohexane to 1-hexene. (**b**) Which has greater enthalpy, cyclohexane or 1-hexene? (**c**) Without doing a further calculation and knowing the answer to (b), do you expect cyclohexane or 1-hexene to have the larger combustion enthalpy?

5.118 Butane $C_4H_{10}(l)$ boils at −0.5 °C; at this temperature it has a density of 0.60 g/cm^3. The enthalpy of formation of $C_4H_{10}(g)$ is −124.7 kJ/mol, and the enthalpy of vaporization of $C_4H_{10}(l)$ is 22.44 kJ/mol. Calculate the enthalpy change when 1 L of liquid $C_4H_{10}(l)$ is burned in air to give $CO_2(g)$ and $H_2O(g)$. How does this compare with ΔH for the complete combustion of 1 L of liquid methanol, $CH_3OH(l)$? For $CH_3OH(l)$, the density at 25 °C is 0.792g/cm^3, and $\Delta H_f° = -239$ kJ/mol.

5.119 Three hydrocarbons that contain four carbons are listed here, along with their standard enthalpies of formation:

Hydrocarbon	Formula	$\Delta H_f°$ (kJ/mol)
Butane	$C_4H_{10}(g)$	−125
1-Butene	$C_4H_8(g)$	−1
1-Butyne	$C_4H_6(g)$	165

(**a**) For each of these substances, calculate the molar enthalpy of combustion to $CO_2(g)$ and $H_2O(l)$. (**b**) Calculate the fuel value, in kJ/g, for each of these compounds. (**c**) For each hydrocarbon, determine the percentage of hydrogen by mass. (**d**) By comparing your answers for parts (b) and (c), propose a relationship between hydrogen content and fuel value in hydrocarbons.

5.120 A 100-kg man decides to add to his exercise routine by walking up six flights of stairs (30 m) 10 times per day. He figures that the work required to increase his potential energy in this way will permit him to eat an extra order of French fries, at 245 Cal, without adding to his weight. Is he correct in this assumption?

5.121 Sucrose ($C_{12}H_{22}O_{11}$) is produced by plants as follows:

$$12\,CO_2(g) + 11\,H_2O(l) \longrightarrow C_{12}H_{22}O_{11} + 12\,O_2(g) \qquad \Delta H = 5645\text{ kJ}$$

About 4.8 g of sucrose is produced per day per square meter of the earth's surface. The energy for this endothermic reaction is supplied by the sunlight. About 0.1 % of the sunlight that reaches the earth is used to produce sucrose. Calculate the

total energy the sun supplies for each square meter of surface area. Give your answer in kilowatts per square meter (kW/m^2 where $1W = 1\,J/s$).

5.122 It is estimated that the net amount of carbon dioxide fixed by photosynthesis on the landmass of Earth is 5.5×10^{16} g/yr of CO_2. Assume that all this carbon is converted into glucose. (**a**) Calculate the energy stored by photosynthesis on land per year, in kJ. (**b**) Calculate the average rate of conversion of solar energy into plant energy in megawatts, MW ($1W = 1\,J/s$). A large nuclear power plant produces about 10^3 MW. The energy of how many such nuclear power plants is equivalent to the solar energy conversion?

Integrative Exercises

5.123 At 25 °C (approximately room temperature) the rms velocity of an Ar atom in air is 1553 km/h. (**a**) What is the rms speed in m/s? (**b**) What is the kinetic energy (in J) of an Ar atom moving at this speed? (**c**) What is the total kinetic energy of 1 mol of Ar atoms moving at this speed?

5.124 Suppose an Olympic diver who weighs 52.0 kg executes a straight dive from a 10-m platform. At the apex of the dive, the diver is 10.8 m above the surface of the water. (**a**) What is the potential energy of the diver at the apex of the dive, relative to the surface of the water? (**b**) Assuming that all the potential energy of the diver is converted into kinetic energy at the surface of the water, at what speed, in m/s, will the diver enter the water? (**c**) Does the diver do work on entering the water? Explain.

5.125 Consider the combustion of a single molecule of $CH_4(g)$, forming $H_2O(l)$ as a product. (**a**) How much energy, in J, is produced during this reaction? (**b**) A typical X-ray light source has an energy of 8 keV (see inside back cover for conversion between eV and J). Is the energy released by the combustion of a CH_4 molecule larger or smaller than the energy of an X-ray from this source?

5.126 Consider the following unbalanced oxidation-reduction reactions in aqueous solution:

$$Ag^+(aq) + Li(s) \longrightarrow Ag(s) + Li^+(aq)$$
$$Fe(s) + Na^+(aq) \longrightarrow Fe^{2+}(aq) + Na(s)$$
$$K(s) + H_2O(l) \longrightarrow KOH(aq) + H_2(g)$$

(**a**) Balance each of the reactions. (**b**) By using data in Appendix C, calculate ΔH° for each of the reactions. (**c**) Based on the values you obtain for ΔH°, which of the reactions would you expect to be thermodynamically favored? (**d**) Use the activity series to predict which of these reactions should occur. Are these results in accord with your conclusion in part (c) of this problem?

5.127 Consider the following acid-neutralization reactions involving the strong base NaOH(*aq*):

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l)$$
$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
$$NH_4^+(aq) + NaOH(aq) \longrightarrow NH_3(aq) + Na^+(aq) + H_2O(l)$$

(**a**) By using data in Appendix C, calculate ΔH° for each of the reactions. (**b**) As we saw in Section 4.3, nitric acid and hydrochloric acid are strong acids. Write net ionic equations for the neutralization of these acids. (**c**) Compare the values of ΔH° for the first two reactions. What can you conclude? (**d**) In the third equation $NH_4^+(aq)$ is acting as an acid. Based on the value of ΔH° for this reaction, do you think it is a strong or a weak acid? Explain.

5.128 Consider two solutions, the first being 50.0 mL of 1.00 *M* $CuSO_4$ and the second 50.0 mL of 2.00 *M* KOH. When the two solutions are mixed in a constant-pressure calorimeter, a precipitate forms and the temperature of the mixture rises from 21.5 to 27.7 °C. (**a**) Before mixing, how many grams of Cu are present in the solution of $CuSO_4$? (**b**) Predict the identity of the precipitate in the reaction. (**c**) Write complete and net ionic equations for the reaction that occurs when the two solutions are mixed. (**d**) From the calorimetric data, calculate ΔH for the reaction that occurs on mixing. Assume that the calorimeter absorbs only a negligible quantity of heat, that the total volume of the solution is 100.0 mL, and that the specific heat and density of the solution after mixing are the same as those of pure water.

5.129 The precipitation reaction between $AgNO_3(aq)$ and NaCl(*aq*) proceeds as follows:

$$AgNO_3(aq) + NaCl(aq) \longrightarrow NaNO_3(aq) + AgCl(s)$$

(**a**) By using data in Appendix C, calculate ΔH° for the net ionic equation of this reaction. (**b**) What would you expect for the value of ΔH° of the overall molecular equation compared to that for the net ionic equation? Explain. (**c**) Use the results from (a) and (b) along with data in Appendix C to determine the value of ΔH_f° for $AgNO_3(aq)$.

5.130 A sample of a hydrocarbon is combusted completely in $O_2(g)$ to produce 21.83 g $CO_2(g)$, 4.47 g $H_2O(g)$, and 311 kJ of heat. (**a**) What is the mass of the hydrocarbon sample that was combusted? (**b**) What is the empirical formula of the hydrocarbon? (**c**) Calculate the value of ΔH_f° per empirical-formula unit of the hydrocarbon. (**d**) Do you think that the hydrocarbon is one of those listed in Appendix C? Explain your answer.

5.131 The methane molecule, CH_4, has the geometry shown in Figure 2.15. Imagine a hypothetical process in which the methane molecule is "expanded," by simultaneously extending all four C—H bonds to infinity. We then have the process

$$CH_4(g) \longrightarrow C(g) + 4\,H(g)$$

(**a**) Compare this process with the reverse of the reaction that represents the standard enthalpy of formation of $CH_4(g)$. (**b**) Calculate the enthalpy change in each case. Which is the more endothermic process? What accounts for the difference in ΔH° values? (**c**) Suppose that 3.45 g $CH_4(g)$ reacts with 1.22 g $F_2(g)$, forming $CF_4(g)$ and HF(*g*) as sole products. What is the limiting reagent in this reaction? If the reaction occurs at constant pressure, what amount of heat is evolved?

Design an Experiment

One of the important ideas of thermodynamics is that energy can be transferred in the form of heat or work. Imagine that you lived 180 years ago when the relationships between heat and work were not well understood. You have formulated a hypothesis that work can be converted to heat with the same amount of work always generating the same amount of heat. To test this idea, you have designed an experiment using a device in which a falling weight is connected through pulleys to a shaft with an attached paddle wheel that is immersed in water. This is actually a classic experiment performed by James Joule in the 1840s. You can see various images of Joule's apparatus by searching the internet for "Joule experiment images."

(**a**) Using this device, what measurements would you need to make to test your hypothesis? (**b**) What equations would you use in analyzing your experiment? (**c**) Do you think you could obtain a reasonable result from a single experiment? Why or why not? (**d**) In what way could the precision of your instruments affect the conclusions that you make? (**e**) List ways that you could modify the equipment to improve the data you obtain if you were performing this experiment today instead of 180 years ago. (**f**) Give an example of how you could demonstrate the relationship between heat and a form of energy other than mechanical work.

WHAT'S AHEAD

6.1 The Wave Nature of Light
6.2 Quantized Energy and Photons
6.3 Line Spectra and the Bohr Model
6.4 The Wave Behavior of Matter
6.5 Quantum Mechanics and Atomic Orbitals
6.6 Representations of Orbitals
6.7 Many-Electron Atoms
6.8 Electron Configurations
6.9 Electron Configurations and the Periodic Table

6

ELECTRONIC STRUCTURE OF ATOMS

6.1 The Wave Nature of Light



The beginning of the twentieth century was truly one of the most revolutionary periods of scientific discovery. Two theoretical developments caused dramatic changes in our view of the universe. The first, Einstein's theory of relativity, forever changed our views of the relationships between space and time. The second—which will be the focus of this chapter—is *quantum theory*, which explains much of the behavior of electrons in atoms.

We begin by looking at the nature of light and how our description of light was changed by quantum theory. We will explore some of the tools used in *quantum mechanics*, the "new" physics that had to be developed to describe atoms correctly. We will then use quantum theory to describe the arrangements of electrons in atoms—what we call

the **electronic structure** of atoms. We will see that the quantum description of the electronic structure of atoms helps us to understand the arrangement of the elements in the periodic table—why, for example, helium and neon are both unreactive gases, whereas sodium and potassium are both soft, reactive metals.

By the end of this section, you should be able to

- Describe a wave in terms of its wavelength and frequency

Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances. To understand electronic structure, therefore, we must first learn more about light. The light we see with our eyes, *visible light*, is one type of **electromagnetic radiation**. Because electromagnetic radiation carries energy through space, it is also known as *radiant energy*.

There are many types of electromagnetic radiation in addition to visible light. These different types—radio waves, infrared radiation (heat), X rays—may seem very different from one another, but they all share certain fundamental characteristics.

All types of electromagnetic radiation move through a vacuum at 2.998×10^8 m/s, the *speed of light*. All have wave-like characteristics similar to those of waves that move through water. Water waves are the result of energy imparted to the water, perhaps by a dropped stone or the movement of a boat across the water's surface (**Figure 6.1**). This energy is expressed as the up-and-down movements of the water.

A cross section of a water wave (**Figure 6.2**) shows that it is *periodic*, which means that the pattern of peaks and troughs repeats itself at regular intervals. The distance between two adjacent peaks (or between two adjacent troughs) is called the **wavelength**. The number of complete wavelengths, or *cycles*, that pass a given point each second is the **frequency** of the wave.

Just as with water waves, we can assign a frequency and wavelength to electromagnetic waves, as illustrated in **Figure 6.3**. These and all other wave characteristics of electromagnetic radiation are due to the periodic oscillations in the intensities of the electric and magnetic fields associated with the radiation.

The speed of water waves can vary depending on how they are created—for example, the waves produced by a speed boat travel faster than those produced by a rowboat. In contrast, *all electromagnetic radiation moves at the same speed, namely, the speed of light*. As a result, the wavelength and frequency of electromagnetic radiation are always related in a straightforward way. If the wavelength is long, fewer cycles of the wave pass a given point per second, and so the frequency is low. Conversely, for a wave to have a high frequency, it must have a short wavelength. This inverse relationship between the frequency and wavelength of electromagnetic radiation is expressed by the equation

$$\lambda\nu = c \qquad [6.1]$$

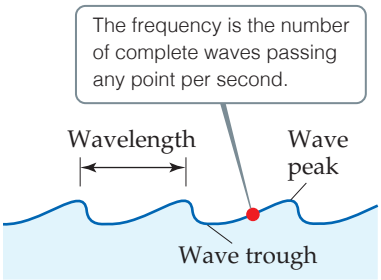
where λ (lambda) is wavelength, ν (nu) is frequency, and c is the speed of light.

Why do different types of electromagnetic radiation have different properties? Their differences are due to their different wavelengths. **Figure 6.4** shows the various types of electromagnetic radiation arranged in order of increasing wavelength, a display called the *electromagnetic spectrum*. Notice that the wavelengths span an enormous range. The wavelengths of gamma rays are comparable to the diameters of atomic nuclei, whereas the wavelengths of radio waves can be longer than a football field. Notice also that visible light, which corresponds to wavelengths of about 400 to 750 nm (4×10^{-7} to 7×10^{-7} m), is an extremely small portion of the electromagnetic spectrum. The unit of length chosen to express wavelength depends on the type of radiation, as shown in **Table 6.1**.

Frequency is expressed in cycles per second, a unit also called a *hertz* (Hz). Because it is understood that cycles are involved, the units of frequency are normally given simply as "per second," which is denoted by s^{-1} or /s. For example, a frequency of 698 megahertz (MHz), a typical frequency for a cellular telephone, could be written as 698 MHz, 698,000,000 Hz, 698,000,000 s^{-1}, or 698,000,000/s.



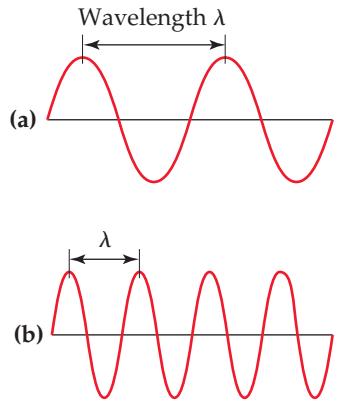
▲ **Figure 6.1 Water waves.** The movement of a boat through the water forms waves. The regular variation of peaks and troughs enables us to sense the motion of the waves away from the boat.



▲ **Figure 6.2 Water waves.** The *wavelength* is the distance between two adjacent peaks or two adjacent troughs.

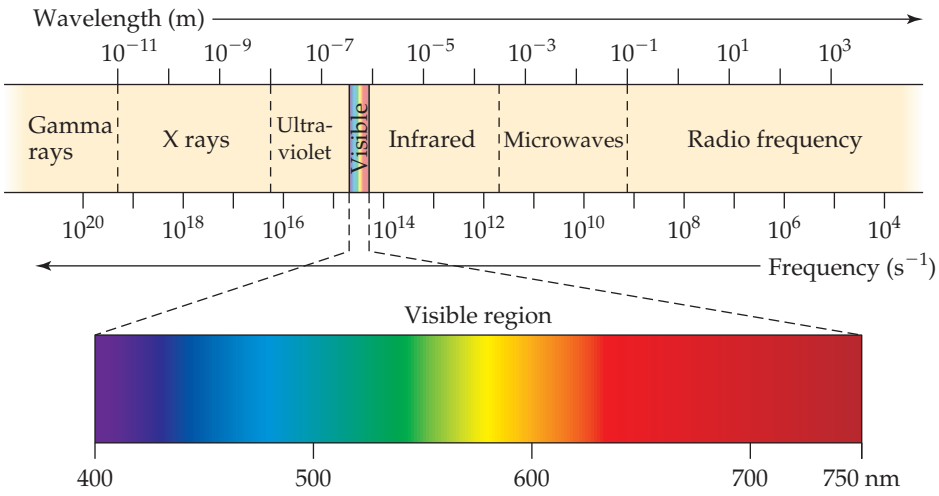
Go Figure

If wave (a) has a wavelength of 2.0 m and a frequency of 1.5×10^8 cycles/s, what are the wavelength and frequency of wave (b)?



▲ **Figure 6.3 Electromagnetic waves.** Like water waves, electromagnetic radiation can be characterized by a wavelength. Notice that the shorter the wavelength, λ, the greater the frequency, ν. The wavelength in (**b**) is half as long as that in (**a**), and the frequency of the wave in (**b**) is therefore twice as great as that in (**a**).

Go Figure Is the wavelength of a microwave longer or shorter than the wavelength of visible light? By how many orders of magnitude do the two waves differ in wavelength?



▲ **Figure 6.4 The electromagnetic spectrum.*** Wavelengths in the spectrum range from very short gamma rays to very long radio waves.

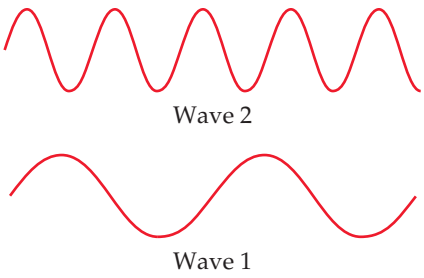
TABLE 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

Sample Exercise 6.1

Concepts of Wavelength and Frequency

Two electromagnetic waves are represented in the margin. (**a**) Which wave has the higher frequency? (**b**) If one wave represents visible light and the other represents infrared radiation, which wave is which?



SOLUTION

(a) Wave 1 has a longer wavelength (greater distance between peaks). The longer the wavelength, the lower the frequency ($\nu = c/\lambda$). Thus, Wave 1 has the lower frequency, and Wave 2 has the higher frequency.

(b) The electromagnetic spectrum (Figure 6.4) indicates that infrared radiation has a longer wavelength than visible light. Thus, Wave 1 is infrared radiation.

Practice Exercise

A source of electromagnetic radiation produces infrared light. Which of the following could be the wavelength of the light? **(a)** 3.0 nm **(b)** 4.7 cm **(c)** 66.8 m **(d)** 34.5 μm **(e)** 16.5 Å

* Based on B. A. Averill and P. Eldredge, *Chemistry: Principles, Patterns, and Applications* 1e, © 2007 Pearson Education, Inc.

Sample Exercise 6.2

Calculating Frequency from Wavelength

The yellow light given off by a sodium vapor lamp used for public lighting has a wavelength of 589 nm. What is the frequency of this radiation?

SOLUTION

Analyze We are given the wavelength, λ, of the radiation and asked to calculate its frequency, ν.

Plan The relationship between the wavelength and the frequency is given by Equation 6.1. We can solve for ν and use the values of λ and c to obtain a numerical answer. (The speed of light, c, is 3.00×10^8 m/s to three significant figures.)

Solve Solving Equation 6.1 for frequency gives $\nu = c/\lambda$. When we insert the values for c and λ, we note that the units of length in these two quantities are different. We use a conversion factor to convert the wavelength from nanometers to meters, so the units cancel:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^8 \text{ m/s}}{589 \text{ nm}}\right)\left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right)$$

$$= 5.09 \times 10^{14} \text{ s}^{-1}$$

Check The high frequency is reasonable because of the short wavelength. The units are proper because frequency has units of "per second," or s^{-1}.

Practice Exercise

(**a**) A laser used in orthopedic spine surgery produces radiation with a wavelength of 2.10 μm. Calculate the frequency of this radiation. (**b**) An FM radio station broadcasts electromagnetic radiation at a frequency of 103.4 MHz (megahertz; 1 MHz = 10^6 s^{-1}). Calculate the wavelength of this radiation. The speed of light is 2.998×10^8 m/s to four significant figures.

Self-Assessment Exercise

6.1 The broadcast frequency of a local radio station is 106.5 MHz. What is the wavelength of the broadcast radio waves?

(a) 0.355 m
(b) 2.82 m
(c) 2.82×10^6 m

Exercises

6.2 Label each of the following statements as true or false. For those that are false, correct the statement. (**a**) Visible light is a form of electromagnetic radiation. (**b**) Ultraviolet light has longer wavelengths than visible light. (**c**) X rays travel faster than microwaves. (**d**) Electromagnetic radiation and sound waves travel at the same speed.

6.3 Arrange the following kinds of electromagnetic radiation in order of increasing wavelength: infrared, green light, red light, radio waves, X rays, ultraviolet light.

6.4 The wavenumber $\bar{\lambda}$ is the number of waves that exist over a specified distance, very often 1 cm. The wavenumber can easily be calculated by taking the reciprocal of the wavelength. Give typical wavenumbers for (**a**) X-rays (λ = 1 nm) (**b**) visible light (λ = 500 nm) (**c**) microwaves (λ = 1 mm).

6.5 (**a**) What is the frequency of radiation that has a wavelength of 10 μm, about the size of a bacterium? (**b**) What is the wavelength of radiation that has a frequency of 5.50×10^{14} s^{-1}? (**c**) Would the radiations in part (a) or part (b) be visible to the human eye? (**d**) What distance does electromagnetic radiation travel in 50.0 μs?

6.6 A laser pointer used in a lecture hall emits light at 650 nm. What is the frequency of this radiation? Using Figure 6.4, predict the color associated with this wavelength.

Answers to Self-Assessment Exercise

6.1 (b)

6.2 | Quantized Energy and Photons



White light, a combination of the colors of the visible spectrum, surrounds us and consists of all the wavelengths in the range 400–750 nm. A little more unusual is the light emitted from a laser, which consists of just a single wavelength, a result of a quantized process. In recent times, the application of laser technology has entered many areas of life: bar code readers, levels used in building construction, welding equipment, surgery, mapping, communication, military applications, and spectacular displays put on for our entertainment. The first laser was built in 1960, the name coming from the acronym 'Light Amplification by Stimulated Emission of Radiation'.

By the end of this section, you should be able to

- Explain what photons are and be able to calculate their energies given either their frequency or wavelength.

Although the wave model of light explains many aspects of the behavior of light, several observations cannot be resolved by this model. Three of these are particularly pertinent to our understanding of how electromagnetic radiation and atoms interact: (1) the emission of light from hot objects (referred to as *blackbody radiation* because the objects studied appear black before heating), (2) the emission of electrons from metal surfaces on which light shines (the *photoelectric effect*), and (3) the emission of light from electronically excited gas atoms (*emission spectra*). We examine the first two phenomena here and the third in Section 6.3.

Hot Objects and the Quantization of Energy

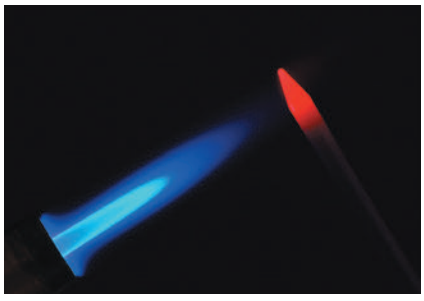
When solids are heated, they emit radiation, as seen in the red glow of an electric stove burner or the bright white light of a tungsten light bulb. The wavelength distribution of the radiation depends on temperature; a red-hot object, for instance, is cooler than a yellowish or white-hot one (**Figure 6.5**). During the late 1800s, a number of physicists studied this phenomenon, trying to understand the relationship between the temperature and the intensity and wavelength of the emitted radiation. The prevailing laws of physics could not account for the observations.

In 1900, a German physicist named Max Planck (1858–1947) solved the problem by making a daring assumption: He proposed that energy can be either released or absorbed by atoms only in discrete "chunks" of some minimum size. Planck gave the name **quantum** (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation. He proposed that the energy, E, of a single quantum equals a constant times the frequency of the radiation:

$$E = h\nu \qquad [6.2]$$

Go Figure

Which is at a higher temperature: the part of the nail glowing yellow or the part glowing red?



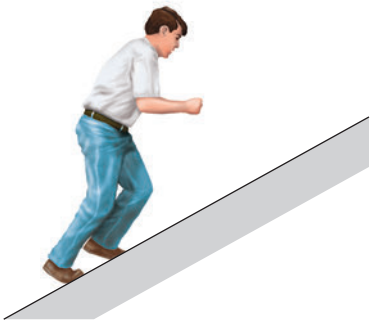
▲ **Figure 6.5 Color and temperature.** The color and intensity of the light emitted by a hot object, such as this nail, depend on the temperature of the object.

The constant h is called the **Planck constant** and has a value of 6.626×10^{-34} joule-second (J-s).

According to Planck's theory, matter can emit and absorb energy only in whole number multiples of $h\nu$, such as $h\nu$, $2h\nu$, $3h\nu$, and so forth. If the quantity of energy emitted by an atom is $3h\nu$, for example, we say that three quanta of energy have been emitted (*quanta* being the plural of *quantum*). Because the energy can be released only in specific amounts, we say that the allowed energies are *quantized*—their values are restricted to certain quantities. Planck's revolutionary proposal that energy is quantized was proved correct, and he was awarded the 1918 Nobel Prize in Physics for his work on quantum theory.

If the notion of quantized energies seems strange, it might be helpful to draw an analogy by comparing a ramp and a staircase (**Figure 6.6**). As you walk up a ramp, your potential energy increases in a uniform, continuous manner. When you climb a staircase, you can step only *on* individual stairs, not *between* them, so that your potential energy is restricted to certain values and is therefore quantized.

If Planck's quantum theory is correct, why are its effects not obvious in our daily lives? Why do energy changes seem continuous rather than quantized, or "jagged"? Notice that the Planck constant is an extremely small number. Thus, a quantum of energy, $h\nu$, is an extremely small amount. Planck's rules regarding the gain or loss of energy are always the same, whether we are concerned with objects on the scale of our ordinary experience or with microscopic objects. With everyday objects, however, the gain or loss of a single quantum of energy is so small that it goes completely unnoticed. In contrast, when dealing with matter at the atomic level, the impact of quantized energies is far more significant.



Potential energy of person walking up ramp increases in uniform, continuous manner



Potential energy of person walking up steps increases in stepwise, quantized manner

▲ **Figure 6.6** **Quantized versus continuous change in energy.**

The Photoelectric Effect and Photons

A few years after Planck presented his quantum theory, scientists began to see its applicability to many experimental observations. In 1905, Albert Einstein (1879–1955) used Planck's theory to explain the **photoelectric effect** (**Figure 6.7**). Light shining on a clean metal surface causes electrons to be emitted from the surface. A minimum frequency of light, different for different metals, is required for the emission of electrons. For example, light with a frequency of $4.60 \times 10^{14}\,s^{-1}$ or greater causes cesium metal to emit electrons, but if the light has frequency less than that, no electrons are emitted.

To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface behaves like a stream of tiny energy packets. Each packet, which is like a "particle" of energy, is called a **photon**. Extending Planck's quantum theory, Einstein deduced that each photon must have an energy equal to the Planck constant times the frequency of the light:

$$\text{Energy of photon} = E = h\nu \qquad [6.3]$$

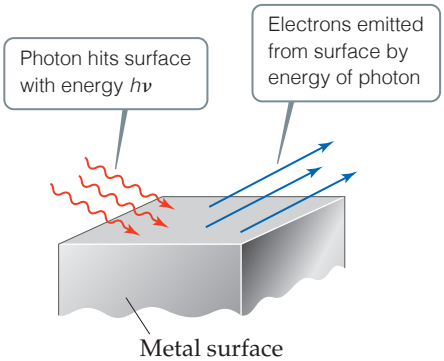
Thus, radiant energy itself is quantized.

Under the right conditions, photons striking a metal surface can transfer their energy to electrons in the metal. A certain amount of energy—called the *work function*—is required for the electrons to overcome the attractive forces holding them in the metal. If the photons striking the metal have less energy than the work function, the electrons do not acquire sufficient energy to escape from the metal. Increasing the intensity of the light source doesn't lead to emission of electrons from the metal; only changing the frequency of the incoming light has that effect. The intensity (brightness) of the light is related to the number of photons striking the surface per unit time but not to the energy of each photon. When the frequency is such that photons have energy greater than the work function of the particular metal, electrons are emitted; any excess energy of the photon is converted into kinetic energy of the emitted electron. Einstein won the Nobel Prize in Physics in 1921 primarily for his explanation of the photoelectric effect.

To better understand what a photon is, imagine you have a light source that produces radiation of a single wavelength. Further suppose that you could switch the light on and off faster and faster to provide ever-smaller bursts of energy. Einstein's photon theory tells us that you would eventually come to the smallest energy burst, given by $E = h\nu$. This smallest burst consists of a single photon of light.

Go Figure

If the frequency of the incoming light is increased, will the energy of the ejected electrons increase, decrease, or stay the same?



▲ **Figure 6.7** **The photoelectric effect.**

Sample Exercise 6.3

Energy of a Photon

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

SOLUTION

Analyze Our task is to calculate the energy, E, of a photon, given its wavelength, $\lambda = 589$ nm.

Plan We can use Equation 6.1 to convert the wavelength to frequency: $\nu = c/\lambda$. We can then use Equation 6.3 to calculate energy: $E = h\nu$

Solve The frequency, ν, is calculated from the given wavelength, as shown in Sample Exercise 6.2:

$$\nu = (3.00 \times 10^8 \cancel{\text{m}}/\text{s})/(589 \times 10^{-9} \cancel{\text{m}}) = 5.09 \times 10^{14}\,\text{s}^{-1}$$

The value of the Planck constant, h, is given both in the text and in the table of physical constants on the inside back cover of the text; thus we can easily calculate E:

$$E = (6.626 \times 10^{-34}\,\text{J}\cdot\cancel{\text{s}})(5.09 \times 10^{14}\,\cancel{\text{s}^{-1}}) = 3.37 \times 10^{-19}\,\text{J}$$

Comment If one photon of radiant energy supplies 3.37×10^{-19} J, we calculate that one mole of these photons will supply:

$$(6.02 \times 10^{23}\,\cancel{\text{photons}}/\text{mol})(3.37 \times 10^{-19}\,\text{J}/\cancel{\text{photon}}) = 2.03 \times 10^5\,\text{J/mol}$$

Practice Exercise

Which of the following expressions correctly gives the energy of a mole of photons with wavelength λ?

(a) $E = \dfrac{h}{\lambda}$ **(b)** $E = N_A\dfrac{\lambda}{h}$ **(c)** $E = \dfrac{hc}{\lambda}$ **(d)** $E = N_A\dfrac{h}{\lambda}$ **(e)** $E = N_A\dfrac{hc}{\lambda}$

The idea that the energy of light depends on its frequency helps us understand the diverse effects that different kinds of electromagnetic radiation have on matter. For example, because of the high frequency (short wavelength) of X rays (Figure 6.4), X-ray photons cause tissue damage, which is why warning signs are posted around X-ray equipment.

Although Einstein's theory of light as a stream of photons rather than a wave explains the photoelectric effect and a great many other observations, it also poses a dilemma. Is light a wave, or does it consist of particles? The only way to resolve this dilemma is to adopt what might seem to be a bizarre position: We must consider that light possesses both wave-like and particle-like characteristics and, depending on the situation, will behave more like waves or more like particles. We will soon see that this dual wave-particle nature is also a characteristic trait of matter.

Self-Assessment Exercise

6.7 Which photon of light has the higher energy?

(a) UV radiation with a wavelength of 450 nm

(b) A red laser pointer with a wavelength of 635 nm

(c) A microwave oven operating with a wavelength of 12.24 cm

Exercises

6.8 If human height were quantized in 1 cm increments, what would happen to the height of a child as she grows up: (i) the child's height would never change, (ii) the child's height would continuously increase, (iii) the child's height would increase in jumps of 6 cm, or (iv) the child's height would increase in "jumps" of 1 cm at a time?

6.9 (**a**) Calculate the energy of a photon of electromagnetic radiation whose frequency is $2.94 \times 10^{14}\,\text{s}^{-1}$. (**b**) Calculate the energy of a photon of radiation whose wavelength is 413 nm. (**c**) What wavelength of radiation has photons of energy 6.06×10^{-19} J?

6.10 (**a**) Calculate and compare the energy of a photon of wavelength 3.0 mm with that of wavelength 0.3 nm. (**b**) Use Figure 6.4 to identify the region of the electromagnetic spectrum to which each belongs.

6.11 One type of sunburn occurs on exposure to UV light of wavelength in the vicinity of 325 nm. **(a)** What is the energy of a photon of this wavelength? **(b)** What is the energy of a mole of these photons? **(c)** How many photons are in a 1.00 mJ burst of this radiation? (**d**) These UV photons can break chemical bonds in your skin to cause sunburn—a form of radiation damage. If the 325-nm radiation provides exactly the energy to break an average chemical bond in the skin, estimate the average energy of these bonds in kJ/mol.

6.12 A diode laser emits at a wavelength of 987 nm. (**a**) In what portion of the electromagnetic spectrum is this radiation found? (**b**) All of its output energy is absorbed in a detector that measures a total energy of 0.52 J over a period of 32 s. How many photons per second are being emitted by the laser?

6.13 Molybdenum metal must absorb radiation with an energy higher than 7.22×10^{-19} J ("energy threshold") before it can eject an electron from its surface via the photoelectric effect. (**a**) What is the frequency threshold for emission of electrons? (**b**) What wavelength of radiation will provide a photon of this energy? (**c**) If molybdenum is irradiated with light of wavelength of 240 nm, what is the maximum possible velocity of the emitted electrons?

Answers to Self-Assessment Exercise

6.7 (a)

6.3 Line Spectra and the Bohr Model



The work of Planck and Einstein paved the way for understanding how electrons are arranged in atoms. In 1913, the Danish physicist Niels Bohr (1885–1962) offered a theoretical explanation of *line spectra*, another phenomenon that had puzzled scientists during the nineteenth century. We will see that Bohr used the ideas of Planck and Einstein to explain the line spectrum of hydrogen.

By the end of this section, you should be able to

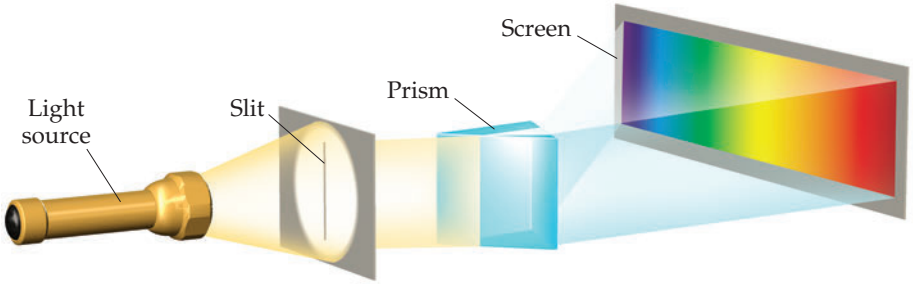
- Explain how line spectra relate to the idea of quantized energy states of electrons in atoms.

Line Spectra

A particular source of radiant energy may emit a single wavelength, as in the light from a laser. Radiation composed of a single wavelength is *monochromatic*. However, most common radiation sources, including incandescent light bulbs and stars, produce radiation containing many different wavelengths, *polychromatic* radiation. A **spectrum** is

produced when radiation from a polychromatic source is separated into its component wavelengths, as shown in Figure 6.8. The resulting spectrum consists of a continuous range of colors—violet merges into indigo, indigo into blue, and so forth, with no (or very few) blank spots. This rainbow of colors, containing light of all wavelengths, is called a **continuous spectrum**. The most familiar example of a continuous spectrum is the rainbow produced when raindrops or mist acts as a prism for sunlight.

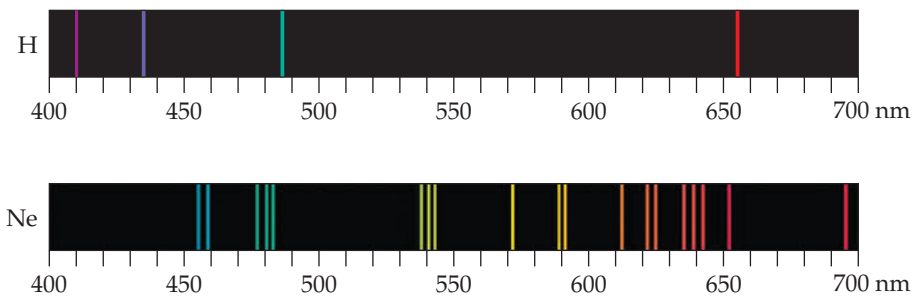
Not all radiation sources produce a continuous spectrum. When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colors of light (Figure 6.9). The light emitted by neon gas is the familiar red-orange glow of many "neon" lights, whereas sodium vapor emits the yellow light characteristic of some streetlights. When light coming from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectra (Figure 6.10). Each colored line in such spectra represents light of one wavelength. A spectrum containing radiation of only specific wavelengths is called a **line spectrum.**



▶ **Figure 6.8 Creating a spectrum.** A continuous visible spectrum is produced when a narrow beam of white light is passed through a prism. The white light could be sunlight or light from an incandescent lamp.



▶ **Figure 6.9 Atomic emission of hydrogen and neon.** Different gases emit light of different characteristic colors when an electric current is passed through them.



▶ **Figure 6.10 Line spectra of hydrogen and neon.** The colored lines occur at wavelengths present in the emission. The black regions are wavelengths for which no light is produced in the emission.

When scientists first detected the line spectrum of hydrogen in the mid-1800s, they were fascinated by its simplicity. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red) were observed (Figure 6.10). In 1885, a Swiss schoolteacher named Johann Balmer showed that the wavelengths of these four lines fit an intriguingly simple formula that relates the wavelengths to integers. Later, additional lines were found in the ultraviolet and infrared regions of hydrogen's line spectrum. Soon Balmer's equation was extended to a more general one, called the *Rydberg equation*, which allows us to calculate the wavelengths of all the spectral lines of hydrogen:

$$\frac{1}{\lambda} = (R_H)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad [6.4]$$

In this formula, λ is the wavelength of a spectral line, R_H is the *Rydberg constant* ($1.096776 \times 10^7\ m^{-1}$), and n_1 and n_2 are positive integers, with n_2 being larger than n_1. How could the remarkable simplicity of this equation be explained? It took nearly 30 more years to answer this question.

Bohr's Model

Rutherford's discovery of the nuclear atom suggested that an atom might be thought of as a "microscopic solar system" in which the electrons orbit the nucleus. To explain the line spectrum of hydrogen, Bohr assumed that electrons in hydrogen atoms move in circular orbits around the nucleus, but this assumption posed a problem. According to classical physics, a charged particle (such as an electron) moving in a circular path should continuously lose energy. As an electron loses energy, therefore, it should spiral into the positively charged nucleus. This behavior, however, does not happen—hydrogen atoms are stable. So how can we explain this apparent violation of the laws of physics? Bohr approached this problem in much the same way that Planck had approached the problem of the nature of the radiation emitted by hot objects: He assumed that the prevailing laws of physics were inadequate to describe all aspects of atoms. Furthermore, he adopted Planck's idea that energies are quantized.

Bohr based his model on three postulates:

1. Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.
2. An electron in a permitted orbit is in an "allowed" energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.
3. Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $E = h\nu$.

The Energy States of the Hydrogen Atom

Starting with his three postulates and using classical equations for motion and for interacting electrical charges, Bohr calculated the energies corresponding to the allowed orbits for the electron in the hydrogen atom. Ultimately, the calculated energies fit the formula

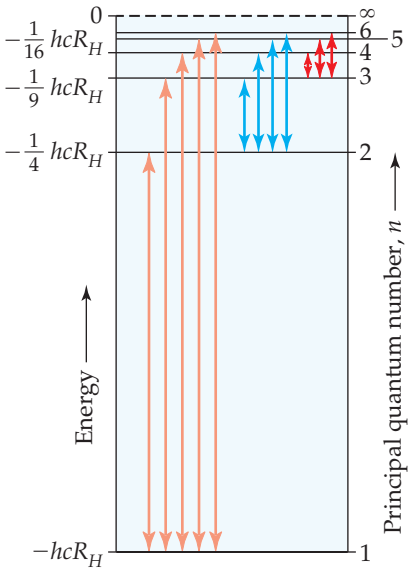
$$E = (-hcR_H)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18}\,J)\left(\frac{1}{n^2}\right) \qquad [6.5]$$

where h, c, and R_H are the Planck constant, the speed of light, and the Rydberg constant, respectively. The integer n, which can have whole-number values of 1, 2, 3, ... ∞, is called the **principal quantum number**.

Each allowed orbit corresponds to a different value of n. The radius of the orbit gets larger as n increases. Thus, the first allowed orbit (the one closest to the nucleus) has $n = 1$, the next allowed orbit (the one second closest to the nucleus) has $n = 2$, and so forth. The electron in the hydrogen atom can be in any allowed orbit, and Equation 6.5 tells us the energy the electron has in each allowed orbit.

Go Figure

If the transition of an electron from the $n = 3$ state to the $n = 2$ state results in emission of visible light, is the transition from the $n = 2$ state to the $n = 1$ state more likely to result in the emission of infrared or ultraviolet radiation?



▲ **Figure 6.11 Energy levels in the hydrogen atom from the Bohr model.** The arrows refer to the transitions of the electron from one allowed energy state to another. The states shown are those for which $n = 1$ through $n = 6$ and the state for $n = \infty$ for which the energy, E, equals zero.

Note that the energies of the electron given by Equation 6.5 are negative for all values of n. The lower (more negative) the energy is, the more stable the atom is. The energy is lowest (most negative) for $n = 1$. As n gets larger, the energy becomes less negative and therefore increases. We can liken the situation to a ladder in which the rungs are numbered from the bottom. The higher one climbs (the greater the value of n), the higher the energy. The lowest-energy state ($n = 1$, analogous to the bottom rung) is called the **ground state** of the atom. When the electron is in a higher-energy state ($n = 2$ or higher), the atom is said to be in an **excited state**. Figure 6.11 shows the allowed energy levels for the hydrogen atom for several values of n.

What happens as n becomes infinitely large? The radius increases and the energy of attraction between the electron and the nucleus approaches zero, so when $n = \infty$ the electron is completely separated from the nucleus and the energy of the electron is zero:

$$E = (-2.18 \times 10^{-18}\,\text{J})\left(\frac{1}{\infty^2}\right) = 0$$

The state in which the electron is completely separated from the nucleus is called the *reference*, or zero-energy, state of the hydrogen atom.

In his third postulate, Bohr assumed that the electron can "jump" from one allowed orbit to another by either absorbing or emitting photons whose radiant energy corresponds exactly to the energy difference between the two orbits. The electron must absorb energy in order to move to a higher-energy state (higher value of n). Conversely, radiant energy is emitted when the electron jumps to a lower-energy state (lower value of n).

Let's consider a case in which the electron jumps from an initial state with principal quantum number n_i and energy E_i to a final state with principal quantum number n_f and energy E_f. Using Equation 6.5, we see that the change in energy for this transition is

$$\Delta E = E_f - E_i = (-2.18 \times 10^{-18}\,\text{J})\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad [6.6]$$

What is the significance of the *sign* of ΔE? Notice that ΔE is positive when n_f is greater than n_i. That makes sense to us because that means the electron is jumping to a higher-energy orbit. Conversely, ΔE is negative when n_f is less than n_i; the electron is falling in energy to a lower-energy orbit.

As noted earlier, transitions from one allowed state to another will involve a photon. *The energy of the photon* (E_{photon}) *must equal the difference in energy between the two states* (ΔE). When ΔE is positive, a photon must be *absorbed* as the electron jumps to a higher energy. When ΔE is negative, a photon is *emitted* as the electron falls to a lower-energy level. In both cases, the energy of the photon must match the energy difference between the states. Because the frequency ν is always a positive number, the energy of the photon ($h\nu$) must always be positive. Thus, the sign of ΔE tells us whether the photon is absorbed or emitted:

$\Delta E > 0$ ($n_f > n_i$): Photon *absorbed* with $E_{photon} = h\nu = \Delta E$

$\Delta E < 0$ ($n_f < n_i$): Photon *emitted* with $E_{photon} = h\nu = -\Delta E$ [6.7]

These two situations are summarized in Figure 6.12. We see that Bohr's model of the hydrogen atom leads to the conclusion that only the specific frequencies of light that satisfy Equation 6.7 can be absorbed or emitted by the atom.

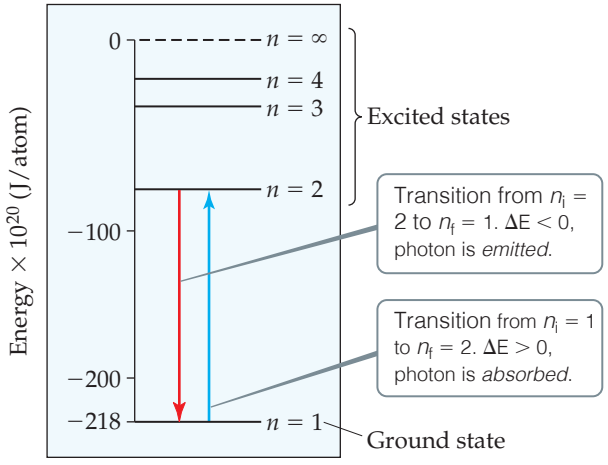
Let's see how to apply these concepts by considering a transition in which the electron moves from $n_i = 3$ to $n_f = 1$. From Equation 6.6 we have

$$\Delta E = (-2.18 \times 10^{-18}\,\text{J})\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$$

$$= (-2.18 \times 10^{-18}\,\text{J})\left(\frac{8}{9}\right) = -1.94 \times 10^{-18}\,\text{J}$$

Go Figure

Which transition will lead to the emission of light with longer wavelength, $n = 3$ to $n = 2$, or $n = 4$ to $n = 3$?



▲ **Figure 6.12 Change in energy states for absorption and emission of a photon in a hydrogen atom.**

The value of ΔE is negative—that makes sense because the electron is falling from a higher-energy orbit ($n = 3$) to a lower-energy orbit ($n = 1$). A photon is *emitted* during this transition, and the energy of the photon is equal to $E_{photon} = h\nu = -\Delta E = +1.94 \times 10^{-18}$ J.

Knowing the energy of the emitted photon, we can calculate either its frequency or its wavelength. For the wavelength, we combine Equations 6.1 ($\lambda = c/\nu$) and 6.3 ($E_{photon} = h\nu$) to obtain

$$\lambda = \frac{c}{\nu} = \frac{hc}{E_{photon}} = \frac{hc}{-\Delta E} = \frac{(6.626 \times 10^{-34}\,\cancel{\text{J-s}})(2.998 \times 10^{8}\,\text{m}/\cancel{\text{s}})}{+1.94 \times 10^{-18}\,\cancel{\text{J}}} = 1.02 \times 10^{-7}\,\text{m}$$

Thus, a photon of wavelength 1.02×10^{-7} m (102 nm) is *emitted*.

We are now in a position to understand the remarkable simplicity of the line spectra of hydrogen, first discovered by Balmer. We recognize that the line spectra are the result of emission, so $E_{photon} = h\nu = hc/\lambda = -\Delta E$ for these transitions. Combining Equations 6.5 and 6.6, we see that

$$E_{photon} = \frac{hc}{\lambda} = -\Delta E = hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{(for emission)}$$

which gives us

$$\frac{1}{\lambda} = \frac{hcR_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \text{where } n_f < n_i$$

Thus, the existence of discrete spectral lines can be attributed to the quantized jumps of electrons between energy levels.

Sample Exercise 6.4

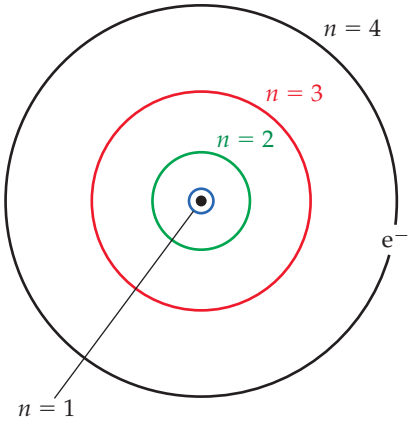
Electronic Transitions in the Hydrogen Atom

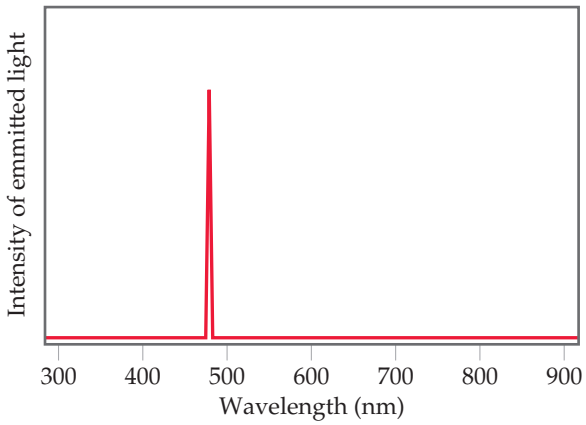
In the Bohr model of the hydrogen atom, electrons are confined to orbits with fixed radii, and those radii can be calculated. The radii of the first four orbits are 0.53, 2.12, 4.76, and 8.46 Å, respectively, as depicted here.

(**a**) If an electron makes a transition from the $n_i = 4$ level to a lower-energy level, $n_f = 3$, 2, or 1, which transition would produce a photon with the shortest wavelength?

(**b**) What are the energy and wavelength of such a photon, and in which region of the electromagnetic spectrum does it lie?

(**c**) The image on the right shows the output of a detector that measures the intensity of light emitted from a sample of hydrogen atoms that have been excited so that each atom begins with an electron in the $n = 4$ state. What is the final state, n_f, of the transition being detected?





SOLUTION

Analyze We are asked to determine the energy and wavelength associated with various transitions involving an electron relaxing from the $n = 4$ state of the hydrogen atom to one of three lower-energy states.

Plan Given the integers representing the initial and final states of the electron, we can use Equation 6.6 to calculate the energy of the photon emitted and then use the relationships $E = h\nu$ and $c = \nu\lambda$ to convert energy to wavelength. The photon with the highest energy will have the shortest wavelength because photon energy is inversely proportional to wavelength.

Continued

Solve

(a) The wavelength of a photon is related to its energy through the relationship $E = h\nu = hc/\lambda$. Hence, the photon with the smallest wavelength will have the largest energy. The energy levels of the electron orbits decrease as n decreases.

The electron loses the most energy on transitioning from the $n_i = 4$ state to the $n_f = 1$ state, and the photon emitted in that transition has the highest energy and the smallest wavelength.

(b) We first calculate the energy of the photon using Equation 6.6 with $n_i = 4$ and $n_f = 1$:

$$\Delta E = -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) = -2.04 \times 10^{-18}\,\text{J}$$

$$E_{\text{photon}} = -\Delta E = 2.04 \times 10^{-18}\,\text{J}$$

Next we rearrange Planck's relationship to calculate the frequency of the emitted photon.

$$\nu = E/h = (2.04 \times 10^{-18}\,\cancel{\text{J}})/(6.626 \times 10^{-34}\,\cancel{\text{J}}\text{-s}) = 3.02 \times 10^{15}\,\text{s}^{-1}$$

Finally, we use the frequency to determine the wavelength.

$$\lambda = c/\nu = (2.998 \times 10^{8}\,\text{m}/\cancel{\text{s}})/(3.02 \times 10^{15}\,\cancel{\text{s}^{-1}}) = 9.72 \times 10^{-8}\,\text{m} = 97.2\,\text{nm}$$

Light with this wavelength falls in the ultraviolet region of the electromagnetic spectrum.

(c) From the graph, we estimate the wavelength of the photon to be approximately 480 nm. Starting from the wavelength, it is easiest to estimate n_f using Equation 6.4:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Rearranging:

$$\frac{1}{n_f^2} = \frac{1}{n_i^2} + \frac{1}{R_H\lambda} = \frac{1}{4^2} + \frac{1}{(1.097 \times 10^{7}\,\cancel{\text{m}^{-1}})(480 \times 10^{-9}\,\cancel{\text{m}})}$$

$$\frac{1}{n_f^2} = 0.25$$

So $n_f = 2$, and the photons seen by the detector are those emitted when an electron transitions from the $n_f = 4$ to the $n_f = 2$ state.

Check Referring back to Figure 6.11, we confirm that the $n = 4$ to $n = 1$ transition should have the largest energy of the three possible transitions.

Practice Exercise

In the top part of Figure 6.10, the four lines in the H atom spectrum are due to transitions from a level for which $n_i > 2$ to the $n_f = 2$ level. What is the value of n_i for the red line in the spectrum? (**a**) 3 (**b**) 4 (**c**) 5 (**d**) 6 (**e**) 7

Limitations of the Bohr Model

Although the Bohr model explains the line spectrum of the hydrogen atom, it can not explain the spectra of other atoms, except in a crude way. Bohr also avoided the problem of why the negatively charged electron would not just fall into the positively charged nucleus, by simply assuming it would not happen. Furthermore, we will see that Bohr's model of an electron orbiting the nucleus at a fixed distance is not a realistic picture. As we will see in Section 6.4, the electron exhibits wave-like properties, a fact that any acceptable model of electronic structure must accommodate.

As it turns out, the Bohr model was only an important step along the way toward the development of a more comprehensive model. What is most significant about Bohr's model is that it introduces two important ideas that are also incorporated into our current model:

1. *Electrons exist only in certain discrete energy levels, which are described by quantum numbers.*
2. *Energy is involved in the transition of an electron from one level to another.*

We will now start to develop the successor to the Bohr model, which requires that we take a closer look at the behavior of matter.

Self-Assessment Exercise

6.14 Which transition would result in emission of the shortest wavelength photon?

(a) from $n = 4$ to $n = 2$

(b) from $n = 6$ to $n = 4$

(c) from $n = 10$ to $n = 6$

(d) from $n = 100$ to $n = 10$

Exercises

6.15 Does the hydrogen atom "expand" or "contract" when an electron is excited from the $n = 1$ state to the $n = 3$ state?

6.16 Is energy emitted or absorbed when the following electronic transitions occur in hydrogen? (**a**) from $n = 3$ to $n = 2$, (**b**) from an orbit of radius 0.846 nm to one of radius 0.212 nm, (**c**) an electron adds to the H^+ ion and ends up in the $n = 2$ shell?

6.17 (**a**) Using Equation 6.5, calculate the energy of an electron in the hydrogen atom when $n = 3$ and when $n = 6$. Calculate the wavelength of the radiation released when an electron moves from $n = 6$ to $n = 3$. (**b**) Is this line in the visible region of the electromagnetic spectrum?

6.18 The visible emission lines observed by Balmer all involved $n_f = 2$. (**a**) Which of the following is the best explanation of why the lines with $n_f = 3$ are not observed in the visible portion of the spectrum: (i) Transitions to $n_f = 3$ are not allowed to happen, (ii) transitions to $n_f = 3$ emit photons in the infrared portion of the spectrum, (iii) transitions to $n_f = 3$ emit photons in the ultraviolet portion of the spectrum, or (iv) transitions to $n_f = 3$ emit photons that are at exactly the same wavelengths as those to $n_f = 2$. (**b**) Calculate the wavelengths of the first three lines in the Balmer series—those for which $n_i = 3, 4$, and 5—and identify these lines in the emission spectrum shown in Figure 6.10.

6.19 One of the emission lines of the hydrogen atom has a wavelength of 94.974 nm. (**a**) In what region of the electromagnetic spectrum is this emission found? (**b**) Determine the initial and final values of n associated with this emission.

6.20 Order the following transitions in the hydrogen atom from smallest to largest frequency of light absorbed: $n = 3$ to $n = 7$, $n = 4$ to $n = 8$, $n = 2$ to $n = 5$, and $n = 1$ to $n = 3$.

Answers to Self-Assessment Exercise

6.14 (a)

6.4 The Wave Behavior of Matter



Sometimes, things are not what they seem! A movie film is based on motion and change yet slow the film down enough and it becomes evident it is made of a

progression of still pictures. We live in a macroscopic world where every object is composed of millions upon millions of atoms. Dial down to an atomic scale and we glimpse another realm.

By the end of this section, you should be able to

- Appreciate that a wave–particle duality and position–momentum uncertainty become significant when dealing with electrons.

In the years following the development of Bohr's model for the hydrogen atom, the dual nature of radiant energy became a familiar concept. Depending on the experimental circumstances, radiation appears to have either a wave-like or a particle-like (photon) character. Louis de Broglie (1892–1987), who was working on his Ph.D. thesis in physics at the Sorbonne in Paris, boldly extended this idea: If radiant energy could, under appropriate conditions, behave as though it were a stream of particles (photons), could matter, under appropriate conditions, possibly show the properties of a wave?

De Broglie suggested that an electron moving about the nucleus of an atom behaves like a wave and therefore has a wavelength. He proposed that the wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity, v:

$$\lambda = \frac{h}{mv} \qquad [6.8]$$

where h is the Planck constant. The quantity mv for any object is called its **momentum**. De Broglie used the term **matter waves** to describe the wave characteristics of material particles.

Because de Broglie's hypothesis is applicable to all matter, any object of mass m and velocity v would give rise to a characteristic matter wave. However, Equation 6.8 indicates that the wavelength associated with an object of ordinary size, such as a golf ball, is so tiny as to be completely unobservable. This is not so for an electron because its mass is so small, as we see in Sample Exercise 6.5.

Sample Exercise 6.5

Matter Waves

What is the wavelength of an electron moving with a speed of 5.97×10^6 m/s? The mass of the electron is 9.11×10^{-31} kg.

SOLUTION

Analyze We are given the mass, m, and velocity, v, of the electron, and we must calculate its de Broglie wavelength, λ.

Plan The wavelength of a moving particle is given by Equation 6.8, so λ is calculated by inserting the known quantities h, m, and v. In doing so, however, we must pay attention to units.

Solve

Using the value of the Planck constant:

$$h = 6.626 \times 10^{-34}\ \text{J-s}$$

we have the following:

$$\lambda = \frac{h}{mv}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J-s})}{(9.11 \times 10^{-31}\ \text{kg})(5.97 \times 10^{6}\ \text{m/s})}\left(\frac{1\ \text{kg-m}^2/\text{s}^2}{1\ \text{J}}\right)$$

$$= 1.22 \times 10^{-10}\ \text{m} = 0.122\ \text{nm} = 122\ \text{pm}$$

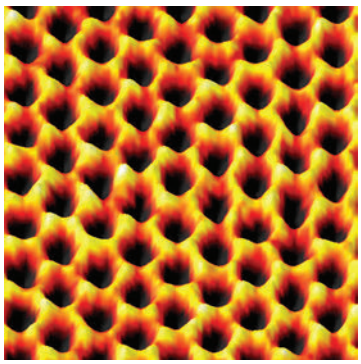
Comment By comparing this value with the wavelengths of electromagnetic radiation shown in Figure 6.4, we see that the wavelength of this electron is about the same as that of X rays.

Practice Exercise

Consider the following three moving objects: (i) a golf ball with a mass of 45.9 g moving at a speed of 50.0 m/s, (ii) An electron moving at a speed of 3.50×10^5 m/s, (iii) A neutron moving at a speed of 2.3×10^2 m/s. List the three objects in order from shortest to longest de Broglie wavelength.
(**a**) i < iii < ii (**b**) ii < iii < i (**c**) iii < ii < i (**d**) i < ii < iii
(**e**) iii < i < ii

A few years after de Broglie published his theory, the wave properties of the electron were demonstrated experimentally. When X rays pass through a crystal, an interference pattern results that is characteristic of the wave-like properties of electromagnetic radiation, a phenomenon called *X-ray diffraction*. As electrons pass through a crystal, they are similarly diffracted. Thus, a stream of moving electrons exhibits the same kinds of wave behavior as X rays and all other types of electromagnetic radiation.

The technique of electron diffraction has been highly developed. In the electron microscope, for instance, the wave characteristics of electrons are used to obtain images at the atomic scale. This microscope is an important tool for studying surface phenomena at very high magnifications (**Figure 6.13**). Electron microscopes can magnify objects by 3,000,000 times, far more than can be done with visible light (1000×), because the wavelength of the electrons is so much smaller than the wavelength of visible light.



▲ **Figure 6.13 Electrons as waves.** Transmission electron micrograph of *graphene*, which has a hexagonal honeycomb arrangement of carbon atoms. Each of the bright yellow "mountains" indicates a carbon atom.

The Uncertainty Principle

The discovery of the wave properties of matter raised some new and interesting questions. Consider, for example, a ball rolling down a ramp. Using the equations of classical physics, we can calculate, with great accuracy, the ball's position, direction of motion, and speed at any instant. Can we do the same for an electron, which exhibits wave properties? A wave extends in space, and its location is not precisely defined. We might therefore anticipate that it is impossible to determine exactly where an electron is located at a specific instant.

The German physicist Werner Heisenberg (**Figure 6.14**) proposed that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of an object at a given instant. The limitation becomes important only when we deal with matter at the subatomic level (that is, with masses as small as that of an electron). Heisenberg's principle is called the **uncertainty principle**. When applied to the electrons in an atom, this principle states that it is impossible for us to know simultaneously both the exact momentum of an electron and its exact location in space.



▲ **Figure 6.14 Werner Heisenberg (1901–1976).** During his postdoctoral assistantship with Niels Bohr, Heisenberg formulated his famous uncertainty principle. At 32 he was one of the youngest scientists to receive a Nobel Prize.

Heisenberg mathematically related the uncertainty in position, Δx, and the uncertainty in momentum, $\Delta(mv)$, to a quantity involving the Planck constant:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi} \qquad [6.9]$$

A brief calculation illustrates the dramatic implications of the uncertainty principle. The electron has a mass of 9.11×10^{-31} kg and moves at an average speed of about 5×10^6 m/s in a hydrogen atom. Let's assume that we know the speed to an uncertainty of 1% [that is, an uncertainty of $(0.01)(5 \times 10^6\ \text{m/s}) = 5 \times 10^4\ \text{m/s}$] and that this is the only important source of uncertainty in the momentum, so that $\Delta(mv) = m\,\Delta v$. We can use Equation 6.9 to calculate the uncertainty in the position of the electron:

$$\Delta x \geq \frac{h}{4\pi m \Delta v} = \left(\frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(9.11 \times 10^{-31}\ \text{kg})(5 \times 10^4\ \text{m/s})}\right) = 1 \times 10^{-9}\ \text{m}$$

Because the diameter of a hydrogen atom is about 1×10^{-10} m, the uncertainty in the position of the electron in the atom is an order of magnitude greater than the size of the atom. Thus, we have essentially no idea where the electron is located in the atom. On the other hand, if we were to repeat the calculation with an object of ordinary mass, such as a tennis ball, the uncertainty would be so small that it would be inconsequential. In that case, m is large and Δx is out of the realm of measurement and therefore of no practical consequence.

De Broglie's hypothesis and Heisenberg's uncertainty principle set the stage for a new and more broadly applicable theory of atomic structure. In this approach, any attempt to define precisely the instantaneous location and momentum of the electron is abandoned. The wave nature of the electron is recognized, and its behavior is described in terms appropriate to waves. The result is a model that precisely describes the energy of the electron while describing its location not precisely but rather in terms of probabilities.

A CLOSER LOOK Measurement and the Uncertainty Principle

Whenever any measurement is made, some uncertainty exists. Our experience with objects of ordinary dimensions, such as balls or trains or laboratory equipment, indicates that using more precise instruments can decrease the uncertainty of a measurement. In fact, we might expect that the uncertainty in a measurement can be made infintesimally small. However, the uncertainty principle states that there is an actual limit to the accuracy of measurements. This limit is not a restriction on how well instruments can be made; rather, it is inherent in nature. This limit has no practical consequences when dealing with ordinary-sized objects, but its implications are enormous when dealing with subatomic particles, such as electrons.

To measure an object, we must disturb it, at least a little, with our measuring device. Imagine using a flashlight to locate a large rubber ball in a dark room. You see the ball when the light from the flashlight bounces off the ball and strikes your eyes. When a beam of photons strikes an object of this size, it does not alter its position or momentum to any practical extent. Imagine, however, that you wish to locate an electron by similarly bouncing light off it into some detector. Objects can be located to an accuracy no greater than the wavelength of the radiation used. Thus, if we want an accurate position measurement for an electron, we must use a short wavelength. This means that photons of high energy must be employed. The more energy the photons have, the more momentum they impart to the electron when they strike it, which changes the electron's motion in an unpredictable way. The attempt to measure accurately the electron's position introduces considerable uncertainty in its momentum; the act of measuring the electron's position at one moment makes our knowledge of its future position inaccurate.

Suppose, then, that we use photons of longer wavelength. Because these photons have lower energy, the momentum of the electron is not so appreciably changed during measurement, but at the same time the longer wavelength limits the accuracy with which the electron's position can be determined. This is the essence of the uncertainty principle: *There is an uncertainty in simultaneously knowing both the position and the momentum of the electron that cannot be reduced beyond a certain minimum level*. The more accurately one is known, the less accurately the other is known.

Although we can never know the exact position and momentum of the electron, we can talk about the probability of its being at certain locations in space. In Section 6.5, we introduce a model of the atom that provides the probability of finding electrons of specific energies at certain positions in atoms.

Related Exercises: 6.25, 6.75, 6.105, 6.106

Self-Assessment Exercises

6.21 Is this statement true or false: *when considering a small fast moving object such as an electron, we can never measure both its position and velocity with great accuracy*?

(a) True

(b) False

6.22 Is this statement true or false: *the wave-particle duality becomes significant with objects the size of an electron*?

(a) True

(b) False

Exercises

6.23 Use the de Broglie relationship to determine the wavelengths of the following objects: (**a**) an 85 kg person skiing at 50 km/hr, (**b**) a 10.0 g bullet fired at 250 m/s, (**c**) a lithium atom of mass 11.5×10^{-27} kg moving at 2.5×10^{5} m/s.

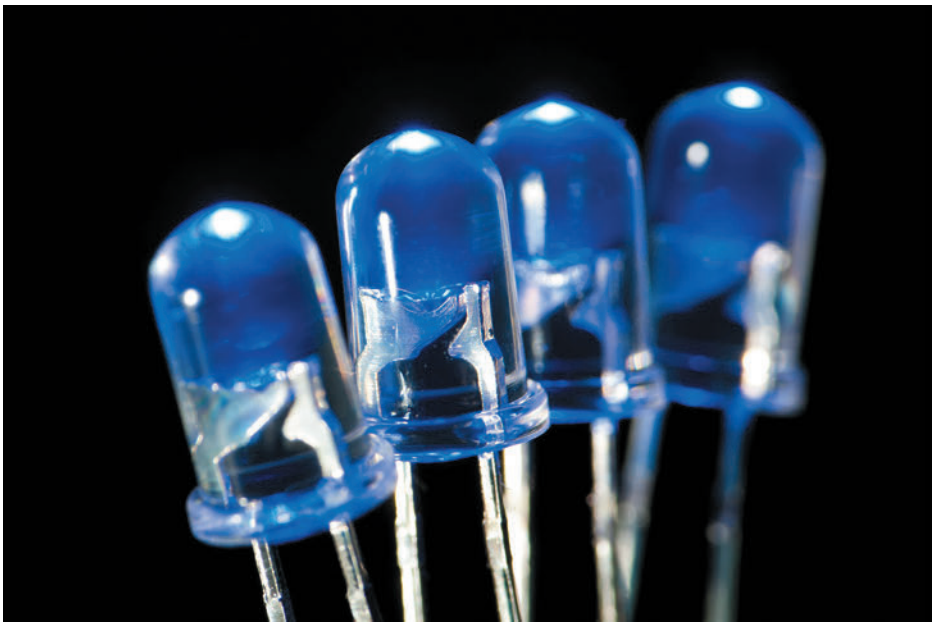
6.24 Neutron diffraction is an important technique for determining the structures of molecules. Calculate the velocity of a neutron needed to achieve a wavelength of 125 pm. (Refer to the inside cover for the mass of the neutron.)

6.25 Using Heisenberg's uncertainty principle, calculate the uncertainty in the position of (**a**) a 1.50-mg mosquito moving at a speed of 1.40 m/s if the speed is known to within ± 0.01 m/s; (**b**) a proton moving at a speed of $(5.00 \pm 0.01) \times 10^{4}$ m/s. (The mass of a proton is given in the table of fundamental constants in the inside cover of the text.)

Answers to Self-Assessment Exercise

6.21 (a) **6.22** (a)

6.5 Quantum Mechanics and Atomic Orbitals



Quantum theory led to the explosion in technological developments in the twentieth century, including remarkable new light sources, such as light-emitting diodes (LEDs), which are now being used as high-quality, low-energy-consumption light sources in many applications, and lasers, which have revolutionized so many aspects of our lives. Quantum theory also led to the development of the solid-state electronics that are at the heart of computers, cellular telephones, and countless other electronic devices.

By the end of this section, you should be able to

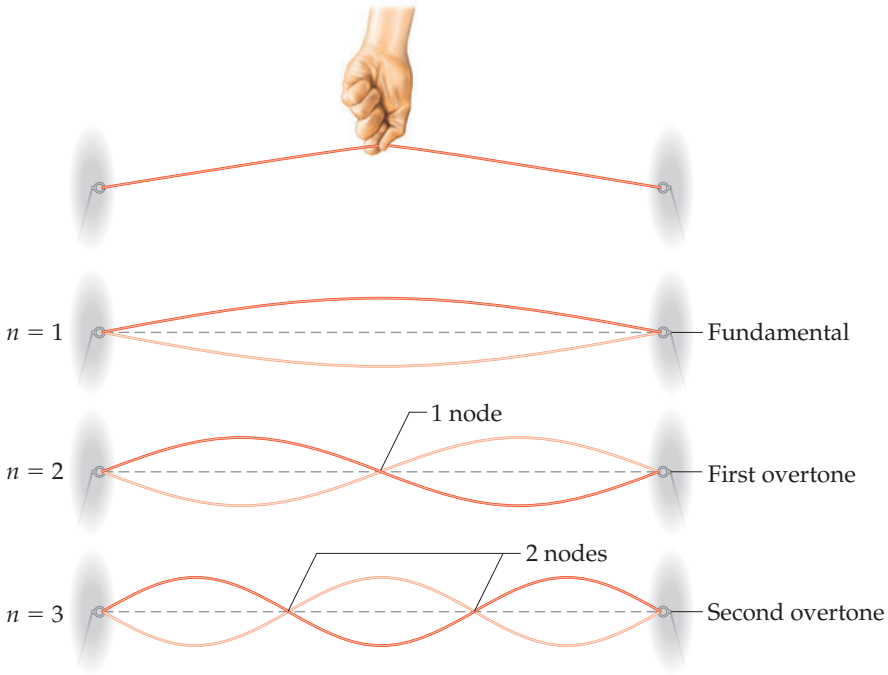
- Relate the quantum numbers to the number and type of orbitals and recognize the different orbital shapes.

In 1926, the Austrian physicist Erwin Schrödinger (1887–1961) proposed an equation, now known as *Schrödinger's wave equation*, that incorporates both the wave-like and particle-like behaviors of the electron. His work opened a new approach to dealing with subatomic particles, an approach known as *quantum mechanics* or *wave mechanics*. The application of Schrödinger's equation requires advanced calculus, and so we will not be concerned with its details. We will, however, qualitatively consider the results Schrödinger obtained because they give us a powerful new way to view electronic structure. Let's begin by examining the electronic structure of the simplest atom, hydrogen.

Schrödinger treated the electron in a hydrogen atom like the wave on a plucked guitar string (**Figure 6.15**). Because such waves do not travel in space, they are called *standing waves*. Just as the plucked guitar string produces a standing wave that has a fundamental frequency and higher overtones (harmonics), the electron exhibits a lowest-energy standing wave and higher-energy ones. Furthermore, just as the overtones of the guitar string have *nodes*, points where the magnitude of the wave is zero, so do the waves characteristic of the electron.

Solving Schrödinger's equation for the hydrogen atom leads to a series of mathematical functions called **wave functions** that describe the electron in the atom. These wave functions are usually represented by the symbol ψ (lowercase Greek letter *psi*). Although the wave function has no direct physical meaning, the square of the wave function, ψ^2, provides information about the electron's location when it is in an allowed energy state.

For the hydrogen atom, the allowed energies are the same as those predicted by the Bohr model. However, the Bohr model assumes that the electron is in a circular orbit of some particular radius about the nucleus. In the quantum-mechanical model, the electron's location cannot be described so simply.



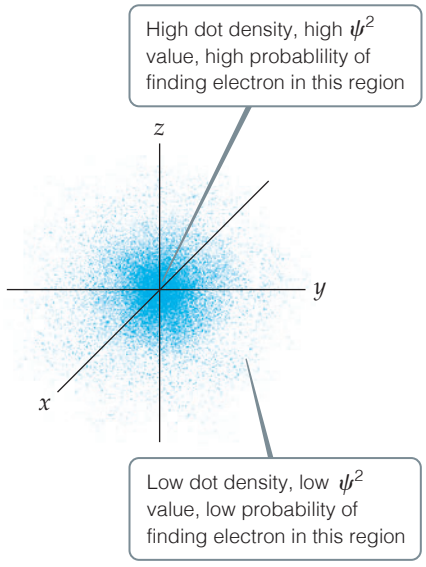
▶ **Figure 6.15** **Standing waves in a vibrating string.**

According to the uncertainty principle, if we know the momentum of the electron with high accuracy, our simultaneous knowledge of its location is very uncertain. Thus, we cannot hope to specify the exact location of an individual electron around the nucleus. Rather, we must be content with a kind of statistical knowledge. We therefore speak of the *probability* that the electron will be in a certain region of space at a given instant. As it turns out, the square of the wave function, ψ^2, at a given point in space represents the probability that the electron will be found at that location. For this reason, ψ^2 is called either the **probability density** or the **electron density**.

One way of representing the probability of finding the electron in various regions of an atom is shown in **Figure 6.16**, where the density of the dots represents the probability of finding the electron. The regions with a high density of dots correspond to relatively large values for ψ^2 and are therefore regions where there is a high probability of finding the electron. Based on this representation, we often describe atoms as consisting of a nucleus surrounded by an electron cloud.

Go Figure

Where in the figure is the region of highest electron density?



▲ **Figure 6.16** **Electron-density distribution.** This rendering represents the probability, ψ^2, of finding the electron in a hydrogen atom in its ground state. The origin of the coordinate system is at the nucleus.

Orbitals and Quantum Numbers

The solution to Schrödinger's equation for the hydrogen atom yields a set of wave functions called **orbitals**. Each orbital has a characteristic shape and energy. For example, the lowest-energy orbital in the hydrogen atom has the spherical shape illustrated in Figure 6.16 and an energy of -2.18×10^{-18} J. Note that an *orbital* (quantum-mechanical model, which describes electrons in terms of probabilities, visualized as "electron clouds") is not the same as an *orbit* (the Bohr model, which visualizes the electron moving in a physical orbit, like a planet around a star). The quantum-mechanical model does not refer to orbits because the motion of the electron in an atom cannot be precisely determined (Heisenberg's uncertainty principle).

The Bohr model introduced a single quantum number, n, to describe an orbit. The quantum-mechanical model uses three quantum numbers, n, l, and m_l, which result naturally from the mathematics used to describe an orbital.

1. The principal quantum number, n, can have positive integral values 1, 2, 3, ... As n increases, the orbital becomes larger, and the electron spends more time farther from the nucleus. An increase in n also means that the electron has a higher energy and is therefore less tightly bound to the nucleus. For the hydrogen atom, $E_n = -(2.18 \times 10^{-18}\text{J})(1/n^2)$, as in the Bohr model.

A CLOSER LOOK Thought Experiments and Schrödinger's Cat

The revolutions in scientific thinking caused by the theory of relativity and quantum theory not only changed science; it also caused deep changes in how we understand the world around us. Before relativity and quantum theory, the prevailing physical theories were inherently *deterministic*: Once the specific conditions of an object were given (position, velocity, forces acting on the object), we could determine exactly the position and motion of the object at any time in the future. These theories, from Newton's laws to Maxwell's theory of electromagnetism, successfully described physical phenomena such as motion of the planets, the trajectories of projectiles, and the diffraction of light.

Relativity and quantum theory both challenged the deterministic view of the universe, and did so in a way that caused a great deal of uneasiness among even the scientists who were developing the theories. One of the common methods scientists used to test these new theories was through so-called thought experiments. Thought experiments are hypothetical scenarios that can lead to paradoxes within a given theory. Let's briefly discuss one of these thought experiments that was used to test ideas within quantum theory.

Quantum theory caused a great deal of discussion with respect to its nondeterministic description of matter. We have touched on two such areas in this chapter. First, we have seen that the descriptions of light and matter have become less distinct—light has particle-like properties and matter has wave-like properties. The description of matter that results—in which we can talk only about the probability of an electron being at a certain place as opposed to knowing exactly where it is—was very bothersome to many. Einstein, for example, famously said that "God doesn't play dice with the world"* about this probabilistic description. Heisenberg's uncertainty principle, which assures that we can't know the position and momentum of a particle exactly, also raised many philosophical questions—so many, in fact, that Heisenberg wrote a book entitled *Physics and Philosophy* in 1958.

One of the most famous thought experiments put forward in the early days of the quantum theory was formulated by Schrödinger and is now known as "Schrödinger's cat." This experiment called into question whether a system could have multiple acceptable wave functions prior to observation of the system. In other words, if we don't actually observe a system, can we know anything about the state it is in? In this paradox, a hypothetical cat is placed in a sealed box with an apparatus that will randomly trigger a lethal dose of poison to the cat (as morbid as that sounds). According to some interpretations of quantum theory, until the box is opened and the cat is observed, the cat must be considered simultaneously alive and dead.

Schrödinger posed this paradox to point out weaknesses in some interpretations of quantum results, but the paradox has led instead to a continuing and lively debate about the fate and meaning of Schrödinger's cat. In 2012, the Nobel Prize in Physics was awarded to Serge Haroche of France and David Wineland of the United States for their ingenious methods for observing the quantum states of photons or particles without having the act of observation destroy the states. In so doing, they observed what is generally called the "cat state" of the systems, in which the photon or particle exists simultaneously in two different quantum states. A puzzling paradox, indeed, but one that might ultimately lead to new ways to harness the simultaneous states to create so-called quantum computers and more accurate clocks.

Related Exercise: 6.106

2. The second quantum number—the **angular momentum quantum number**, l—can have integral values from 0 to $(n - 1)$ for each value of n. This quantum number defines the shape of the orbital. The value of l for a particular orbital is generally designated by the letters s, p, d, and f,** corresponding to l values of 0, 1, 2, and 3:

Value of l	0	1	2	3
Letter used	s	p	d	f

3. The **magnetic quantum number**, m_l, can have integral values between $-l$ and l, including zero. This quantum number describes the orientation of the orbital in space, as we discuss in Section 6.6.

Notice that because the value of n can be any positive integer, there is an infinite number of orbitals for the hydrogen atom. At any given instant, however, the electron in a hydrogen atom is described by only one of these orbitals—we say that the electron *occupies* a certain orbital. The remaining orbitals are *unoccupied* for that particular state of the hydrogen atom. We will focus mainly on orbitals that have small values of n.

The collection of orbitals with the same value of n is called an **electron shell**. All the orbitals that have $n = 3$, for example, are said to be in the third shell. The set of orbitals that have the same n and l values is called a **subshell**. Each subshell is designated by a number (the value of n) and a letter (s, p, d, or f, corresponding to the value of l). For example, the orbitals that have $n = 3$ and $l = 2$ are called $3d$ orbitals and are in the $3d$ subshell.

*Hermanns, William, *Einstein and the Poet*: *In Search of the Cosmic Man*, 1st edition, Branden Books, 1983.

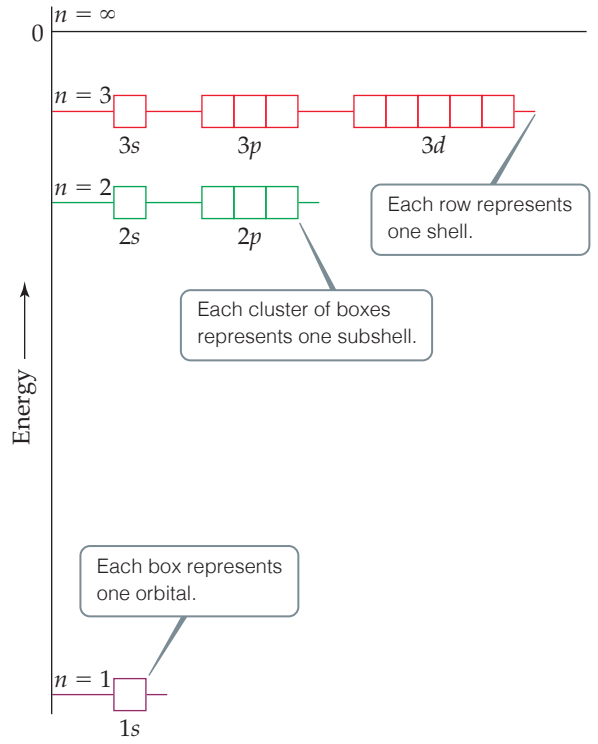
**The letters come from the words *sharp, principal, diffuse,* and *fundamental,*which were used to describe certain features of spectra before quantum mechanics was developed.

TABLE 6.2 Relationship among Values of n, l, and m_l through $n = 4$

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

Go Figure

Are the energies of the $n = 1$, 2, and 3 shells shown here the same as or different from those of the Bohr model of the atom shown in Figure 6.11?



$n = 1$ shell has one orbital
$n = 2$ shell has two subshells composed of four orbitals
$n = 3$ shell has three subshells composed of nine orbitals

▲ **Figure 6.17** Energy levels in the hydrogen atom.

Table 6.2 summarizes the possible values of l and m_l for values of n through $n = 4$. The restrictions on possible values give rise to the following very important observations:

1. *The shell with principal quantum number* n *consists of exactly* n *subshells*. Each subshell corresponds to a different allowed value of l from 0 to $(n - 1)$. Thus, the first shell $(n = 1)$ consists of only one subshell, the 1*s* $(l = 0)$; the second shell $(n = 2)$ consists of two subshells, the 2*s* $(l = 0)$ and 2*p* $(l = 1)$; the third shell consists of three subshells, 3*s*, 3*p*, and 3*d*, and so forth.
2. *Each subshell consists of a specific number of orbitals*. Each orbital corresponds to a different allowed value of m_l. For a given value of l, there are $(2l + 1)$ allowed values of m_l, ranging from $-l$ to $+l$. Thus, each *s* $(l = 0)$ subshell consists of one orbital; each *p* $(l = 1)$ subshell consists of three orbitals; each *d* $(l = 2)$ subshell consists of five orbitals, and so forth.
3. *The total number of orbitals in a shell is* n^2, *where* n *is the principal quantum number of the shell*. The resulting number of orbitals for the shells—1, 4, 9, 16—is related to a pattern seen in the periodic table: We see that the number of elements in the rows of the periodic table—2, 8, 18, and 32—equals twice these numbers. We will discuss this relationship further in Section 6.9.

Figure 6.17 shows the relative energies of the hydrogen atom orbitals through $n = 3$. Each box represents an orbital, and orbitals of the same subshell, such as the three 2*p* orbitals, are grouped together. When the electron occupies the lowest-energy orbital (1*s*), the hydrogen atom is said to be in its *ground state*. When the electron occupies any other orbital, the atom is in an *excited state*. (The electron can be excited to a higher-energy orbital by absorption of a photon of appropriate energy.) At ordinary temperatures, essentially all hydrogen atoms are in the ground state.

Sample Exercise 6.6

Subshells of the Hydrogen Atom

(**a**) Without referring to Table 6.2, predict the number of subshells in the fourth shell, that is, for $n = 4$. (**b**) Give the label for each of these subshells. (**c**) How many orbitals are in each of these subshells?

SOLUTION

Analyze and Plan We are given the value of the principal quantum number, n. We need to determine the allowed values of l and m_l for this given value of n and then count the number of orbitals in each subshell.

Solve There are four subshells in the fourth shell, corresponding to the four possible values of l (0, 1, 2, and 3).

These subshells are labeled 4*s*, 4*p*, 4*d*, and 4*f*. The number given in the designation of a subshell is the principal quantum number, n; the letter designates the value of the angular momentum quantum number, l: for $l = 0$, *s*; for $l = 1$, *p*; for $l = 2$, *d*; for $l = 3$, *f*.

There is one 4*s* orbital (when $l = 0$, there is only one possible value of m_l: 0). There are three 4*p* orbitals (when $l = 1$, there are three possible values of m_l: 1, 0, −1). There are five 4*d* orbitals (when $l = 2$, there are five allowed values of m_l: 2, 1, 0, −1, −2). There are seven 4*f* orbitals (when $l = 3$, there are seven permitted values of m_l: 3, 2, 1, 0, −1, −2, −3).

Practice Exercise

(**a**) What is the designation for the subshell with $n = 5$ and $l = 1$? (**b**) How many orbitals are in this subshell? (**c**) Indicate the values of m_l for each of these orbitals.

Self-Assessment Exercise

6.26 Which set of quantum numbers is a valid description of an orbital?

(a) $n = 2; l = 2; m_l = 0$

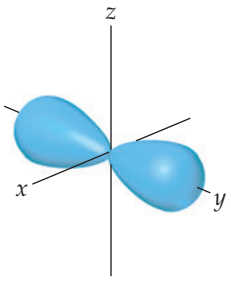
(b) $n = 0; l = 2; m_l = 2$

(c) $n = 3; l = 2; m_l = 1$

(d) $n = 2; l = 0; m_l = 1$

Exercises

6.27 Classify the following statements as either true or false: (**a**) In a contour representation of an orbital, such as the one shown here for a 2*p* orbital, the electron is confined to move about the nucleus on the outer surface of the shape. (**b**) The probability density $[\psi(r)]^2$ gives the probability of finding the electron at a specific distance from the nucleus.



6.28 (**a**) For $n = 4$, what are the possible values of l? (**b**) For $l = 2$, what are the possible values of m_l? (**c**) If m_l is 2, what are the possible values for l?

6.29 Give the numerical values of n and l corresponding to each of the following orbital designations: (**a**) 3*p*, (**b**) 2*s*, (**c**) 4*f*, (**d**) 5*d*.

6.30 A certain orbital of the hydrogen atom has $n = 4$ and $l = 3$. (**a**) What are the possible values of m_l for this orbital? (**b**) What are the possible values of m_s for the orbital?

6.31 Which of the following represent impossible combinations of n and l? (**a**) 1*p*, (**b**) 4*s*, (**c**) 5*f*, (**d**) 2*d*

Answers to Self-Assessment Exercise

6.26 (c)

6.6 Representations of Orbitals



Watching the waves break on the shore of a large lake or at the seaside can be both fascinating and relaxing. We can, perhaps, imagine waves of different sorts—a wave in one dimension might be represented by the shape of a plucked guitar string or a moving skipping rope. A wave in two dimensions is typified by the ripples in a pond after a stone has been thrown into the water. For a wave in three dimensions, think of the surface of a balloon that is pulsing in size. To simplify the situation, we may draw a cross-section of the wave as a snapshot in time, but we should always bear in mind that waves are in motion.

By the end of this section, you should be able to

- Recognize the shape and size of orbitals of a given n and l quantum number

So far, we have emphasized orbital energies, but the wave function also provides information about an electron's probable location in space. Let's examine the ways in which we can picture orbitals, because their shapes help us visualize how the electron density is distributed around the nucleus.

The s Orbitals

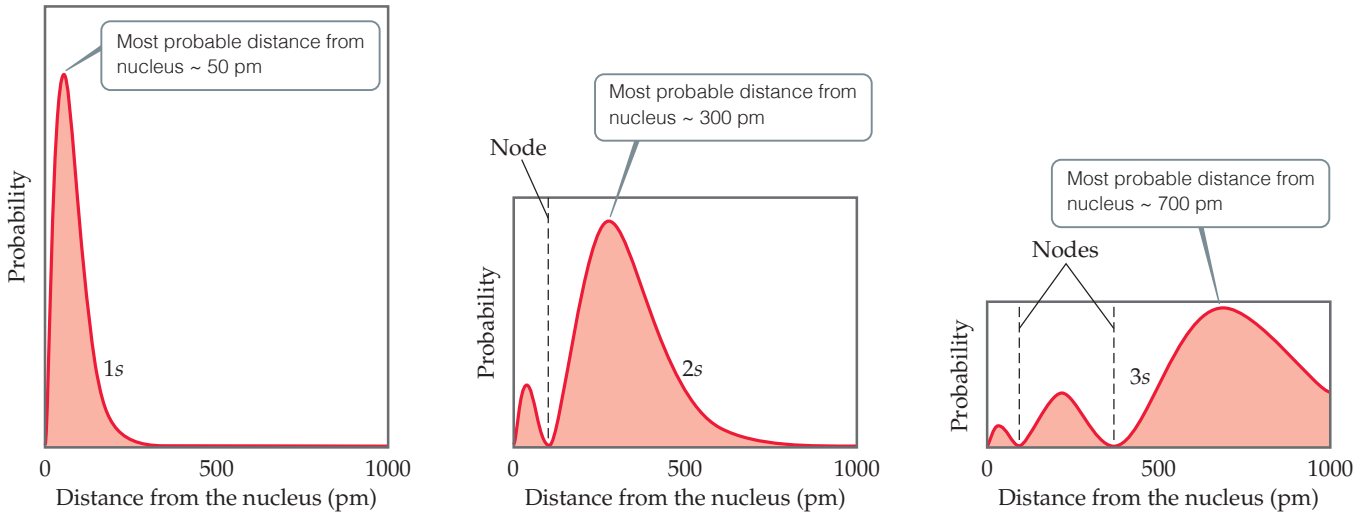
We have already seen one representation of the lowest-energy orbital of the hydrogen atom, the 1*s* (Figure 6.16). The first thing we notice about the electron density for the 1*s* orbital is that it is *spherically symmetric*—in other words, the electron density at a given distance from the nucleus is the same regardless of the direction in which we proceed from the nucleus. All of the other *s* orbitals (2*s*, 3*s*, 4*s*, and so forth) are also spherically symmetric and centered on the nucleus.

Recall that the l quantum number for the *s* orbitals is 0; therefore, the m_l quantum number must be 0. Thus, for each value of n, there is only one *s* orbital. So how do *s* orbitals differ as the value of n changes? For example, how does the electron-density distribution of the hydrogen atom change when the electron is excited from the 1*s* orbital to the 2*s* orbital? To address this question, we will look at the *radial probability density*, which is the probability that the electron is at a specific distance from the nucleus.

Figure 6.18 shows the radial probability densities for the 1*s*, 2*s*, and 3*s* orbitals of hydrogen as a function of r, the distance from the nucleus—each resulting curve is the **radial probability function** for the orbital. Three features of these plots are noteworthy: the number of peaks, the number of points at which the probability function goes to zero (called **nodes**), and how spread out the distribution is, which gives a sense of the size of the orbital.

For the 1*s* orbital, we see that the probability rises rapidly as we move away from the nucleus, maximizing at about 50 pm. Thus, when the electron occupies the 1*s* orbital, it is *most likely* to be found this distance from the nucleus*—we still use the probabilistic

Go Figure How many maxima would you expect to find in the radial probability function for the 4*s* orbital of the hydrogen atom? How many nodes would you expect in this function?



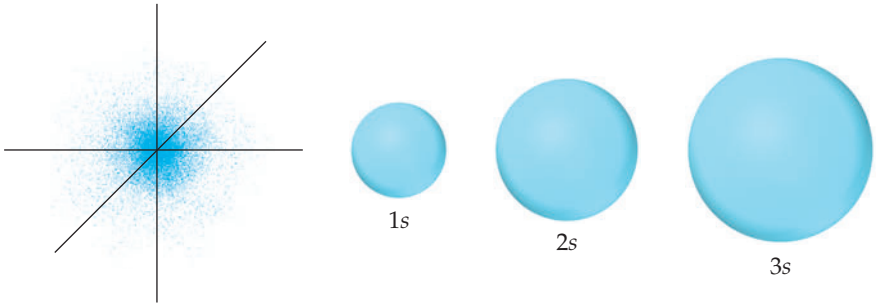
▲ **Figure 6.18 Radial probability functions for the 1*s*, 2*s*, and 3*s* orbitals of hydrogen.** These plots show the probability of finding the electron as a function of distance from the nucleus. As *n* increases, the most likely distance at which to find the electron (the highest peak) moves farther from the nucleus.

description, consistent with the uncertainty principle. Notice also that in the 1*s* orbital the probability of finding the electron at a distance greater than about 300 pm from the nucleus is essentially zero.

Comparing the radial probability distributions for the 1*s*, 2*s*, and 3*s* orbitals reveals three trends:

1. *For an* ns *orbital, the number of peaks is equal to* n, *with the outermost peak being larger than inner ones.*
2. *For an* ns *orbital, the number of nodes is equal to* $n - 1$.
3. *As* n *increases, the electron density becomes more spread out; that is, there is a greater probability of finding the electron further from the nucleus.*

One widely used method of representing orbital *shape* is to draw a boundary surface that encloses some substantial portion, say 90%, of the electron density for the orbital. This type of drawing is called a *contour representation*, and the contour representations for the *s* orbitals are spheres (**Figure 6.19**). All the orbitals have the same shape, but they differ in size, becoming larger as *n* increases, reflecting the fact that the electron density becomes more spread out as *n* increases. Although the details of how electron density varies within a given contour representation are lost in these representations, this is not a



(a) An electron density model **(b)** Contour models

◀ **Figure 6.19 Comparison of the 1*s*, 2*s*, and 3*s* orbitals.** (**a**) Electron-density distribution of a 1*s* orbital. (**b**) Contour representations of the 1*s*, 2*s*, and 3*s* orbitals. Each sphere is centered on the atom's nucleus and encloses the volume in which there is a 90% probability of finding the electron.

*In the quantum-mechanical model, the most probable distance at which to find the electron in the 1*s* orbital is actually 52.9 pm, the same as the radius of the orbit predicted by Bohr for $n = 1$. The distance 52.9 pm is often called the Bohr radius.

A CLOSER LOOK Probability Density and Radial Probability Functions

According to quantum mechanics, we must describe the position of the electron in the hydrogen atom in terms of probabilities rather than exact locations. The information about the probability is contained in the wave functions, ψ, obtained from Schrödinger's equation. The square of the wave function, ψ^2, called either the probability density or the electron density, as noted earlier, gives the probability that the electron is at any *point* in space. Because *s* orbitals are spherically symmetric, the value of ψ for an *s* electron depends only on its distance from the nucleus, *r*. Thus, the probability density can be written as $[\psi(r)]^2$, where $\psi(r)$ is the value of ψ at *r*. This function $[\psi(r)]^2$ gives the probability density for any point located a distance *r* from the nucleus.

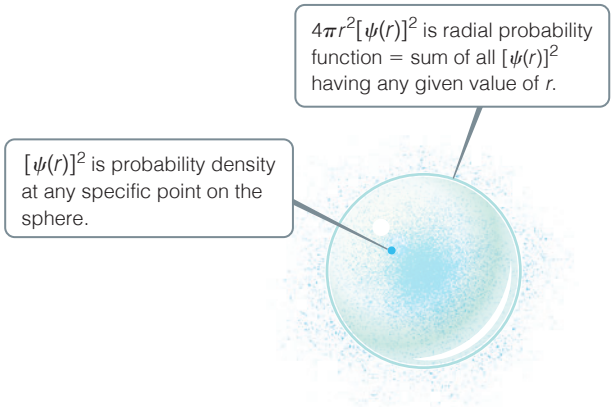
The radial probability function, which we used in Figure 6.18, differs from the probability density. The radial probability function equals the *total* probability of finding the electron at all the points at any distance *r* from the nucleus. In other words, to calculate this function, we need to "add up" the probability densities $[\psi(r)]^2$ over all points located a distance *r* from the nucleus. **Figure 6.20** compares the probability density at a point $[\psi(r)]^2$ with the radial probability function.

Let's examine the difference between probability density and radial probability function more closely. **Figure 6.21** shows plots of $[\psi(r)]^2$ as a function of *r* for the 1*s*, 2*s*, and 3*s* orbitals of the hydrogen atom. You will notice that these plots look distinctly different from the radial probability functions shown in Figure 6.18.

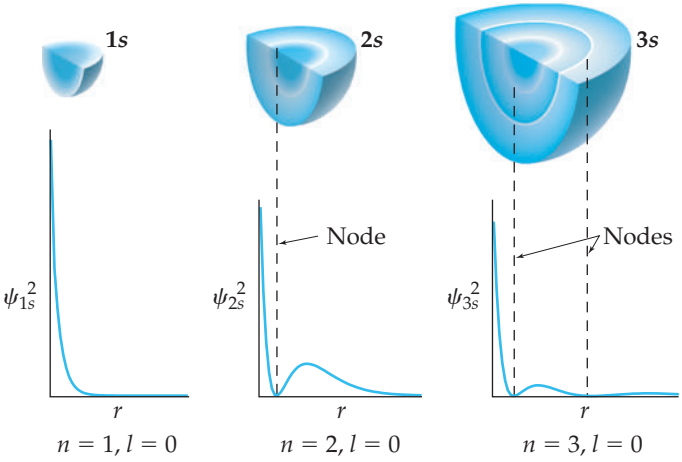
As shown in Figure 6.20, the collection of points a distance *r* from the nucleus is the surface of a sphere of radius *r*. The probability density *at each point* on that spherical surface is $[\psi(r)]^2$. To add up all the individual probability densities requires calculus and so is beyond the scope of this text. However, the result of that calculation tells us that the radial probability function is the probability density, $[\psi(r)]^2$, multiplied by the surface area of the sphere, $4\pi r^2$:

$$\text{Radial probability function at distance } r = 4\pi r^2[\psi(r)]^2$$

Thus, the plots of radial probability function in Figure 6.18 are equal to the plots of $[\psi(r)]^2$ in Figure 6.21 multiplied by $4\pi r^2$. The fact that $4\pi r^2$ increases rapidly as we move away from the nucleus makes the two sets of plots look very different from each other. For example, the plot of $[\psi(r)]^2$ for the 3*s* orbital in Figure 6.21 shows that the function generally gets smaller the farther we go from the nucleus. But when we multiply by $4\pi r^2$, we see peaks that get larger and larger (up to a certain point) as we move away from the nucleus (Figure 6.18).



▲ **Figure 6.20 Comparin g probability density $[\psi(r)]^2$ and radial probability function $4\pi r^2[\psi(r)]^2$.**



▲ **Figure 6.21 Probability density $[\psi(r)]^2$ in the 1*s*, 2*s*, and 3*s* orbitals of hydrogen.**

The radial probability functions in Figure 6.18 provide us with the more use ful information because they tell us the probability of finding the electron at *all* points a distance *r* from the nucleus, not just one particular point.

Related Exercises: 6.34, 6.76, 6.82, 107

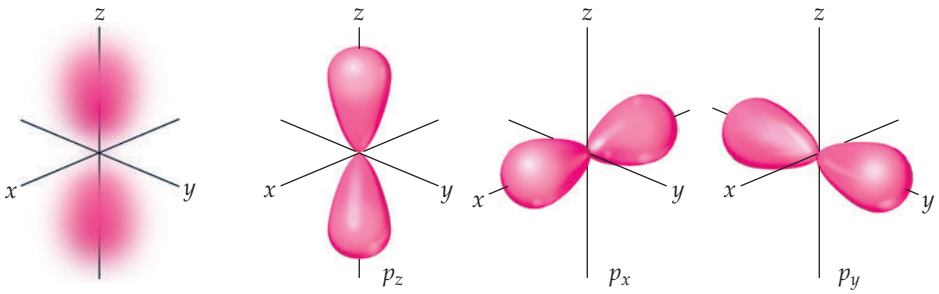
serious disadvantage. For qualitative discussions, the most important features of orbitals are shape and relative size, which are adequately displayed by contour representations.

The *p* Orbitals

Recall that the orbitals for which $l = 1$ are the *p* orbitals. Each *p* subshell has three orbitals, corresponding to the three allowed values of m_l: −1, 0, and 1. The distribution of electron density for a 2*p* orbital is shown in **Figure 6.22(a)**. The electron density is not distributed spherically as in an *s* orbital. Instead, the density is concentrated in two regions on either side of the nucleus, separated by a node at the nucleus. We say that this dumbbell-shaped orbital has two *lobes*. Recall that we are making no statement of how the electron is moving within the orbital. Figure 6.22(a) portrays only the *averaged* distribution of the electron density in a 2*p* orbital.

Beginning with the $n = 2$ shell, each shell has three *p* orbitals (Table 6.2), one for each allowed value of m_l. Thus, there are three 2*p* orbitals, three 3*p* orbitals, and so forth. Each set of *p* orbitals has the dumbbell shapes shown in Figure 6.22(a) for the 2*p* orbitals. For each value of *n*, the three *p* orbitals have the same size and shape but differ from one another in spatial orientation. We usually represent *p* orbitals by drawing the shape and orientation of their wave functions, as shown in the contour representations in

Go Figure Each *p* orbital has what is called a nodal plane, a plane or sheet where the probability density goes to zero. For which of the orbitals below is the *yz* plane a nodal plane?



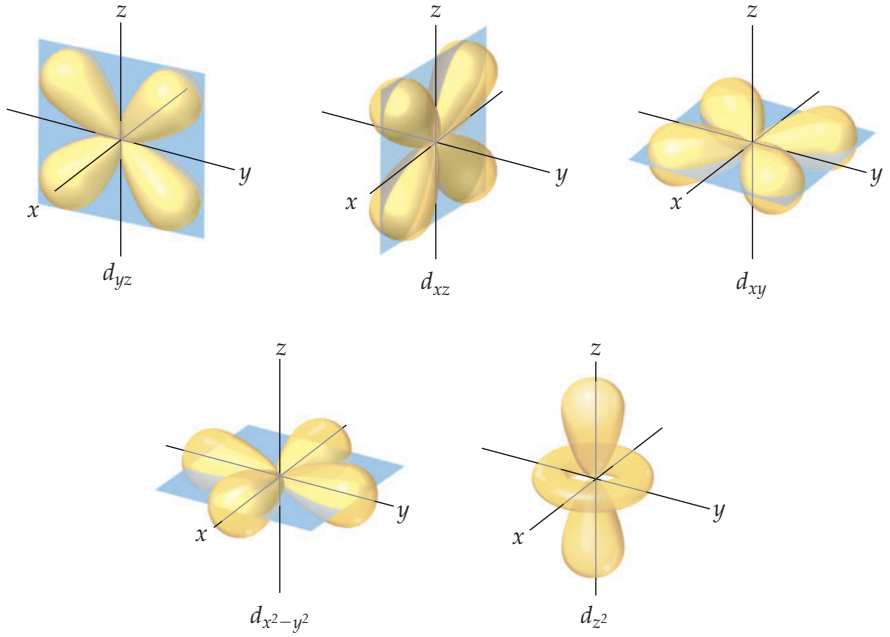
▲ **Figure 6.22 The *p* orbitals.** (**a**) Electron-density distribution of a 2*p* orbital. (**b**) Contour representations of the three *p* orbitals. The subscript on the orbital label indicates the axis along which the orbital lies.

Figure 6.22(**b**). It is convenient to label these as p_x, p_y, and p_z orbitals. The letter subscript indicates the Cartesian axis along which the orbital is oriented. Thus, we see that two orbitals with the same value of n and l, but different values of m_l, differ from each other in the way they are oriented in space.* Like *s* orbitals, *p* orbitals increase in size as we move from 2*p* to 3*p* to 4*p*, and so forth.

The *d* and *f* Orbitals

When n is 3 or greater, we encounter the *d* orbitals (for which $l = 2$). There are five 3*d* orbitals, five 4*d* orbitals, and so forth, because in each shell there are five possible values for the m_l quantum number: −2, −1, 0, 1, and 2. The different *d* orbitals in a given shell have different shapes and orientations in space, as shown in **Figure 6.23**. Four of

Go Figure How many nodal planes, two-dimensional sheets where the probability density goes to zero, are there for the d_{xy} orbital?



▲ **Figure 6.23 Contour representations of the five *d* orbitals.**

*We cannot make a simple correspondence between the subscripts (x, y, and z) and the allowed m_l values (1, 0, and −1). To explain why this is so is beyond the scope of an introductory text.

the *d*-orbital contour representations have a "four-leaf clover" shape, with four lobes, and each lies primarily in a plane. The d_{xy}, d_{xz}, and d_{yz} orbitals lie in the *xy, xz,* and *yz* planes, respectively, with the lobes oriented *between* the axes. The lobes of the $d_{x^2-y^2}$ orbital also lie in the *xy* plane, but the lobes lie *along* the *x* and *y* axes. The d_{z^2} orbital looks very different from the other four: It has two lobes along the *z* axis and a "doughnut" in the *xy* plane. Even though the d_{z^2} orbital looks different from the other *d* orbitals, it has the same energy as the other four *d* orbitals. The representations in Figure 6.23 are commonly used for all *d* orbitals, regardless of the principal quantum number.

When *n* is 4 or greater, there are seven equivalent *f* orbitals (for which $l = 3$). The shapes of the *f* orbitals are even more complicated than those of the *d* orbitals and are not presented here. As you will see in the next section, however, you must be aware of *f* orbitals as we consider the electronic structure of atoms in the lower part of the periodic table.

In many instances later in the text, you will find that knowing the number and shapes of atomic orbitals will help you understand chemistry at the molecular level. You will therefore find it useful to memorize the shapes of the *s, p,* and *d* orbitals shown in Figures 6.19, 6.22, and 6.23.

Self-Assessment Exercise

6.32 How many nodes does a 5*s* orbital have?

(a) 4 **(b)** 5 **(c)** 6

Exercises

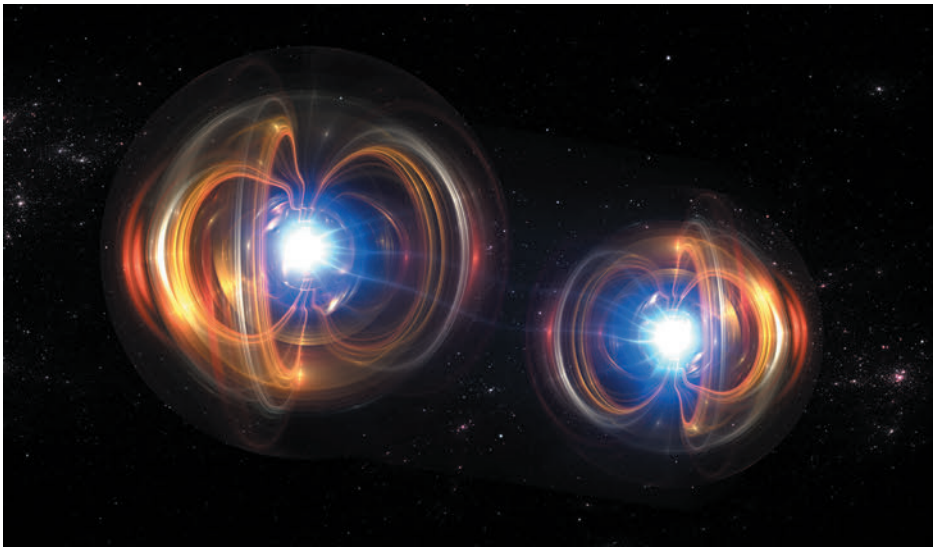
6.33 Sketch the shape and orientation of the following types of orbitals: (**a**) *s*, (**b**) p_z, (**c**) d_{xy}.

6.34 (**a**) What are the similarities of and differences between the 1*s* and 2*s* orbitals of the hydrogen atom? (**b**) In what sense does a 2*p* orbital have directional character? Compare the "directional" characteristics of the p_x and $d_{x^2-y^2}$ orbitals. (That is, in what direction or region of space is the electron density concentrated?) (**c**) What can you say about the average distance from the nucleus of an electron in a 2*s* orbital as compared with a 3*s* orbital? (**d**) For the hydrogen atom, list the following orbitals in order of increasing energy (that is, most stable ones first): 4*f*, 6*s*, 3*d*, 1*s*, 2*p*.

Answers to Self-Assessment Exercise

6.32 (a)

6.7 Many-Electron Atoms



When we propose a model to explain some set of observations, we generally start with the simplest case and work towards more complex situations to test the robustness of our model. One of our goals in this chapter has been to determine the electronic structures of atoms. So far, we have seen that quantum mechanics leads to an elegant description of the hydrogen atom. This atom, however, has only one electron. How does our description change when we consider an atom with two or more electrons (a *many-electron* atom)? To describe such an atom, we must consider the nature of orbitals and their relative energies as well as how the electrons populate the available orbitals.

By the end of this section, you should be able to

- Explain how and why the energies of the orbitals are different in a many-electron atom from those in the hydrogen atom.

Orbitals and Their Energies

We can describe the electronic structure of a many-electron atom by using the orbitals we described for the hydrogen atom in Table 6.2. Thus, the orbitals of a many-electron atom are designated 1*s*, $2p_x$, and so forth (Table 6.2) and have the same general shapes as the corresponding hydrogen orbitals.

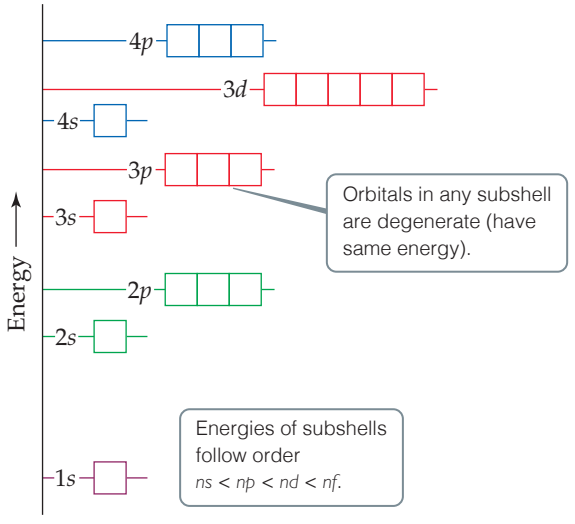
Although the shapes of the orbitals of a many-electron atom are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, *n* (Figure 6.17). For instance, in a hydrogen atom, the 3*s*, 3*p*, and 3*d* subshells all have the same energy. In a many-electron atom, however, the energies of the various subshells in a given shell are *different* because of electron–electron repulsions. To explain why this happens, we must consider the forces between the electrons and how these forces are affected by the shapes of the orbitals. We will, however, forgo this analysis until Chapter 7.

The important idea is this: *In a many-electron atom, for a given value of* n, *the energy of an orbital increases with increasing value of* l, as illustrated in **Figure 6.24**. For example, notice in Figure 6.24 that the $n = 3$ orbitals increase in energy in the order $3s < 3p < 3d$. Notice also that all orbitals of a given subshell (such as the five 3*d* orbitals) have the same energy, just as they do in the hydrogen atom. Orbitals with the same energy are said to be **degenerate**.

Figure 6.24 is a *qualitative* energy-level diagram; the exact energies of the orbitals and their spacings differ from one atom to another.

Go Figure

Not all of the orbitals in the $n = 4$ shell are shown in this figure. Which subshells are missing?



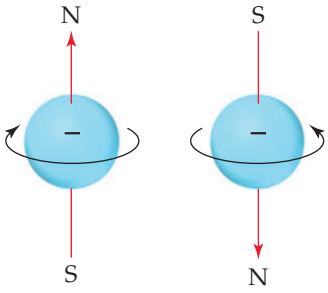
▲ **Figure 6.24** **General energy ordering of orbitals for a many-electron atom.**

Electron Spin and the Pauli Exclusion Principle

We have now seen that we can use hydrogen-like orbitals to describe many-electron atoms. What, however, determines which orbitals the electrons occupy? That is, how do the electrons of a many-electron atom populate the available orbitals? To answer this question, we must consider an additional property of the electron.

When scientists studied the line spectra of many-electron atoms in great detail, they noticed a very puzzling feature: Lines that were originally thought to be single were actually closely spaced pairs. This meant, in essence, that there were twice as many energy levels as there were "supposed" to be. In 1925, the Dutch physicists George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978) proposed a solution to this dilemma. They postulated that electrons have an intrinsic property, called **electron spin**, that causes each electron to behave as if it were a tiny sphere spinning on its own axis.

By now, it may not surprise you to learn that electron spin is quantized. This observation led to the assignment of a new quantum number for the electron, in addition to *n*, *l*, and m_l, which we have



▲ **Figure 6.25 Electron spin.** The electron behaves as if it were spinning about an axis, thereby generating a magnetic field whose direction depends on the direction of spin. The two directions for the magnetic field correspond to the two possible values for the spin quantum number, m_s. The magnetic fields that emanate from materials, like iron, arise because there are more electrons with one spin direction than the other.

already discussed. This new quantum number, the **spin magnetic quantum number**, is denoted m_s (the subscript *s* stands for *spin*). Two possible values are allowed for m_s, $+\frac{1}{2}$ or $-\frac{1}{2}$, which were first interpreted as indicating the two opposite directions in which the electron can spin. A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields (**Figure 6.25**).* These two opposite magnetic fields lead to the splitting of spectral lines into closely spaced pairs.

Electron spin is crucial for understanding the electronic structures of atoms. In 1925, the Austrian-born physicist Wolfgang Pauli (1900–1958) discovered the principle that governs the arrangement of electrons in many-electron atoms. The **Pauli exclusion principle** states that *no two electrons in an atom can have the same set of four quantum numbers* n, l, m_l, *and* m_s. For a given orbital, the values of *n*, *l*, and m_l are fixed. Thus, if we want to put more than one electron in an orbital *and* satisfy the Pauli exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two such values, we conclude that *an orbital can hold a maximum of two electrons and they must have opposite spins*. This restriction allows us to index the electrons in an atom, giving their quantum numbers and thereby defining the region in space where each electron is most likely to be found. It also provides the key to understanding the remarkable structure of the periodic table of the elements.

Self-Assessment Exercise

6.35 what is the maximum number of electrons that can occupy a 3*d* subshell?

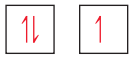
(a) 3
(b) 5
(c) 10

Exercises

6.36 (**a**) For an He^+ ion, do the 2*s* and 2*p* orbitals have the same energy? If not, which orbital has a lower energy? (**b**) If we add one electron to form the He atom, would your answer to part (a) change?

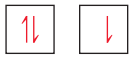
6.37 Two possible electron configurations for an Li atom are shown here. (**a**) Does either configuration violate the Pauli exclusion principle? (**b**) Does either configuration violate Hund's rule? (**c**) In the absence of an external magnetic field, can we say that one electron configuration has a lower energy than the other? If so, which one has the lowest energy?

Configuration A



1*s* 2*s*

Configuration B



1*s* 2*s*

6.38 What is the maximum number of electrons that can occupy each of the following subshells? (**a**) 3*s*, (**b**) 2*p*, (**c**) 4*d*, (**d**) 5*s*.

Answers to Self-Assessment Exercise

6.35 (c)

*As we discussed earlier, the electron has both particle-like and wave-like properties. Thus, the picture of an electron as a spinning charged sphere is, strictly speaking, just a useful pictorial representation that helps us understand the two directions of magnetic field that an electron can possess.

6.8 | Electron Configurations



The line spectrum of hydrogen can only be seen if the light from a hydrogen discharge tube is passed through a prism, or similar device. What we see is the amalgamation of the different wavelengths emitted by hydrogen—a pale purple color. Colored fireworks represent the atomic emission spectrum of different elements. If we were to pass their light through a prism, we would see a different line spectrum for each different element present. We can measure the spectrum and use it to test our theories of electron configuration. So, while quantum mechanics may appear theoretical, we can validate the predictions it makes in the study of spectroscopy.

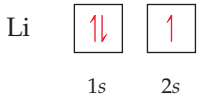
By the end of this section, you should be able to

- Draw an energy-level diagram for the orbitals in a many-electron atom and describe how electrons populate the orbitals in the ground state of an atom using the Pauli exclusion principle and Hund's rule.

Armed with knowledge of the relative energies of orbitals and the Pauli exclusion principle, we are in a position to consider the arrangements of electrons in atoms. The way electrons are distributed among the various orbitals of an atom is called the **electron configuration** of the atom.

The most stable electron configuration—the ground state—is that in which the electrons are in the lowest possible energy states. If there were no restrictions on the possible values for the quantum numbers of the electrons, all the electrons would crowd into the 1*s* orbital because it is the lowest in energy (Figure 6.24). The Pauli exclusion principle tells us, however, that there can be at most two electrons in any single orbital. Thus, *the orbitals are filled in order of increasing energy, with no more than two electrons per orbital.* For example, consider the lithium atom, which has three electrons. (Recall that the number of electrons in a neutral atom equals its atomic number.) The 1*s* orbital can accommodate two of the electrons. The third one goes into the next lowest-energy orbital, the 2*s*.

We can represent any electron configuration by writing the symbol for the occupied subshell and adding a superscript to indicate the number of electrons in that subshell. For example, for lithium we write $1s^2 2s^1$ (read "1*s* two, 2*s* one"). We can also show the arrangement of the electrons as



CHEMISTRY AND LIFE Nuclear Spin and Magnetic Resonance Imaging

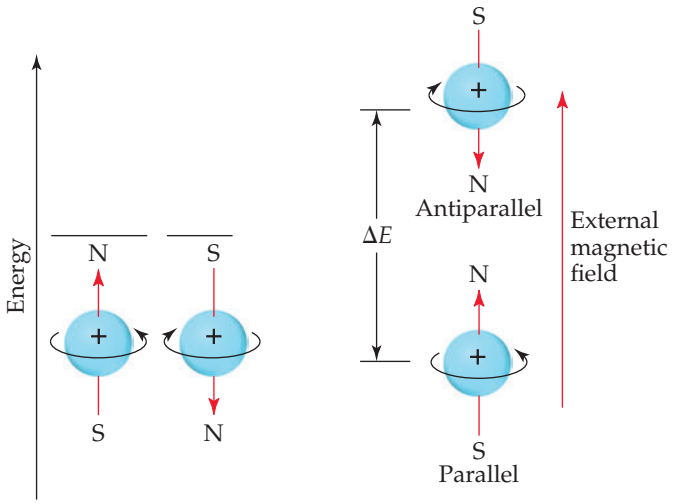
A major challenge facing medical diagnosis is seeing inside the human body. Until recently, this was accomplished primarily by X-ray technology. X rays do not, however, give well-resolved images of overlapping physiological structures, and sometimes fail to discern diseased or injured tissue. Moreover, because X rays are high-energy radiation, they potentially can cause physiological harm, even in low doses. An imaging technique developed in the 1980s called *magnetic resonance imaging* (*MRI*) does not have these disadvantages.

The foundation of MRI is a phenomenon called *nuclear magnetic resonance (NMR)*, which was discovered in the mid-1940s. Today NMR has become one of the most important spectroscopic methods used in chemistry. NMR is based on the observation that, like electrons, the nuclei of many elements possess an intrinsic spin. Like electron spin, nuclear spin is quantized. For example, the nucleus of ^1H has two possible magnetic nuclear spin quantum numbers, $+\frac{1}{2}$ and $-\frac{1}{2}$.

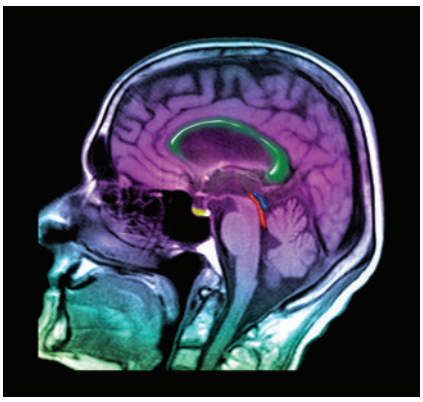
A spinning hydrogen nucleus acts like a tiny magnet. In the absence of external effects, the two spin states have the same energy. However, when the nuclei are placed in an external magnetic field, they can align either parallel or opposed (antiparallel) to the field, depending on their spin. The parallel alignment is lower in energy than the antiparallel one by a certain amount, ΔE (**Figure 6.26**). If the nuclei are irradiated with photons having energy equal to ΔE, the spin of the nuclei can be "flipped," that is, excited from the parallel to the antiparallel alignment. Detection of the flipping of nuclei between the two spin states leads to an NMR spectrum. The radiation used in an NMR experiment is in the radiofrequency range, typically 100 to 900 MHz, which is far less energetic per photon than X rays.

Because hydrogen is a major constituent of aqueous body fluids and fatty tissue, the hydrogen nucleus is the most convenient one for study by MRI. In MRI a person's body is placed in a strong magnetic field. By irradiating the body with pulses of radiofrequency radiation and using sophisticated detection techniques, medical technicians can image tissue at specific depths in the body, giving pictures with spectacular detail (**Figure 6.27**). The ability to sample at different depths allows the technicians to construct a three-dimensional picture of the body.

MRI has had such a profound influence on the modern practice of medicine that Paul Lauterbur, a chemist, and Peter Mansfield, a physicist, were awarded the 2003 Nobel Prize in Physiology or Medicine for their discoveries concerning MRI. The major drawback of this technique is expense: The current cost of a new standard MRI instrument for clinical applications is typically $1.5 million. In the 2000s, a new technique was developed, called *prepolarized MRI*, that requires much less expensive equipment and will lead to an even greater application of this important diagnostic tool.



▲ **Figure 6.26 Nuclear spin.** Like electron spin, nuclear spin generates a small magnetic field and has two allowed values. (**a**) In the absence of an external magnetic field, the two spin states have the same energy. (**b**) When an external magnetic field is applied, the spin state in which the spin direction is parallel to the direction of the external field is lower in energy than the spin state in which the spin direction is antiparallel to the field direction. The energy difference, ΔE, is in the radio frequency portion of the electromagnetic spectrum.



▲ **Figure 6.27 MRI image.** This image of a human head, obtained using magnetic resonance imaging, shows a normal brain, airways, and facial tissues.

In this representation, which we call an **orbital diagram**, each orbital is denoted by a box and each electron by a half arrow. A half arrow pointing up (↑) represents an electron with a positive spin magnetic quantum number ($m_s = +\frac{1}{2}$), and a half arrow pointing down (↓) represents an electron with a negative spin magnetic quantum number ($m_s = -\frac{1}{2}$). This pictorial representation of electron spin, which corresponds to the directions of the magnetic fields in Figure 6.25, is quite convenient. Chemists refer to the two possible spin states as "spin-up" and "spin-down" corresponding to the directions of the half arrows.

Electrons having opposite spins are said to be *paired* when they are in the same orbital (↑↓). An *unpaired electron* is one not accompanied by a partner of opposite spin. In the lithium atom the two electrons in the 1*s* orbital are paired and the electron in the 2*s* orbital is unpaired.

Hund's Rule

Consider now how the electron configurations of the elements change as we move from element to element across the periodic table.

Hydrogen Hydrogen has one electron, which occupies the 1*s* orbital in its ground state:

$$\text{H} \quad \boxed{\uparrow} \quad : 1s^1$$

1*s*

The choice of a spin-up electron here is arbitrary; we could equally well show the ground state with one spin-down electron. It is customary, however, to show unpaired electrons with their spins up.

Helium The next element, helium, has two electrons. Because two electrons with opposite spins can occupy the same orbital, both of helium's electrons are in the 1*s* orbital:

$$\text{He} \quad \boxed{\uparrow\downarrow} \quad : 1s^2$$

1*s*

The two electrons present in helium complete the filling of the first shell. This arrangement represents a very stable configuration, as is evidenced by the chemical inertness of helium.

Lithium The electron configurations of lithium and several elements that follow it in the periodic table are shown in **Table 6.3**. For the third electron of lithium, the change in the principal quantum number from $n = 1$ for the first two electrons to $n = 2$ for the third electron represents a large jump in energy and a corresponding jump in the average distance of the electron from the nucleus. In other words, it represents the start of a new shell occupied with electrons. As you can see by examining the periodic table, lithium starts a new row of the table. It is the first member of the alkali metals (Group 1).

Beryllium and Boron The element that follows lithium is beryllium; its electron configuration is $1s^2 2s^2$ (Table 6.3). Boron, atomic number 5, has the electron configuration $1s^2 2s^2 2p^1$. The fifth electron must be placed in a 2*p* orbital because the 2*s* orbital is filled. Because all three of the 2*p* orbitals are of equal energy, it does not matter which 2*p* orbital we place this fifth electron in.

TABLE 6.3 Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram				Electron Configuration
		1*s*	2*s*	2*p*	3*s*	
Li	3	↑↓	↑			$1s^2 2s^1$
Be	4	↑↓	↑↓			$1s^2 2s^2$
B	5	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^2 2s^2 2p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Carbon With the next element, carbon, we encounter a new situation. We know that the sixth electron must go into a 2*p* orbital. However, does this new electron go into the 2*p* orbital that already has one electron or into one of the other two 2*p* orbitals?

> ***Hund's rule*** *states that that when filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized.*

This means that electrons occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell all have the same spin magnetic quantum number. Electrons arranged in this way are said to have *parallel spins*. For a carbon atom to achieve its lowest energy, therefore, the two 2*p* electrons must have the same spin. For this to happen, the electrons must be in different 2*p* orbitals, as shown in Table 6.3. Thus, a carbon atom in its ground state has two unpaired electrons.

Nitrogen, Oxygen, Fluorine Similarly, for nitrogen in its ground state, Hund's rule requires that the three 2*p* electrons singly occupy each of the three 2*p* orbitals. This is the only way that all three electrons can have the same spin. For oxygen and fluorine, we place four and five electrons, respectively, in the 2*p* orbitals. To achieve this, we pair up electrons in the 2*p* orbitals, as we will see in Sample Exercise 6.7.

Hund's rule is based in part on the fact that electrons repel one another. By occupying different orbitals, the electrons remain as far as possible from one another, thus minimizing electron–electron repulsions.

Condensed Electron Configurations

The filling of the 2*p* subshell is complete at neon (Table 6.3), which has a stable configuration with eight electrons (an *octet*) in the outermost occupied shell. The next element, sodium, atomic number 11, marks the beginning of a new row of the periodic table. Sodium has a single 3*s* electron beyond the stable configuration of neon. We can therefore abbreviate the electron configuration of sodium as

$$\text{Na: } [\text{Ne}]3s^1$$

The symbol [Ne] represents the electron configuration of the ten electrons of neon, $1s^2 2s^2 2p^6$. Writing the electron configuration as $[\text{Ne}]3s^1$ focuses attention on the

Sample Exercise 6.7

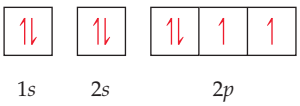
Orbital Diagrams and Electron Configurations

Draw the orbital diagram for the electron configuration of oxygen, atomic number 8. How many unpaired electrons does an oxygen atom possess?

SOLUTION

Analyze and Plan Because oxygen has an atomic number of 8, each oxygen atom has eight electrons. Figure 6.24 shows the ordering of orbitals. The electrons (represented as half arrows) are placed in the orbitals (represented as boxes) beginning with the lowest-energy orbital, the 1*s*. Each orbital can hold a maximum of two electrons (the Pauli exclusion principle). Because the 2*p* orbitals are degenerate, we place one electron in each of these orbitals (spin-up) before pairing any electrons (Hund's rule).

Solve Two electrons each go into the 1*s* and 2*s* orbitals with their spins paired. This leaves four electrons for the three degenerate 2*p* orbitals. Following Hund's rule, we put one electron into each 2*p* orbital until all three orbitals have one electron each. The fourth electron is then paired up with one of the three electrons already in a 2*p* orbital, so that the orbital diagram is



The corresponding electron configuration is written $1s^2 2s^2 2p^4$. The atom has two unpaired electrons.

Practice Exercise

How many of the elements in the second row of the periodic table (Li through Ne) will have at least one unpaired electron in their electron configurations?
(**a**) 3 (**b**) 4 (**c**) 5 (**d**) 6 (**e**) 7

outermost electron of the atom, which is the one largely responsible for how sodium behaves chemically.

We can generalize what we have just done for the electron configuration of sodium. In writing the *condensed electron configuration* of an element, the electron configuration of the nearest noble-gas element of lower atomic number is represented by its chemical symbol in brackets. For lithium, for example, we can write

$$\text{Li: } [\text{He}]2s^1$$

We refer to the electrons represented by the bracketed symbol as the *noble-gas core* of the atom. More usually, these inner-shell electrons are referred to as the **core electrons**. The electrons given after the noble-gas core are called the *outer-shell electrons*. The outer-shell electrons include the electrons involved in chemical bonding, which are called the **valence electrons**. For the elements with atomic number of 30 or less, all of the outer-shell electrons are valence electrons. By comparing the condensed electron configurations of lithium and sodium, we can appreciate why these two elements are so similar chemically. They have the same type of electron configuration in the outermost occupied shell. Indeed, all the members of the alkali metal group (1) have a single *s* valence electron beyond a noble-gas configuration (**Figure 6.28**).

1

3 **Li** $[\text{He}]2s^1$
11 **Na** $[\text{Ne}]3s^1$
19 **K** $[\text{Ar}]4s^1$
37 **Rb** $[\text{Kr}]5s^1$
55 **Cs** $[\text{Xe}]6s^1$
87 **Fr** $[\text{Rn}]7s^1$

Alkali metals

▲ **Figure 6.28** **The condensed electron configurations of the alkali metals (Group 1 in the periodic table).**

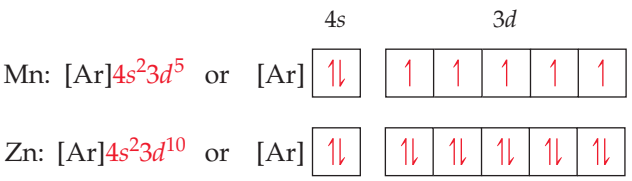
Transition Metals

The noble-gas element argon ($1s^2 2s^2 2p^6 3s^2 3p^6$) marks the end of the row started by sodium. The element following argon in the periodic table is potassium (K), atomic number 19. In all its chemical properties, potassium is clearly a member of the alkali metal group. The experimental facts about the properties of potassium leave no doubt that the outermost electron of this element occupies an *s* orbital. But this means that the electron with the highest energy has *not* gone into a 3*d* orbital, which we might expect it to do. Because the 4*s* orbital is lower in energy than the 3*d* orbital (Figure 6.24), the condensed electron configuration of potassium is

$$\text{K: } [\text{Ar}]4s^1$$

Following the complete filling of the 4*s* orbital (this occurs in the calcium atom), the next set of orbitals to be filled is the 3*d*. (You will find it helpful as we go along to refer often to the periodic table on the front-inside cover.) Beginning with scandium and extending through zinc, electrons are added to the five 3*d* orbitals until they are completely filled. Thus, the fourth row of the periodic table is ten elements wider than the two previous rows. These ten elements are known as either **transition elements** or **transition metals**. Note the position of these elements in the periodic table.

In writing the electron configurations of the transition elements, we fill orbitals in accordance with Hund's rule—we add them to the 3*d* orbitals singly until all five orbitals have one electron each and then place additional electrons in the 3*d* orbitals with spin pairing until the shell is completely filled. The condensed electron configurations and the corresponding orbital diagram representations of two transition elements are as follows:



Once all the 3*d* orbitals have been filled with two electrons each, the 4*p* orbitals begin to be occupied until the completed octet of outer electrons ($4s^2 4p^6$) is reached with krypton (Kr), atomic number 36, another of the noble gases. Rubidium (Rb) marks the beginning of the fifth row. Refer again to the periodic table on the front-inside cover. Notice that this row is in every respect like the preceding one, except that the value for *n* is greater by 1.

The Lanthanides and Actinides

The sixth row of the periodic table begins with Cs and Ba, which have [Xe]$6s^1$ and [Xe]$6s^2$ configurations, respectively. Notice, however, that the periodic table then has a break, with elements 57–70 placed below the main portion of the table. This break point is where we begin to encounter a new set of orbitals, the 4*f*.

There are seven degenerate 4*f* orbitals, corresponding to the seven allowed values of m_l, ranging from 3 to −3. Thus, it takes 14 electrons to fill the 4*f* orbitals completely. The 14 elements corresponding to the filling of the 4*f* orbitals are known as either the **lanthanide elements** or the **rare earth elements**. These elements are set below the other elements to avoid making the periodic table unduly wide. The properties of the lanthanide elements are all quite similar, and these elements occur together in nature. For many years it was virtually impossible to separate them from one another.

Because the energies of the 4*f* and 5*d* orbitals are very close to each other, the electron configurations of some of the lanthanides involve 5*d* electrons. For example, the elements lanthanum (La), cerium (Ce), and praseodymium (Pr) have the following electron configurations:

[Xe]$6s^2 5d^1$	[Xe]$6s^2 5d^1 4f^1$	[Xe]$6s^2 4f^3$
Lanthanum	Cerium	Praseodymium

Because La has a single 5*d* electron, it is sometimes placed below yttrium (Y) as the first member of the third series of transition elements; Ce is then placed as the first member of the lanthanides. Based on its chemical properties, however, La can be considered the first element in the lanthanide series. Arranged this way, there are fewer apparent exceptions to the regular filling of the 4*f* orbitals among the subsequent members of the series.

After the lanthanide series, the third transition element series is completed by the filling of the 5*d* orbitals, followed by the filling of the 6*p* orbitals. This brings us to radon (Rn), the heaviest naturally occurring noble-gas element.

The final row of the periodic table begins by filling the 7*s* orbitals. The **actinide elements**, of which uranium (U, element 92) and plutonium (Pu, element 94) are the best known, are then built up by completing the 5*f* orbitals. All of the actinide elements are radioactive, and most of them are not found in nature.

Self-Assessment Exercise

6.39 What is the condensed electron configuration of Se?

(a) [Ar] $4s^2 3d^{10} 4p^4$

(b) [Ar] $4s^2 4d^{10} 4p^4$

(c) [Ar] $4s^2 5d^{10} 4p^4$

Exercises

6.40 (**a**) What are "valence electrons"? (**b**) What are "core electrons"? (**c**) What does each box in an orbital diagram represent? (**d**) What object is represented by the half arrows in an orbital diagram? What does the direction of the arrow signify?

6.41 Write the condensed electron configurations for the following atoms, using the appropriate noble-gas core abbreviations: (**a**) Cs, (**b**) Ni, (**c**) Se, (**d**) Cd, (**e**) U, (**f**) Pb.

6.42 Identify the specific element that corresponds to each of the following electron configurations and indicate the number of unpaired electrons for each: (**a**) $1s^2 2s^2$, (**b**) $1s^2 2s^2 2p^4$, (**c**) [Ar]$4s^1 3d^5$, (**d**) [Kr]$5s^2 4d^{10} 5p^4$.

6.43 The following do not represent valid ground-state electron configurations for an atom either because they violate the Pauli exclusion principle or because orbitals are not filled in order of increasing energy. Indicate which of these two principles is violated in each example. (**a**) [Ne]$3s^2 3p^6 3d^5$ (**b**) [Xe]$6s^3$ (**c**) $1s^2 3s^1$.

Answers to Self-Assessment Exercise

6.39 (a)

6.9 Electron Configurations and the Periodic Table



In almost every chemistry lecture theatre and teaching space, there is a periodic table. It plays a central role in our thinking about chemistry. The pattern it portrays reflects the electron configuration of the atoms and hence the chemistry they undergo. It is our 'road map' to understanding the reactivity of the elements.

By the end of this section, you should be able to

- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom

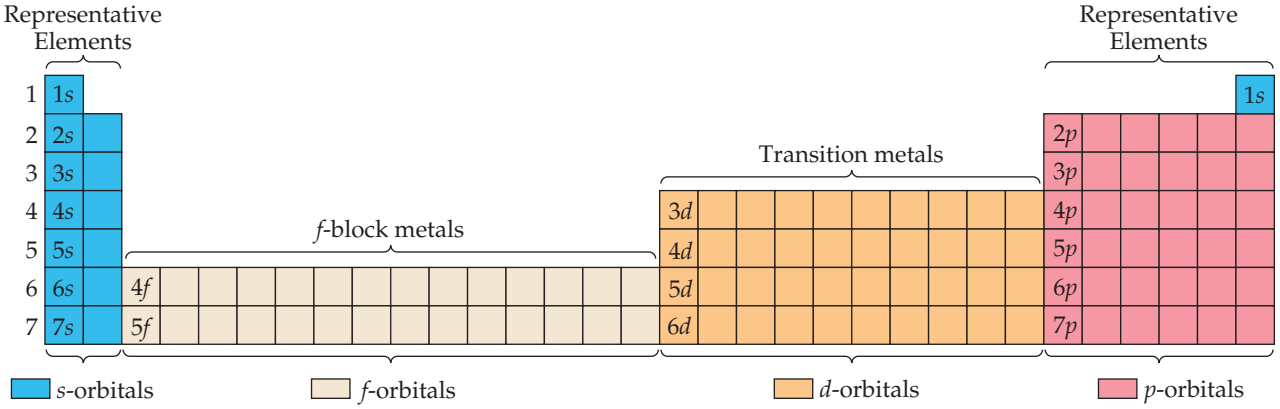
We just saw that the electron configurations of the elements correspond to their locations in the periodic table. Thus, elements in the same column of the table have related outer-shell (valence) electron configurations. As **Table 6.4** shows, for example, all Group 2 elements have an ns^2 outer configuration, and all Group 13 elements have an ns^2np^1 outer configuration, with the value of n increasing as we move down each column.

In Table 6.2 we saw that the total number of orbitals in each shell equals n^2: 1, 4, 9, or 16. Because we can place two electrons in each orbital, each shell accommodates up to $2n^2$ electrons: 2, 8, 18, or 32. We see that the overall structure of the periodic table reflects these electron numbers: Each row of the table has 2, 8, 18, or 32 elements in it. As shown in **Figure 6.29**, the periodic table can be further divided into four blocks based on the filling order of orbitals. On the left are *two* blue columns of elements. These elements, known as the alkali metals (Group 1) and alkaline earth metals (Group 2), are

TABLE 6.4 Electron Configurations of Group 2 and 13 Elements

Group 2	
Be	$[He]2s^2$
Mg	$[Ne]3s^2$
Ca	$[Ar]4s^2$
Sr	$[Kr]5s^2$
Ba	$[Xe]6s^2$
Ra	$[Rn]7s^2$
Group 13	
B	$[He]2s^2 2p^1$
Al	$[Ne]3s^2 3p^1$
Ga	$[Ar]3d^{10}4s^2 4p^1$
In	$[Kr]4d^{10}5s^2 5p^1$
Tl	$[Xe]4f^{14}5d^{10}6s^2 6p^1$

▼ Figure 6.29 Regions of the periodic table. The order in which electrons are added to orbitals is read left to right beginning in the top-left corner.

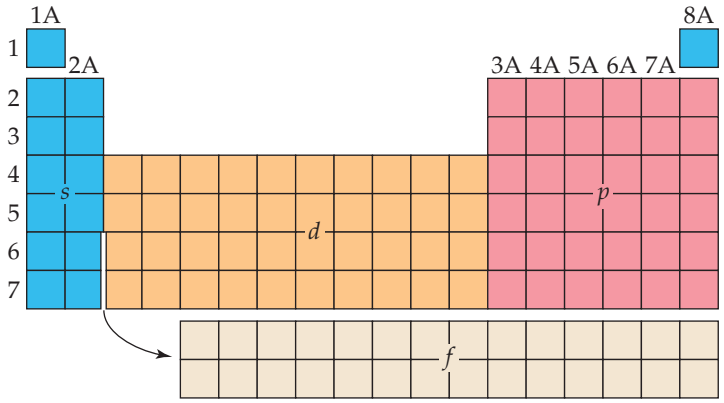


those in which the valence *s* orbitals are being filled. These two columns make up the *s* block of the periodic table.

On the right is a block of *six* pink columns that comprises the *p* block, where the valence *p* orbitals are being filled. The *s* block and the *p* block elements together are the **representative elements**, sometimes called the **main-group elements**.

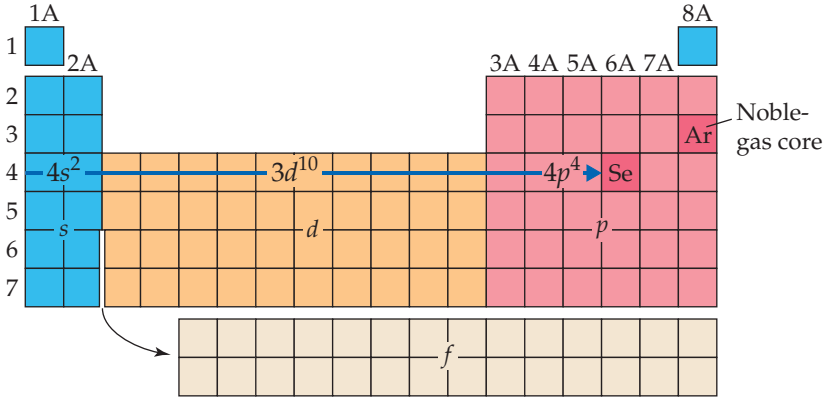
The orange block in Figure 6.29 has *ten* columns containing the **transition metals**. These are the elements in which the valence *d* orbitals are being filled and make up the *d* block.

The elements in the two tan rows containing *14* columns are the ones in which the valence *f* orbitals are being filled and make up the *f* block. Consequently, these elements are often referred to as the ***f*-block metals**. In most tables, the *f* block is positioned below the periodic table to save space:



The number of columns in each block corresponds to the maximum number of electrons that can occupy each kind of subshell. Recall that 2, 6, 10, and 14 are the numbers of electrons that can fill the *s*, *p*, *d*, and *f* subshells, respectively. Thus, the *s* block has 2 columns, the *p* block has 6, the *d* block has 10, and the *f* block has 14. Recall also that 1*s* is the first *s* subshell, 2*p* is the first *p* subshell, 3*d* is the first *d* subshell, and 4*f* is the first *f* subshell, as Figure 6.29 shows. Using these facts, you can write the electron configuration of an element based merely on its position in the periodic table. Remember: *The periodic table is your best guide to the order in which orbitals are filled.*

Let's use the periodic table to write the electron configuration of selenium (Se, element 34). We first locate Se in the table and then move backward from it through the table, from element 34 to 33 to 32, and so forth, until we come to the noble gas that precedes Se. In this case, the noble gas is argon, Ar, element 18. Thus, the noble-gas core for Se is [Ar]. Our next step is to write symbols for the outer electrons. We do this by moving across Period 4 from K, the element following Ar, to Se:



Because K is in the fourth period and the *s* block, we begin with the 4*s* electrons, meaning our first two outer electrons are written $4s^2$. We then move into the *d* block, which begins with the 3*d* electrons. (The principal quantum number in the *d* block is always

one less than that of the preceding elements in the *s* block, as seen in Figure 6.29.) Traversing the *d* block adds ten electrons, $3d^{10}$. Finally, we move into the *p* block, whose principal quantum number is always the same as that of the *s* block. Counting the squares as we move across the *p* block to Se tells us that we need four electrons, $4p^4$. The electron configuration for Se is therefore $[Ar]4s^23d^{10}4p^4$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Ar]3d^{10}4s^24p^4$.

As a check, we add the number of electrons in the [Ar] core, 18, to the number of electrons we added to the 4*s,* 3*d,* and 4*p* subshells. This sum should equal the atomic number of Se, 34: 18 + 2 + 10 + 4 = 34.

Sample Exercise 6.8

Electron Configurations for a Group

What is the characteristic valence electron configuration of the Group 17 elements, the halogens?

SOLUTION

Analyze and Plan We first locate the halogens in the periodic table, write the electron configurations for the first two elements, and then determine the general similarity between the configurations.

Solve The first member of the halogen group is fluorine (F, element 9). Moving backward from F, we find that the noble-gas core is [He]. Moving from He to the element of next higher atomic number brings us to Li, element 3. Because Li is in the second period of the *s* block, we add electrons to the 2*s* subshell. Moving across this block gives $2s^2$. Continuing to move to the right, we enter the *p* block. Counting the squares to F gives $2p^5$. Thus, the condensed electron configuration for fluorine is

F: $[He]2s^22p^5$

The electron configuration for chlorine, the second halogen, is

Cl: $[Ne]3s^23p^5$

From these two examples, we see that the characteristic valence electron configuration of a halogen is ns^2np^5, where *n* ranges from 2 in the case of fluorine to 6 in the case of astatine.

Practice Exercise

Which group of elements is characterized by an ns^2np^2 electron configuration in the outermost occupied shell?

Sample Exercise 6.9

Electron Configurations from the Periodic Table

(**a**) Based on its position in the periodic table, write the condensed electron configuration for bismuth, element 83. (**b**) How many unpaired electrons does a bismuth atom have?

SOLUTION

(**a**) Our first step is to write the noble-gas core. We do this by locating bismuth, element 83, in the periodic table. We then move backward to the nearest noble gas, which is Xe, element 54. Thus, the noble-gas core is [Xe].

Next, we trace the path in order of increasing atomic numbers from Xe to Bi. Moving from Xe to Cs, element 55, we find ourselves in Period 6 of the *s* block. Knowing the block and the period identifies the subshell in which we begin placing outer electrons, 6*s*. As we move through the *s* block, we add two electrons: $6s^2$.

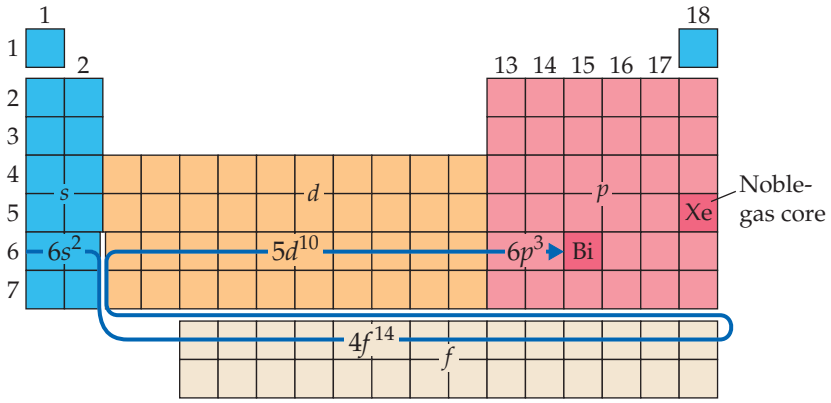
As we move beyond the *s* block, from element 56 to element 57, the curved arrow below the periodic table reminds us that we are entering the *f* block. The first row of the *f* block corresponds to the 4*f* subshell. As we move across this block, we add 14 electrons: $4f^{14}$.

With element 71, we move into the third row of the *d* block. Because the first row of the *d* block is 3*d,* the second row is 4*d* and the third row is 5*d*. Thus, as we move through the ten elements of the *d* block, from element 71 to element 80, we fill the 5*d* subshell with ten electrons: $5d^{10}$.

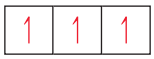
Moving from element 80 to element 81 puts us into the *p* block in the 6*p* subshell. (Remember that the principal quantum number in the *p* block is the same as that in the *s* block.) Moving across to Bi requires three electrons: $6p^3$. Putting the parts together, we obtain the condensed electron configuration: $[Xe]6s^24f^{14}5d^{10}6p^3$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Xe]4f^{14}5d^{10}6s^26p^3$.

Finally, we check our result to see if the number of electrons equals the atomic number of Bi, 83: Because Xe has 54 electrons (its atomic number), we have 54 + 2 + 14 + 10 + 3 = 83. (If we had 14 electrons too few, we would realize that we have missed the *f* block.)

Continued



(**b**) We see from the condensed electron configuration that the only partially occupied subshell is 6*p*. The orbital diagram representation for this subshell is



In accordance with Hund's rule, the three 6*p* electrons occupy the three 6*p* orbitals singly, with their spins parallel. Thus, there are three unpaired electrons in the bismuth atom.

Practice Exercise

A certain atom has a [noble gas]$5s^2 4d^{10} 5p^4$ electron configuration. Which element is it?
(**a**) Cd (**b**) Te (**c**) Sm (**d**) Hg (**e**) More information is needed

Figure 6.30 gives, for all the elements, the ground-state electron configurations for the outer-shell electrons. You can use this figure to check your answers as you practice writing electron configurations. We have written these configurations with orbitals listed in order of increasing principal quantum number. As we saw in Sample Exercise 6.9, the orbitals can also be listed in order of filling, as they would be read off of the periodic table.

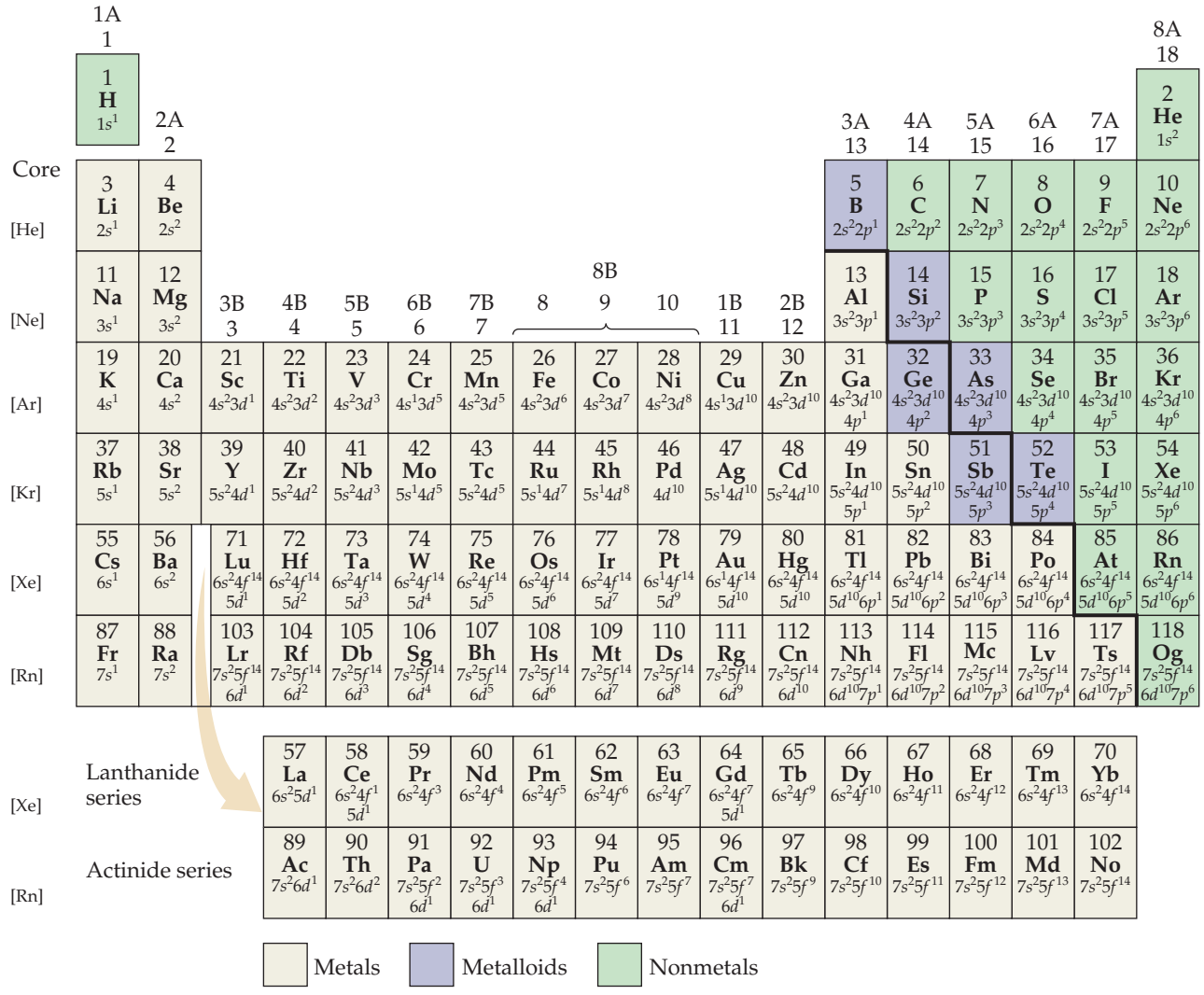
Figure 6.30 allow us to reexamine the concept of *valence electrons*. Notice, for example, that as we proceed from Cl ([Ne]$3s^2 3p^5$) to Br ([Ar]$3d^{10} 4s^2 4p^5$) we add a complete subshell of 3*d* electrons to the electrons beyond the [Ar] core. Although the 3*d* electrons are outer-shell electrons, they are not involved in chemical bonding and are therefore not considered valence electrons. Thus, we consider only the 4*s* and 4*p* electrons of Br to be valence electrons. Similarly, if we compare the electron configurations of Ag (element 47) and Au (element 79), we see that Au has a completely full $4f^{14}$ subshell beyond its noble-gas core, but those 4*f* electrons are not involved in bonding. In general, *for representative elements we do not consider the electrons in completely filled* d *or* f *subshells to be valence electrons,* and *for transition elements we do not consider the electrons in a completely filled* f *subshell to be valence electrons*.

Anomalous Electron Configurations

The electron configurations of certain elements appear to violate the rules we have just discussed. For example, Figure 6.30 shows that the electron configuration of chromium (element 24) is [Ar]$3d^5 4s^1$ rather than the [Ar]$3d^4 4s^2$ configuration we might expect. Similarly, the configuration of copper (element 29) is [Ar]$3d^{10} 4s^1$ instead of [Ar]$3d^9 4s^2$.

This anomalous behavior is largely a consequence of the closeness of the 3*d* and 4*s* orbital energies. It frequently occurs when there are enough electrons to form precisely half-filled sets of degenerate orbitals (as in chromium) or a completely filled *d* subshell (as in copper). There are a few similar cases among the heavier transition metals (those with partially filled 4*d* or 5*d* orbitals) and among the *f*-block metals. Although these minor departures from the expected are interesting, they are not of great chemical significance.

Go Figure A friend tells you that her favorite element has an electron configuration of [noble gas]$6s^2 4f^{14} 5d^6$. Which element is it?



▲ **Figure 6.30** **Outer-shell electron configurations of the elements.**

Sample Integrative Exercise

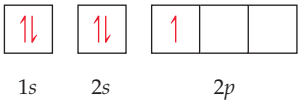
Putting Concepts Together

Boron, atomic number 5, occurs naturally as two isotopes, ^{10}B and ^{11}B, with natural abundances of 19.9% and 80.1%, respectively. (**a**) In what ways do the two isotopes differ from each other? Does the electronic configuration of ^{10}B differ from that of ^{11}B? (**b**) Draw the orbital diagram for an atom of ^{11}B. Which electrons are the valence electrons? (**c**) Indicate three ways in which the 1*s* electrons in boron differ from its 2*s* electrons. (**d**) Elemental boron reacts with fluorine to form BF_3, a gas. Write a balanced chemical equation for the reaction of solid boron with fluorine gas. (**e**) ΔH_f° for $BF_3(g)$ is -1135.6 kJ/mol. Calculate the standard enthalpy change in the reaction of boron with fluorine. (**f**) Will the mass percentage of F be the same in $^{10}BF_3$ and $^{11}BF_3$? If not, why is that the case?

SOLUTION

(**a**) The two isotopes of boron differ in the number of neutrons in the nucleus. Each of the isotopes contains five protons, but ^{10}B contains five neutrons, whereas ^{11}B contains six neutrons. The two isotopes of boron have identical electron configurations, $1s^2 2s^2 2p^1$, because each has five electrons.

(**b**) The complete orbital diagram is



Continued

The valence electrons are the ones in the outermost occupied shell, the $2s^2$ and $2p^1$ electrons. The $1s^2$ electrons constitute the core electrons, which we represent as [He] when we write the condensed electron configuration, $[He]2s^22p^1$.

(**c**) The 1*s* and 2*s* orbitals are both spherical, but they differ in three important respects: First, the 1*s* orbital is lower in energy than the 2*s* orbital. Second, the average distance of the 2*s* electrons from the nucleus is greater than that of the 1*s* electrons, so the 1*s* orbital is smaller than the 2*s*. Third, the 2*s* orbital has one node, whereas the 1*s* orbital has no nodes (Figure 6.18).

(**d**) The balanced chemical equation is

$$2\,B(s) + 3\,F_2(g) \longrightarrow 2\,BF_3(g)$$

(**e**) $\Delta H^\circ = 2(-1135.6) - [0 + 0] = -2271.2$ kJ. The reaction is strongly exothermic.

(**f**) As we saw in Equation 3.10 (Section 3.3), the mass percentage of an element in a substance depends on the formula weight of the substance. The formula weights of $^{10}BF_3$ and $^{11}BF_3$ are different because of the difference in the masses of the two isotopes (the isotope masses of ^{10}B and ^{11}B are 10.01294 and 11.00931 amu, respectively). The denominators in Equation 3.10 would therefore be different for the two isotopes, whereas the numerators would remain the same.

Chapter Summary and Key Terms

WAVELENGTHS AND FREQUENCIES OF LIGHT (INTRODUCTION AND SECTION 6.1) The **electronic structure** of an atom describes the energies and arrangement of electrons around the atom. Much of what is known about the electronic structure of atoms was obtained by observing the interaction of light with matter.

Visible light and other forms of **electromagnetic radiation** (also known as radiant energy) move through a vacuum at the speed of light, $c = 2.998 \times 10^8$ m/s. Electromagnetic radiation has both electric and magnetic components that vary periodically in wavelike fashion. The wave characteristics of radiant energy allow it to be described in terms of **wavelength**, λ, and **frequency**, ν, which are interrelated: $\lambda\nu = c$.

QUANTIZED ENERGY AND PHOTONS (SECTION 6.2) Planck proposed that the minimum amount of radiant energy that an object can gain or lose is related to the frequency of the radiation: $E = h\nu$. This smallest quantity is called a **quantum** of energy. The constant h is called the **Planck constant**: $h = 6.626 \times 10^{-34}$ J-s.

In the quantum theory, energy is quantized, meaning that it can have only certain allowed values. Einstein used the quantum theory to explain the **photoelectric effect**, the emission of electrons from metal surfaces when exposed to light. He proposed that light behaves as if it consists of quantized energy packets called **photons**. Each photon carries energy, $E = h\nu$.

BOHR MODEL OF THE HYDROGEN ATOM (SECTION 6.3) Dispersion of radiation into its component wavelengths produces a **spectrum**. If the spectrum contains all wavelengths, it is called a **continuous spectrum**; if it contains only certain specific wavelengths, the spectrum is called a **line spectrum**. The radiation emitted by excited hydrogen atoms forms a line spectrum.

Bohr proposed a model of the hydrogen atom that explains its line spectrum. In this model, the energy of the electron in the hydrogen atom depends on the value of a quantum number, n, called the **principal quantum number**. The value of n must be a positive integer (1, 2, 3, . . .), and each value of n corresponds to a different specific energy, E_n. The energy of the atom increases as n increases. The lowest energy is achieved for $n = 1$; this is called the **ground state** of the hydrogen atom. Other values of n correspond to **excited states**. Light is emitted when the electron drops from a higher-energy state to a lower-energy state; light is absorbed to excite the electron from a lower-energy state to a higher one. The frequency of light emitted or absorbed is such that $h\nu$ equals the difference in energy between two allowed states.

WAVE BEHAVIOR OF MATTER (SECTION 6.4) De Broglie proposed that matter, such as electrons, should exhibit wave-like properties. This hypothesis of **matter waves** was proved experimentally by observing the diffraction of electrons. An object has a characteristic wavelength that depends on its **momentum**, mv: $\lambda = h/mv$.

Discovery of the wave properties of the electron led to Heisenberg's **uncertainty principle**, which states that there is an inherent limit to the accuracy with which the position and momentum of a particle can be measured simultaneously.

QUANTUM MECHANICS AND ORBITALS (SECTION 6.5) In the quantum-mechanical model of the hydrogen atom, the behavior of the electron is described by mathematical functions called **wave functions**, denoted with the Greek letter ψ. Each allowed wave function has a precisely known energy, but the location of the electron cannot be determined exactly; rather, the probability of it being at a particular point in space is given by the **probability density**, ψ^2. The **electron-density** distribution is a map of the probability of finding the electron at all points in space.

The allowed wave functions of the hydrogen atom are called **orbitals**. An orbital is described by a combination of an integer and a letter, corresponding to values of three quantum numbers. The *principal quantum number*, n, is indicated by the integers 1, 2, 3, ... This quantum number relates most directly to the size and energy of the orbital. The **angular momentum quantum number**, l, is indicated by the letters *s*, *p*, *d*, *f*, and so on, corresponding to the values of 0, 1, 2, 3, ... The l quantum number defines the shape of the orbital. For a given value of n, l can have integer values ranging from 0 to $(n - 1)$. The **magnetic quantum number**, m_l, relates to the orientation of the orbital in space. For a given value of l, m_l can have integral values ranging from $-l$ to l, including 0. Subscripts can be used to label the orientations of the orbitals. For example, the three 3*p* orbitals are designated $3p_x$, $3p_y$, and $3p_z$, with the subscripts indicating the axis along which the orbital is oriented.

An electron shell is the set of all orbitals with the same value of n, such as 3*s*, 3*p*, and 3*d*. In the hydrogen atom all the orbitals in an electron shell have the same energy. A **subshell** is the set of one or more orbitals with the same n and l values; for example, 3s, 3*p*, and 3*d* are each subshells of the $n = 3$ shell. There is one orbital in an *s* subshell, three in a *p* subshell, five in a *d* subshell, and seven in an *f* subshell.

REPRESENTATIONS OF ORBITALS (SECTION 6.6) Contour representations are useful for visualizing the shapes of the orbitals. Represented this way, *s* orbitals appear as spheres that increase in size as n increases. The **radial probability function** tells us the probability that the electron will be found at a certain distance from the nucleus. The wave function for each *p* orbital has two lobes on opposite sides of the nucleus. They are oriented along the *x*, *y*, and *z* axes. Four of the *d* orbitals appear as shapes with four lobes around the nucleus; the fifth one, the d_{z^2} orbital, is represented as two lobes along the *z* axis and a "doughnut" in the *xy* plane. Regions in which the wave function is zero are called **nodes**. There is zero probability that the electron will be found at a node.

MANY-ELECTRON ATOMS (SECTION 6.7) In many-electron atoms, different subshells of the same electron shell have different energies. For a given value of n, the energy of the subshells increases as the value of l increases: $ns < np < nd < nf$. Orbitals within the same subshell are **degenerate**, meaning they have the same energy.

Electrons have an intrinsic property called **electron spin**, which is quantized. The **spin magnetic quantum number**, m_s, can have two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, which can be envisioned as the two directions of an electron spinning about an axis. The **Pauli exclusion principle** states that no two electrons in an atom can have the same values for n, l, m_l, and m_s. This principle places a limit of two on the number of electrons that can occupy any one atomic orbital. These two electrons differ in their value of m_s.

ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE (SECTIONS 6.8 AND 6.9) The **electron configuration** of an atom describes how the electrons are distributed among the orbitals of the atom. The ground-state electron configurations are generally obtained by placing the electrons in the atomic orbitals of lowest possible energy with the restriction that each orbital can hold no more than two electrons. We depict the arrangement of the electrons pictorially using an **orbital diagram**. When electrons occupy a subshell with more than one degenerate orbital, such as the $2p$ subshell, **Hund's rule** states that the lowest energy is attained by maximizing the number of electrons with the same electron spin. For example, in the ground-state electron configuration of carbon, the two $2p$ electrons have the same spin and must occupy two different $2p$ orbitals.

Elements in any given group in the periodic table have the same type of electron arrangements in their outermost shells. For example, the electron configurations of the halogens fluorine and chlorine are $[He]2s^2 2p^5$ and $[Ne]3s^2 3p^5$, respectively. The outer-shell electrons are those that lie outside the orbitals occupied in the next lowest noble-gas element. The outer-shell electrons that are involved in chemical bonding are the **valence electrons** of an atom; for the elements with atomic number 30 or less, all of the outer-shell electrons are valence electrons. The electrons that are not valence electrons are called **core electrons**.

The periodic table is partitioned into different types of elements, based on their electron configurations. Those elements in which the outermost subshell is an s or p subshell are called the **representative** (or **main-group**) **elements**. Those elements in which a d subshell is being filled are called the **transition elements** (or **transition metals**). The elements in which the $4f$ subshell is being filled are called the **lanthanide** (or **rare earth**) **elements**. The actinide elements are those in which the $5f$ subshell is being filled. The lanthanide and **actinide elements** are collectively referred to as the ***f*-block metals**. These elements are shown as two rows of 14 elements below the main part of the periodic table. The structure of the periodic table, summarized in Figure 6.30, allows us to write the electron configuration of an element from its position in the periodic table.

Learning Outcomes After studying this chapter, you should be able to:

- Calculate the wavelength of electromagnetic radiation given its frequency or its frequency given its wavelength. (Section 6.1) *Related Exercises: 6.5, 6.6, 6.59,*
- Order the common kinds of radiation in the electromagnetic spectrum according to their wavelengths or energy. (Section 6.1) *Related Exercises: 6.2, 6.3, 6.57, 6.58*
- Explain what photons are and be able to calculate their energies given either their frequency or wavelength. (Section 6.2) *Related Exercises: 6.9, 6.11, 6.12, 6.62*
- Explain how line spectra relate to the idea of quantized energy states of electrons in atoms. (Section 6.3) *Related Exercises: 6.18, 6.67, 6.70, 6.71*
- Calculate the wavelength of a moving object. (Section 6.4) *Related Exercises: 6.23, 6.24, 6.73, 6.74*
- Explain how the uncertainty principle limits how precisely we can specify the position and the momentum of subatomic particles such as electrons. (Section 6.4) *Related Exercises: 6.25, 6.75*
- Relate the quantum numbers to the number and type of orbitals and recognize the different orbital shapes. (Section 6.5) *Related Exercises: 6.28, 6.29, 6.31, 6.80*
- Interpret radial probability function graphs for atomic orbitals. (Section 6.6) *Related Exercises: 6.27, 6.76, 6.82*
- Explain how and why the energies of the orbitals are different in a many-electron atom from those in the hydrogen atom (Section 6.7) *Related Exercises: 6.36, 6.83*
- Draw an energy-level diagram for the orbitals in a many-electron atom and describe how electrons populate the orbitals in the ground state of an atom, using the Pauli exclusion principle and Hund's rule. (Section 6.8) *Related Exercises: 6.37, 6.54*
- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom. (Section 6.9) *Related Exercises: 6.41, 6.42, 6.87, 6.88*

Key Equations

- $\lambda\nu = c$ [6.1] light as a wave: λ = wavelength in meters, ν = frequency in s^{-1}, c = speed of light (2.998×10^8 m/s)
- $E = h\nu$ [6.2] light as a particle (photon): E = energy of photon in joules, h = Planck constant (6.626×10^{-34} J-s), ν = frequency in s^{-1}
- $E = (-hcR_H)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18}\,\text{J})\left(\frac{1}{n^2}\right)$ [6.5] energies of the allowed states of the hydrogen atom: h = Planck constant; c = speed of light; R_H = Rydberg constant ($1.096776 \times 10^7\ m^{-1}$); $n = 1, 2, 3, \ldots$ (any positive integer)
- $\lambda = h/mv$ [6.8] matter as a wave: λ = wavelength, h = Planck constant, m = mass of object in kg, v = speed of object in m/s
- $\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$ [6.9] Heisenberg's uncertainty principle. The uncertainty in position (Δx) and momentum [$\Delta(mv)$] of an object cannot be zero; the smallest value of their product is $h/4\pi$

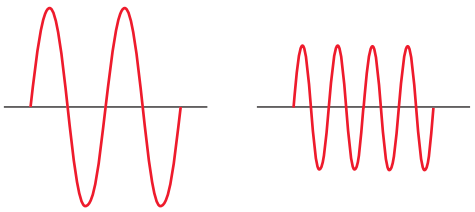
Exercises

Visualizing Concepts

6.44 The speed of sound in dry air at 20 °C is 343 m/s and the lowest frequency sound wave that the human ear can detect is approximately 20 Hz. (**a**) What is the wavelength of such a sound wave? (**b**) What would be the frequency of electromagnetic radiation with the same wavelength? (**c**) What type of electromagnetic radiation would that correspond to? [Section 6.1]

6.45 A popular kitchen appliance produces electromagnetic radiation with a frequency of 2450 MHz. With reference to Figure 6.4, answer the following: (**a**) Estimate the wavelength of this radiation. (**b**) Would the radiation produced by the appliance be visible to the human eye? (**c**) If the radiation is not visible, do photons of this radiation have more or less energy than photons of visible light? (**d**) Which of the following is the appliance likely to be? (i) A toaster oven, (ii) A microwave oven, or (iii) An electric hotplate. [Section 6.1]

6.46 The following diagrams represent two electromagnetic waves, drawn on the same scale. (**a**) Which wave has a longer wavelength? (**b**) Which wave has a higher frequency? (**c**) Which wave has a higher energy? [Section 6.2]



(a) **(b)**

6.47 Stars do not all have the same temperature. The color of light emitted by stars is characteristic of the light emitted by hot objects. Telescopic photos of three stars are shown: (i) the Sun, which is classified as a *yellow* star, (ii) *Rigel*, in the constellation Orion, which is classified as a *blue-white* star, and (iii) *Betelgeuse*, also in Orion, which is classified as a *red* star. (**a**) Place these three stars in order of increasing temperature. (**b**) Which of the following principles is relevant to your choice of answer for part (a): The uncertainty principle, the photoelectric effect, blackbody radiation, or line spectra? [Section 6.2]

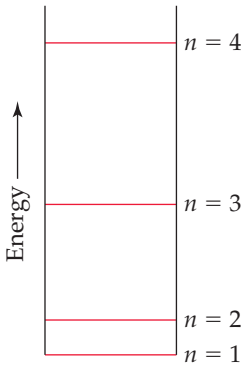


(i) Sun **(ii)** Rigel **(iii)** Betelgeuse

6.48 The familiar phenomenon of a rainbow results from the diffraction of sunlight through raindrops. (**a**) Does the wavelength of light increase or decrease as we proceed outward from the innermost band of the rainbow? (**b**) Does the frequency of light increase or decrease as we proceed outward? [Section 6.3]

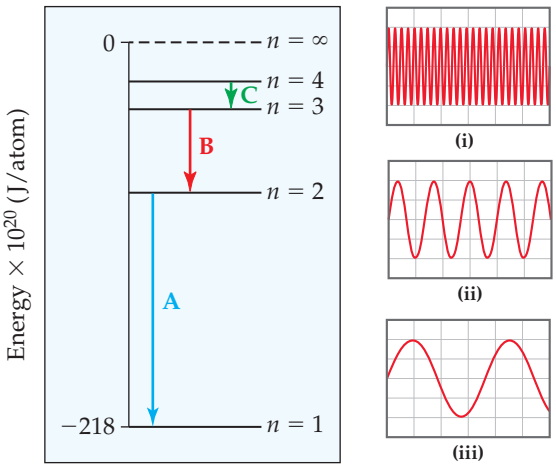


6.49 A certain quantum-mechanical system has the energy levels shown in the accompanying diagram. The energy levels are indexed by a single quantum number n that is an integer. (**a**) As drawn, which quantum numbers are involved in the transition that requires the most energy? (**b**) Which quantum numbers are involved in the transition that requires the least energy? (**c**) Based on the drawing, put the following in order of increasing wavelength of the light absorbed during the transition: (i) $n = 1$ to $n = 2$; (ii) $n = 2$ to $n = 3$; (iii) $n = 2$ to $n = 4$; (iv) $n = 1$ to $n = 3$. [Section 6.3]



6.50 Consider the three electronic transitions in a hydrogen atom shown here, labeled A, B, and C.

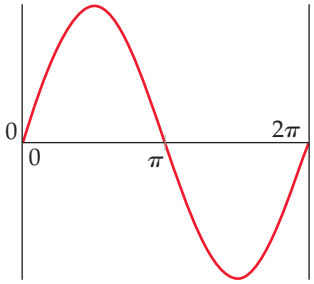
(**a**) Three electromagnetic waves, all drawn on the same scale, are also shown. Each corresponds to one of the transitions. Which electromagnetic wave (i), (ii), or (iii), is associated with electronic transition C?



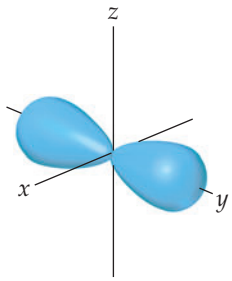
(**b**) Calculate the energy of the photon emitted for each transition.

(**c**) Calculate the wavelength of the photon emitted for each transition. Do any of these transitions lead to the emission of visible light? If so which one(s)? [Section 6.3]

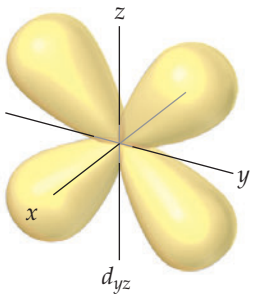
6.51 Consider a fictitious one-dimensional system with one electron. The wave function for the electron, as shown here, is $\psi(x) = \sin x$ from $x = 0$ to $x = 2\pi$. (**a**) Sketch the probability density, $\psi^2(x)$, from $x = 0$ to $x = 2\pi$. (**b**) At what value or values of x will there be the greatest probability of finding the electron? (**c**) What is the probability that the electron will be found at $x = \pi$? What is such a point in a wave function called? [Section 6.5]



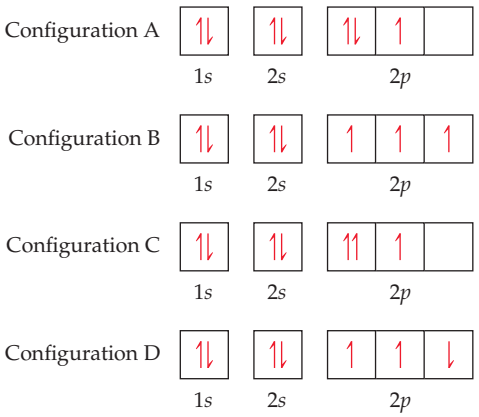
6.52 The contour representation of one of the orbitals for the $n = 3$ shell of a hydrogen atom is shown here. (**a**) What is the quantum number l for this orbital? (**b**) How do we label this orbital? (**c**) In which of the following ways would you modify this sketch if the value of the magnetic quantum number, m_l, were to change? (i) It would be drawn larger, (ii) the number of lobes would change, (iii) the lobes of the orbital would point in a different direction, (iv) there would be no change in the sketch. [Section 6.6]



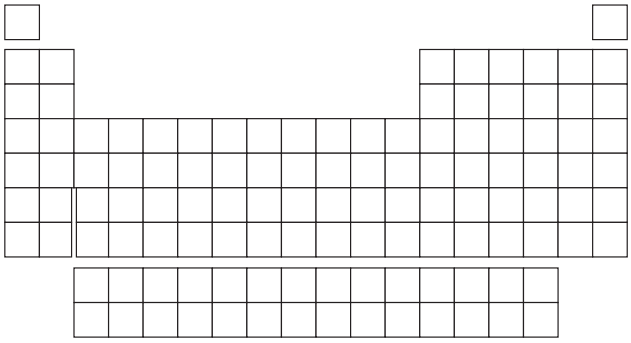
6.53 The accompanying drawing shows a contour plot for a d_{yz} orbital. Consider the quantum numbers that could potentially correspond to this orbital. (**a**) What is the smallest possible value of the principal quantum number, n? (**b**) What is the value of the angular momentum quantum number, l? (**c**) What is the largest possible value of the magnetic quantum number, m_l? (**d**) The probability density goes to zero along which of the following planes: xy, xz, or yz?



6.54 Four possible electron configurations for a nitrogen atom are shown here, but only one schematic represents the correct configuration for a nitrogen atom in its ground state. Which one is the correct electron configuration? Which configurations violate the Pauli exclusion principle? Which configurations violate Hund's rule? [Section 6.8]



6.55 State where in the periodic table these elements appear:
(**a**) elements with the valence-shell electron configuration ns^2np^5
(**b**) elements that have three unpaired p electrons
(**c**) an element whose valence electrons are $4s^24p^1$
(**d**) the d-block elements [Section 6.9]



The Wave Nature of Light (Section 6.1)

6.56 Carbon dioxide in the atmosphere absorbs energy in the 4.0–4.5 μm range of the spectrum. (**a**) Calculate the frequency of the 4.0 μm radiation. (**b**) In what region of the electromagnetic spectrum does this radiation occur?

6.57 Determine which of the following statements are false and correct them. (**a**) The frequency of radiation increases as the wavelength increases. (**b**) Electromagnetic radiation travels through a vacuum at a constant speed, regardless of wavelength. (**c**) Infrared light has higher frequencies than visible light. (**d**) The glow from a fireplace, the energy within a microwave oven, and a foghorn blast are all forms of electromagnetic radiation.

6.58 List the following types of electromagnetic radiation in order of descending wavelength: (**a**) UV lights used in tanning salons (300–400 nm); (**b**) radiation from an FM radio station at 93.1 MHz on the dial; (**c**) radiation from mobile phones (450–2100 MHz); (**d**) the yellow light from sodium vapor streetlights; (**e**) the red light of a light-emitting diode, such as in an appliance's display.

6.59 (**a**) What is the frequency of radiation whose wavelength is 0.86 nm? (**b**) What is the wavelength of radiation that has a frequency of $6.4 \times 10^{11}\ s^{-1}$? (**c**) Would the radiations in part (a) or part (b) be detected by an X-ray detector? (**d**) What distance does electromagnetic radiation travel in 0.38 ps?

6.60 It is possible to convert radiant energy into electrical energy using photovoltaic cells. Assuming equal efficiency of conversion, would infrared or ultraviolet radiation yield more electrical energy on a per-photon basis?

Quantized Energy and Photons (Section 6.2)

6.61 Einstein's 1905 paper on the photoelectric effect was the first important application of Planck's quantum hypothesis. Describe Planck's original hypothesis, and explain how Einstein made use of it in his theory of the photoelectric effect.

6.62 (**a**) A green laser pointer emits light with a wavelength of 532 nm. What is the frequency of this light? (**b**) What is the energy of one of these photons? (**c**) The laser pointer emits light because electrons in the material are excited (by a battery) from their ground state to an upper excited state. When the electrons return to the ground state, they lose the excess energy in the form of 532-nm photons. What is the energy gap between the ground state and excited state in the laser material?

6.63 An AM radio station broadcasts at 1000 kHz and its FM partner broadcasts at 100 MHz. Calculate and compare the energy of the photons emitted by these two radio stations.

6.64 The energy from radiation can be used to rupture chemical bonds. A minimum energy of 192 kJ/mol is required to break the bromine–bromine bond in Br_2. What is the longest wavelength of radiation that possesses the necessary energy to break the bond? What type of electromagnetic radiation is this?

6.65 A stellar object is emitting radiation at 3.0 mm. (**a**) What type of electromagnetic spectrum is this radiation? (**b**) If a detector is capturing 3.0×10^8 photons per second at this wavelength, what is the total energy of the photons detected in 1 day?

6.66 Titanium metal requires light with a maximum wavelength of 286 nm to emit electrons. (**a**) What is the minimum energy of the photons necessary to emit electrons from titanium via the photoelectric effect? (**b**) What is the frequency of this radiation? (**c**) Is it possible to eject electrons from titanium metal using infrared light? (**d**) If titanium is irradiated with light of wavelength 276 nm, what is the maximum possible kinetic energy of the emitted electrons?

Bohr's Model; Matter Waves (Sections 6.3 and 6.4)

6.67 Classify each of the following statements as either true or false: (**a**) A hydrogen atom in the $n = 3$ state can emit light at only two specific wavelengths, (**b**) a hydrogen atom in the $n = 2$ state is at a lower energy than one in the $n = 1$ state, and (**c**) the energy of an emitted photon equals the energy difference of the two states involved in the emission.

6.68 Indicate whether energy is emitted or absorbed when the following electronic transitions occur in hydrogen: (**a**) from $n = 2$ to $n = 3$, (**b**) from an orbit of radius 0.529 to one of radius 0.476 nm, (**c**) from the $n = 9$ to the $n = 6$ state.

6.69 Consider a transition of the electron in the hydrogen atom from $n = 8$ to $n = 3$. (**a**) Is ΔE for this process positive or negative? (**b**) Determine the wavelength of light that is associated with this transition. Will the light be absorbed or emitted? (**c**) In which portion of the electromagnetic spectrum is the light in part (b)?

6.70 The Lyman series of emission lines of the hydrogen atom are those for which $n_f = 1$. (**a**) Determine the region of the electromagnetic spectrum in which the lines of the Lyman series are observed. (**b**) Calculate the wavelengths of the first three lines in the Lyman series—those for which $n_i = 2$, 3, and 4.

6.71 The hydrogen atom can absorb light of wavelength 1094 nm. (**a**) In what region of the electromagnetic spectrum is this absorption found? (**b**) Determine the initial and final values of n associated with this absorption.

6.72 Place the following transitions of the hydrogen atom in order from shortest to longest wavelength of the photon emitted: $n = 5$ to $n = 2$, $n = 4$ to $n = 3$, $n = 8$ to $n = 4$, and $n = 4$ to $n = 2$.

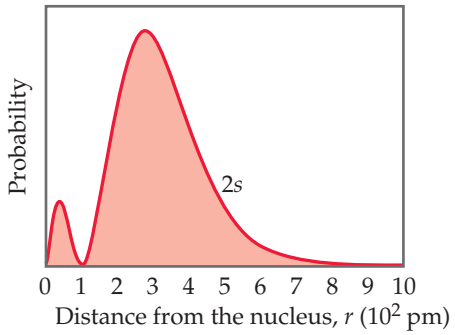
6.73 Among the elementary subatomic particles of physics is the muon, which decays within a few microseconds after formation. The muon has a rest mass 206.8 times that of an electron. Calculate the de Broglie wavelength associated with a muon traveling at 8.85×10^5 cm/s.

6.74 The electron microscope has been widely used to obtain highly magnified images of biological and other types of materials. When an electron is accelerated through a particular potential field, it attains a speed of 9.47×10^6 m/s. What is the characteristic wavelength of this electron? Is the wavelength comparable to the size of atoms?

6.75 Calculate the uncertainty in the position of (**a**) an electron moving at a speed of $(3.00 \pm 0.01) \times 10^5$ m/s, (**b**) a neutron moving at this same speed. (The masses of an electron and a neutron are given in the table of fundamental constants in the inside cover of the text.) (**c**) Based on your answers to parts (a) and (b), which can we know with greater precision, the position of the electron or of the neutron?

Quantum Mechanics and Atomic Orbitals (Sections 6.5 and 6.6)

6.76 The radial probability function for a 2s orbital is shown here.



Classify the following statements as either true or false: (**a**) There are two maxima in this function because one electron spends most of its time at an approximate distance of 50 pm from the nucleus and the other electron spends most of its time at an approximate distance of 300 pm from the nucleus. (**b**) The radial probability function shown here and the probability density $[\psi(r)]^2$ both go to zero at the same distance from the nucleus, approximately 100 pm. (**c**) For an s orbital, the number of radial nodes is equal to the principal quantum number, n.

6.77 How many unique combinations of the quantum numbers l and m_l are there when (**a**) $n = 1$, (**b**) $n = 5$?

6.78 Give the values for n, l, and m_l for (**a**) each orbital in the $3p$ subshell, (**b**) each orbital in the $4f$ subshell.

6.79 A hydrogen atom orbital has $n = 4$ and $m_l = -2$. (**a**) What are the possible values of l for this orbital? (**b**) What are the possible values of m_s for the orbital?

6.80 For the table that follows, write which orbital goes with the quantum numbers. Don't worry about x, y, z subscripts. If the quantum numbers are not allowed, write "not allowed."

n	l	m_l	Orbital
2	1	−1	2p (example)
1	0	0	
3	−3	2	
3	2	−2	
2	0	−1	
0	0	0	
4	2	1	
5	3	0	

6.81 Sketch the shape and orientation of the following types of orbitals: (**a**) p_x, (**b**) d_{z^2}, (**c**) $d_{x^2-y^2}$.

6.82 (**a**) With reference to Figure 6.18, what is the relationship between the number of nodes in an s orbital and the value of the principal quantum number? (**b**) Identify the number of nodes; that is, identify places where the electron density is zero, in the $2p_x$ orbital; in the $3s$ orbital. (**c**) What information is obtained from the radial probability functions in Figure 6.18? (**d**) For the hydrogen atom, list the following orbitals in order of increasing energy: $3s$, $2s$, $2p$, $5s$, $4d$.

Many-Electron Atoms and Electron Configurations (Sections 6.7–6.9)

6.83 (**a**) The average distance from the nucleus of a 3*s* electron in a chlorine atom is smaller than that for a 3*p* electron. In light of this fact, which orbital is higher in energy? (**b**) Would you expect it to require more or less energy to remove a 3*s* electron from the chlorine atom, as compared with a 2*p* electron?

6.84 An experiment called the Stern–Gerlach experiment helped establish the existence of electron spin. In this experiment, a beam of silver atoms is passed through a magnetic field, which deflects half of the silver atoms in one direction and half in the opposite direction. The separation between the two beams increases as the strength of the magnetic field increases. (**a**) What is the electron configuration for a silver atom? (**b**) Would this experiment work for a beam of cadmium (Cd) atoms? (**c**) Would this experiment work for a beam of fluorine (F) atoms?

6.85 What is the maximum number of electrons in an atom that can have the following quantum numbers? (**a**) $n = 3, m_l = -1$; (**b**) $n = 4, l = 2$; (**c**) $n = 4, l = 3, m_l = -2$; (**d**) $n = 5, l = 2, m_l = 0$.

6.86 For each element, indicate the number of valence electrons, core electrons, and unpaired electrons in the ground state: (**a**) sodium, (**b**) sulfur, (**c**) fluorine.

6.87 Write the condensed electron configurations for the following atoms and indicate how many unpaired electrons each has: (**a**) Mg, (**b**) Ge, (**c**) Br, (**d**) V, (**e**) Y, (**f**) Lu.

6.88 Identify the group of elements that corresponds to each of the following generalized electron configurations and indicate the number of unpaired electrons for each:

(**a**) [noble gas]ns^2np^5

(**b**) [noble gas]$ns^2(n-1)d^2$

(**c**) [noble gas]$ns^2(n-1)d^{10}np^1$

(**d**) [noble gas]$ns^2(n-2)f^6$

6.89 The following electron configurations represent excited states. Identify the element and write its ground-state condensed electron configuration. (**a**) $1s^22s^22p^43s^1$, (**b**) $[Ne]3s^13p^44p^1$, (**c**) $[Ar]4s^23d^64p^1$.

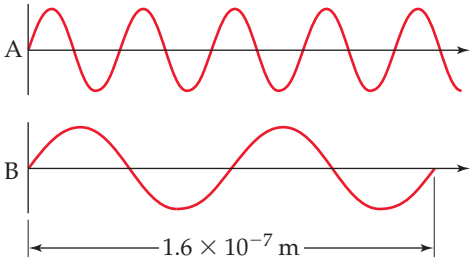
Additional Exercises

6.90 Consider the two waves shown here, which we will consider to represent two electromagnetic radiations:

(**a**) What is the wavelength of wave A? Of wave B?

(**b**) What is the frequency of wave A? Of wave B?

(**c**) Identify the regions of the electromagnetic spectrum to which waves A and B belong.



6.91 If a sample of calcium chloride is introduced into a non-luminous flame, the color of the flame turns to orange ("flame test"). The light is emitted because calcium atoms become excited; their return to the ground state results in light emission. (**a**) The wavelength of this emitted light is 422.7 nm. Calculate its frequency. (**b**) What is the energy of 1.00 mol of these photons (a mole of photons is called an Einstein)? (**c**) Calculate the energy gap between the excited and ground states for the calcium atom.

6.92 Certain elements emit light of a specific wavelength when they are burned or heated in a non-luminous flame. Historically, chemists used such emission wavelengths to determine whether specific elements were present in a sample. Some characteristic wavelengths for a few of the elements are given in the following table:

Ag	328.1 nm	Fe	372.0 nm
Au	267.6 nm	K	404.7 nm
Ba	455.4 nm	Mg	285.2 nm
Ca	422.7 nm	Na	589.6 nm
Cu	324.8 nm	Ni	341.5 nm

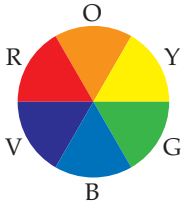
(**a**) Determine which of these emissions occur in the ultraviolet part of the spectrum. (**b**) Which emission has the highest frequency and which one has the lowest frequency? (**c**) When burned, a sample of an unknown substance is found to emit light of frequency $6.58 \times 10^{14}\ s^{-1}$. Which of these elements is probably in the sample?

6.93 In January 2006, the *New Horizons* space probe was launched from Earth with the mission to perform a flyby study of Pluto. The arrival at the dwarf planet was estimated to happen after nine years, in 2015. The distance between Earth and Pluto varies depending on the location of the planets in their orbits, but at their closest, the distance is 4.2 billion kilometers (2.6 billion miles). Calculate the minimum amount of time it takes for a transmitted signal from Pluto to reach the Earth.

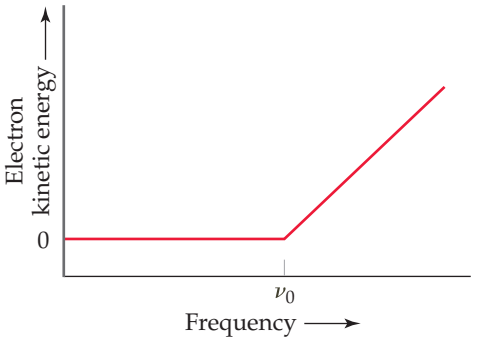
6.94 The rays of the Sun that cause tanning and burning are in the ultraviolet portion of the electromagnetic spectrum. These rays are categorized by wavelength. So-called UV-A radiation has wavelengths in the range of 320–380 nm, whereas UV-B radiation has wavelengths in the range of 290–320 nm. (**a**) Calculate the frequency of light that has a wavelength of 380 nm. (**b**) Calculate the energy of a mole of 380 nm photons. (**c**) Which are more energetic, photons of UV-A radiation or photons of UV-B radiation? (**d**) The UV-B radiation from the Sun is considered a more important cause of sunburn in humans than UV-A radiation. Is this observation consistent with your answer to part (c)?

6.95 The watt is the derived SI unit of power, the measure of energy per unit time: 1 W = 1 J/s. A semiconductor laser in a DVD player has an output wavelength of 650 nm and a power level of 5.0 mW. How many photons strike the DVD surface during the playing of a DVD 90 minutes in length?

6.96 Carotenoids are yellow, orange, and red pigments synthesized by plants. The observed color of an object is not the color of light it absorbs but rather the complementary color, as described by a color wheel such as the one shown here. On this wheel, complementary colors are across from each other. (**a**) Based on this wheel, what color is absorbed most strongly if a plant is orange? (**b**) If a particular carotenoid absorbs photons at 455 nm, what is the energy of the photon?

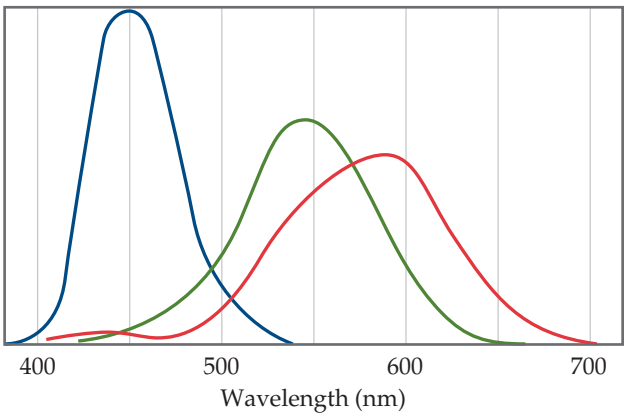


6.97 In an experiment to study the photoelectric effect, a scientist measures the kinetic energy of ejected electrons as a function of the frequency of radiation hitting a metal surface. She obtains the following plot. The point labeled "ν_0" corresponds to light with a wavelength of 542 nm. (**a**) What is the value of ν_0 in s^{-1}? (**b**) What is the value of the work function of the metal in units of kJ/mol of ejected electrons? (**c**) Note that when the frequency of the light is greater than ν_0, the plot shows a straight line with a nonzero slope. What is the slope of this line segment?



6.98 Consider a transition in which the electron of a hydrogen atom is excited from $n = 1$ to $n = \infty$. (**a**) What is the end result of this transition? (**b**) What is the wavelength of light that must be absorbed to accomplish this process? (**c**) What will occur if light with a shorter wavelength than that in part (b) is used to excite the hydrogen atom? (**d**) How are the results of parts (b) and (c) related to the plot shown in Exercise 6.97?

6.99 The human retina has three types of receptor cones, each sensitive to a different range of wavelengths of visible light, as shown in this figure (the colors are merely to differentiate the three curves from one another; they do not indicate the actual colors represented by each curve):



(**a**) Estimate the energies of photons with wavelengths at the maximum for each type of cone. (**b**) The color of the sky is due to scattering of solar light by the molecules of the atmosphere. Lord Rayleigh was one of the first to study scattering of this kind. He showed that the amount of scattering for very small particles such as molecules is inversely proportional to the fourth power of the wavelength. Estimate the ratio of the scattering efficiency of light at the wavelength of the maximum for the "blue" cones, as compared with that for the "green" cones. (**c**) Explain why the sky appears blue even though all wavelengths of solar light are scattered by the atmosphere.

6.100 The series of emission lines of the hydrogen atom for which $n_f = 4$ is called the *Brackett series*. (**a**) Determine the region of the electromagnetic spectrum in which the lines of the Brackett series are observed. (**b**) Calculate the wavelengths of the first three lines in the Brackett series—those for which $n_i = 5$, 6, and 7.

6.101 When the spectrum of light from the Sun is examined in high resolution in an experiment similar to that illustrated in Figure 6.8, dark lines are evident. These are called Fraunhofer lines, after the scientist who studied them extensively in the early nineteenth century. Altogether, about 25,000 lines have been identified in the solar spectrum between 1000 nm and 295 nm. The Fraunhofer lines are attributed to absorption of certain wavelengths of the Sun's "white" light by gaseous elements in the Sun's atmosphere. (**a**) Describe the process that causes absorption of specific wavelengths of light from the solar spectrum. (**b**) To determine which Fraunhofer lines belong to a given element, say, neon, what experiments could a scientist conduct here on Earth?

6.102 Determine whether each of the following sets of quantum numbers for the hydrogen atom are valid. If a set is not valid, indicate which of the quantum numbers has a value that is not valid:
(**a**) $n = 3, l = 3, m_l = 2, m_s = +\frac{1}{2}$
(**b**) $n = 4, l = 3, m_l = -3, m_s = +\frac{1}{2}$
(**c**) $n = 3, l = 1, m_l = 2, m_s = +\frac{1}{2}$
(**d**) $n = 5, l = 0, m_l = 0, m_s = 0$
(**e**) $n = 2, l = 1, m_l = 1, m_s = -\frac{1}{2}$

6.103 Bohr's model can be used for hydrogen-like ions—ions that have only one electron, such as He^+ and Li^{2+}. (**a**) Why is the Bohr model applicable to Li^{2+} ions but not to neutral Li atoms? (**b**) The ground-state energies of B^{4+}, C^{5+}, and N^{6+} are tabulated as follows:

Atom or ion	B^{4+}	C^{5+}	N^{6+}
Ground-state energy	-5.45×10^{-17} J	-7.85×10^{-17} J	-1.07×10^{-16} J

By examining these numbers, propose a relationship between the ground-state energy of hydrogen-like systems and the nuclear charge, Z. (*Hint:* Divide by the ground-state energy of hydrogen -2.18×10^{-18} J) (**c**) Use the relationship you derive in part (b) to predict the ground-state energy of the Be^{3+} ion.

6.104 An electron is accelerated through an electric potential to a kinetic energy of 1.6×10^{-15} J. What is its characteristic wavelength? [*Hint:* Recall that the kinetic energy of a moving object is $E = \frac{1}{2}mv^2$, where m is the mass of the object and v is the speed of the object.]

6.105 In the television series *Star Trek,* the transporter beam is a device used to "beam down" people from the *Starship Enterprise* to another location, such as the surface of a planet. The writers of the show put a "Heisenberg compensator" into the transporter beam mechanism. Explain why such a compensator (which is entirely fictional) would be necessary to get around Heisenberg's uncertainty principle.

6.106 As discussed in the A Closer Look box on "Measurement and the Uncertainty Principle," the essence of the uncertainty principle is that we can't make a measurement without disturbing the system that we are measuring. (**a**) Why can't we measure the position of a subatomic particle without disturbing it? (**b**) How is this concept related to the paradox discussed in the Closer Look box on "Thought Experiments and Schrödinger's Cat"?

6.107 Consider the discussion of radial probability functions in "A Closer Look" in Section 6.6. (**a**) What is the difference between the probability density as a function of r and the radial probability function as a function of r? (**b**) What is the significance of the term $4\pi r^2$ in the radial probability functions for the s orbitals? (**c**) Based on Figures 6.18 and 6.21, make sketches of what you think the probability density as a function of r and the radial probability function would look like for the 4s orbital of the hydrogen atom.

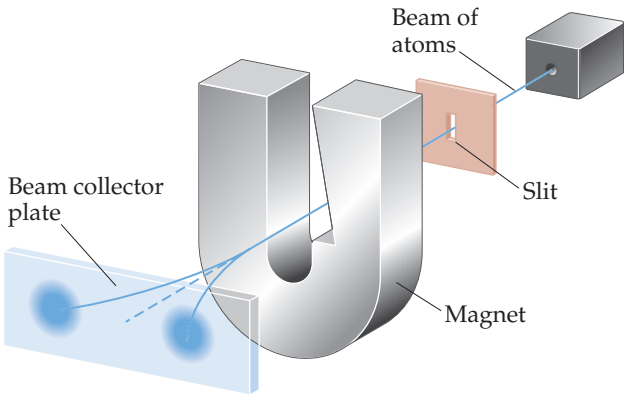
6.108 For orbitals that are symmetric but not spherical, the contour representations (as in Figures 6.22 and 6.23) suggest where nodal planes exist (that is, where the electron density is zero). For example, the p_x orbital has a node wherever $x = 0$. This equation is satisfied by all points on the yz plane, so this plane is called a nodal plane of the p_x orbital. (**a**) Determine the nodal plane of the p_z orbital. (**b**) What are the two nodal planes of the d_{xy} orbital? (**c**) What are the two nodal planes of the $d_{x^2-y^2}$ orbital?

6.109 Suppose that the spin quantum number, m_s, could have *three* allowed values instead of two. How would this affect the number of elements in the first four rows of the periodic table?

6.110 Using the periodic table as a guide, write the condensed electron configuration and determine the number of unpaired electrons for the ground state of (**a**) Cl, (**b**) Al, (**c**) Zr, (**d**) As, (**e**) Sb, (**f**) W.

6.111 Scientists have speculated that element 126 might have a moderate stability, allowing it to be synthesized and characterized. Predict what the condensed electron configuration of this element might be.

6.112 In the experiment shown schematically with this question, a beam of neutral atoms is passed through a magnetic field. Atoms that have unpaired electrons are deflected in different directions in the magnetic field depending on the value of the electron spin quantum number. In the experiment illustrated, we envision that a beam of hydrogen atoms splits into two beams. (**a**) What is the significance of the observation that the single beam splits into two beams? (**b**) What do you think would happen if the strength of the magnet were increased? (**c**) What do you think would happen if the beam of hydrogen atoms were replaced with a beam of helium atoms? Why? (**d**) The relevant experiment was first performed by Otto Stern and Walter Gerlach in 1921. They used a beam of Ag atoms in the experiment. By considering the electron configuration of a silver atom, explain why the single beam splits into two beams.



Integrative Exercises

6.113 Microwave ovens use microwave radiation to heat food. The energy of the microwaves is absorbed by water molecules in food and then transferred to other components of the food. (**a**) Suppose that the microwave radiation has a wavelength of 10 cm. How many photons are required to heat 200 mL of water from 25 to 75 °C? (**b**) Suppose the microwave's power is 1000 W (1 watt = 1 joule-second). How long would you have to heat the water in part (a)?

6.114 The stratospheric ozone (O_3) layer helps to protect us from harmful ultraviolet radiation. It does so by absorbing ultraviolet light and falling apart into an O_2 molecule and an oxygen atom, a process known as photodissociation.

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

Use the data in Appendix C to calculate the enthalpy change for this reaction. What is the maximum wavelength a photon can have if it is to possess sufficient energy to cause this dissociation? In what portion of the spectrum does this wavelength occur?

6.115 The discovery of hafnium, element number 72, provided a controversial episode in chemistry. G. Urbain, a French chemist, claimed in 1911 to have isolated an element number 72 from a sample of rare earth (elements 58–71) compounds. However, Niels Bohr believed that hafnium was more likely to be found along with zirconium than with the rare earths. D. Coster and G. von Hevesy, working in Bohr's laboratory in Copenhagen, showed in 1922 that element 72 was present in a sample of Norwegian zircon, an ore of zirconium. (The name *hafnium* comes from the Latin name for Copenhagen, *Hafnia*). (**a**) How would you use electron configuration arguments to justify Bohr's prediction? (**b**) Zirconium, hafnium's neighbor in Group 4, can be produced as a metal by reduction of solid $ZrCl_4$ with molten sodium metal. Write a balanced chemical equation for the reaction. Is this an oxidation-reduction reaction? If yes, what is reduced and what is oxidized? (**c**) Solid zirconium dioxide, ZrO_2, reacts with chlorine gas in the presence of carbon. The products of the reaction are $ZrCl_4$ and two gases, CO_2 and CO in the ratio 1:2. Write a balanced chemical equation for the reaction. Starting with a 55.4 g sample of ZrO_2, calculate the mass of $ZrCl_4$ formed, assuming that ZrO_2 is the limiting reagent and assuming 100% yield. (**d**) Using their electron configurations, account for the fact that Zr and Hf form chlorides MCl_4 and oxides MO_2.

6.116 (**a**) Account for formation of the following series of oxides in terms of the electron configurations of the elements and the discussion of ionic compounds in Section 2.7: K_2O, CaO, Sc_2O_3, TiO_2, V_2O_5, CrO_3. (**b**) Name these oxides. (**c**) Consider the metal oxides whose enthalpies of formation (in kJ mol^{-1}) are listed here.

Oxide	$K_2O(s)$	$CaO(s)$	$TiO_2(s)$	$V_2O_5(s)$
ΔH_f°	−363.2	−635.1	−938.7	−1550.6

Calculate the enthalpy changes in the following general reaction for each case:

$$M_nO_m(s) + H_2(g) \longrightarrow nM(s) + mH_2O(g)$$

(You will need to write the balanced equation for each case and then compute ΔH°.) (**d**) Based on the data given, estimate a value of ΔH_f° for $Sc_2O_3(s)$.

6.117 The first 25 years of the twentieth century were momentous for the rapid pace of change in scientists' understanding of the nature of matter. (**a**) How did Rutherford's experiments on the scattering of α particles by a gold foil set the stage for Bohr's theory of the hydrogen atom? (**b**) In what ways is de Broglie's hypothesis, as it applies to electrons, consistent with J. J. Thomson's conclusion that

the electron has mass? In what sense is it consistent with proposals preceding Thomson's work that the cathode rays are a wave phenomenon?

6.118 The two most common isotopes of uranium are ^{235}U and ^{238}U. (**a**) Compare the number of protons, the number of electrons, and the number of neutrons in atoms of these two isotopes. (**b**) Using the periodic table in the front-inside cover, write the electron configuration for a U atom. (**c**) Compare your answer to part (b) to the electron configuration given in Figure 6.29. How can you explain any differences between these two electron configurations? (**d**) ^{238}U undergoes radioactive decay to ^{234}Th. How many protons, electrons, and neutrons are gained or lost by the ^{238}U atom during this process? (**e**) Examine the electron configuration for Th in Figure 6.30. Are you surprised by what you find? Explain.

Design an Experiment

In this chapter, we have learned about the *photoelectric effect* and its impact on the formulation of light as photons. We have also seen that some anomalous electron configurations of the elements are particularly favorable if each atom has one or more half-filled shell, such as the case for the Cr atom with its [Ar]$4s^1 3d^5$ electron configuration. Let's suppose it is hypothesized that it requires more energy to remove an electron from a metal that has atoms with one or more half-filled shells than from those that do not. (**a**) Design a series of experiments involving the photoelectric effect that would test the hypothesis. (**b**) What experimental apparatus would be needed to test the hypothesis? It's not necessary that you name actual equipment but rather that you imagine how the apparatus would work—think in terms of the types of measurements that would be needed, and what capability you would need in your apparatus. (**c**) Describe the type of data you would collect and how you would analyze the data to see whether the hypothesis were correct. (**d**) Could your experiments be extended to test the hypothesis for other parts of the periodic table, such as the lanthanide or actinide elements?

7

PERIODIC PROPERTIES OF THE ELEMENTS

WHAT'S AHEAD

7.1 Development of the Periodic Table
7.2 Effective Nuclear Charge
7.3 Sizes of Atoms and Ions
7.4 Ionization Energy
7.5 Electron Affinity
7.6 Metals, Nonmetals, and Metalloids
7.7 Trends for Group 1 and Group 2 Metals
7.8 Trends for Selected Nonmetals

7.1 | Development of the Periodic Table



The discovery of chemical elements has been ongoing since ancient times. Certain elements, such as gold (Au), appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements, such as technetium (Tc), are radioactive and intrinsically unstable. We know about them only because of technology developed during the twentieth century.

The majority of elements readily form compounds and, consequently, are not found in nature in their elemental form. For centuries, therefore, scientists were unaware of their existence. During the early nineteenth century, advances in chemistry made it easier to isolate elements from their compounds. As a result, the number of known elements more than doubled from 31 in 1800 to 63 by 1865.

By the end of this section, you should

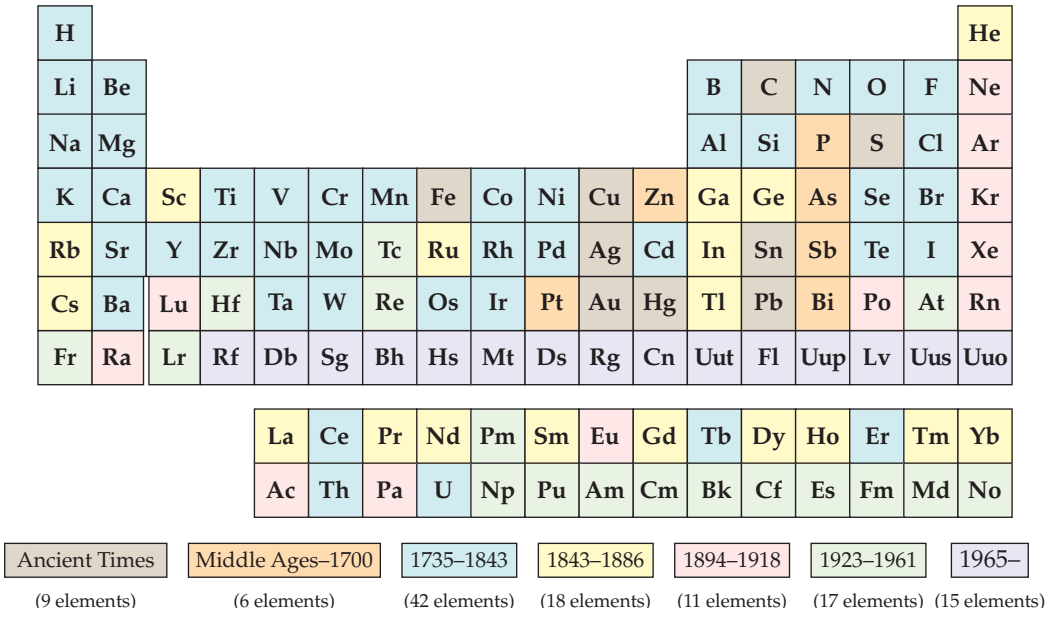
- Have an appreciation for the historical context of the periodic table

As the number of known elements increased (**Figure 7.1**), scientists began classifying them. In 1869, Dmitri Mendeleev (1834–1907) in Russia and Lothar Meyer (1830–1895) in Germany published nearly identical classification schemes. Both noted that similar chemical and physical properties recur periodically when the elements are arranged in order of increasing atomic weight. Scientists at that time had no knowledge of atomic numbers. Atomic weights, however, generally increase with increasing atomic number, so both Mendeleev and Meyer fortuitously arranged the elements in nearly the proper sequence.

Although Mendeleev and Meyer came to essentially the same conclusion about the periodicity of elemental properties, Mendeleev is given credit for advancing his ideas more vigorously and stimulating new work. His insistence that elements with similar characteristics be listed in the same column forced him to leave blank spaces in his table. For example, both gallium (Ga) and germanium (Ge) were unknown to Mendeleev. He boldly predicted their existence and properties, referring to them as *eka-aluminum* ("under" aluminum) and *eka-silicon* ("under" silicon), respectively, after the elements under which they appeared in his table. When these elements were discovered, their properties closely matched those predicted by Mendeleev, as shown in **Table 7.1**.

In 1913, two years after Rutherford proposed the nuclear model of the atom, English physicist Henry Moseley (1887–1915) developed the concept of atomic numbers. Bombarding different elements with high-energy electrons, Moseley found that each element produced X rays of a unique frequency and that the frequency generally increased as the atomic mass increased. He arranged the X-ray frequencies in order by assigning a unique whole number, called an *atomic number*, to each element. Moseley correctly identified the atomic number as the number of protons in the nucleus of the atom.

Go Figure Copper, silver, and gold have all been known since ancient times, whereas most of the other metals were not isolated until much later. Can you suggest an explanation?



▲ **Figure 7.1** **Discovering the elements.**

TABLE 7.1 Comparison of the Properties of Eka-Silicon Predicted by Mendeleev with the Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-K)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

The concept of atomic number clarified some problems in the periodic table of Moseley's day, which was based on atomic weights. For example, the atomic weight of Ar (atomic number 18) is greater than that of K (atomic number 19), yet the chemical and physical properties of Ar are much more like those of Ne and Kr than like those of Na and Rb. When the elements are arranged in order of increasing atomic number, Ar and K appear in their correct places in the table. Moseley's studies also made it possible to identify "holes" in the periodic table, which led to the discovery of new elements.

Self-Assessment Exercise

7.1 Around the start of the twentieth century, improvements in refrigeration techniques allowed Sir William Ramsay to discover which elements?

(a) Copper, silver, and gold

(b) Sodium, potassium, and rubidium

(c) Neon, argon, and krypton

Exercises

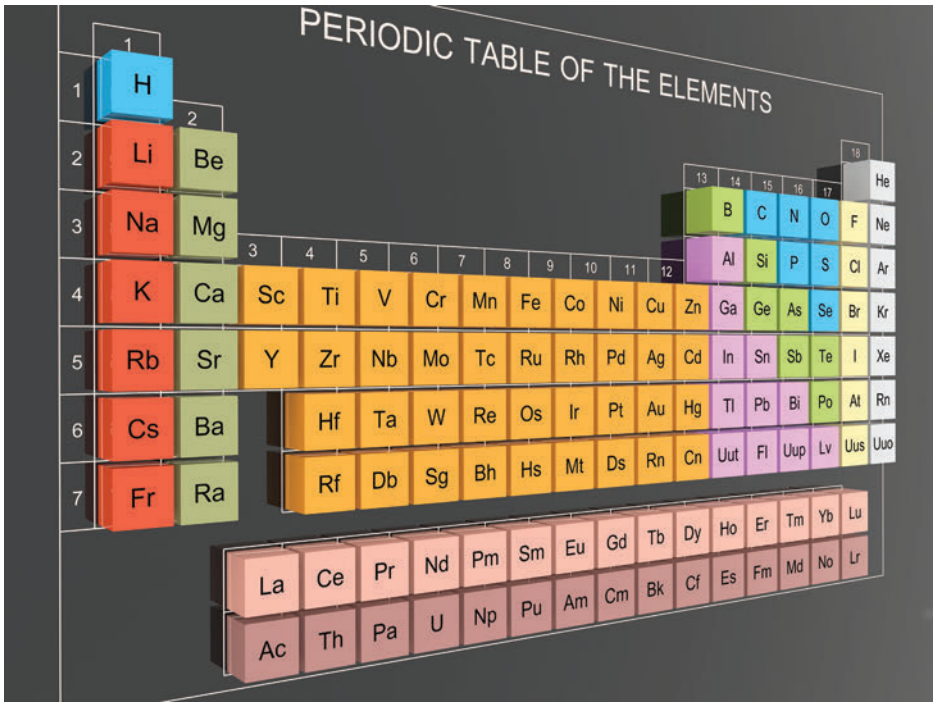
7.2 The prefix *eka-* comes from the Sanskrit word for "one." Mendeleev used this prefix to indicate that the unknown element was one place away from the known element that followed the prefix. For example, *eka-silicon*, which we now call germanium, is one element below silicon. Mendeleev also predicted the existence of *eka-manganese*, which was not experimentally confirmed until 1937 because this element is radioactive and does not occur in nature. Based on the periodic table shown in Figure 7.1, what do we now call the element Mendeleev called *eka-manganese*?

7.3 (**a**) The five most abundant elements in the Earth's crust are O, Si, Al, Fe, and Ca. Referring to Figure 7.1, are any of these elements among those known before 1700? If so which ones? (**b**) Seven of the nine elements known since ancient times are metals. Referring to Table 4.5, are these metals mostly found at the bottom or top of the activity series?

Answers to Self-Assessment Exercises

7.1 (c)

7.2 | Effective Nuclear Charge



The periodic table is a powerful tool for understanding and predicting the physical and chemical properties of elements. Typically, elements share common characteristics with neighbors that occupy the same column of the periodic table. Sodium, potassium, and rubidium are soft metals that react violently when they come in contact with water. Neon, argon, and krypton are colorless, chemically inert gases. Copper, silver, and gold are highly conductive metals that react slowly, if at all, with air and water. It is also possible to understand trends observed across a period, all of which are based on the attraction between the nuclear charge and the surrounding electrons.

By the end of this section, you should be able to

- Understand the factors that contribute to effective nuclear charge

Many properties of atoms depend on electron configuration and on how strongly the outer electrons in the atoms are attracted to the nucleus. Coulomb's law tells us that the strength of the interaction between two electrical charges depends on the magnitudes of the charges and on the distance between them. Thus, the attractive force between an electron and the nucleus depends on the magnitude of the nuclear charge and on the average distance between the nucleus and the electron. The force increases as the nuclear charge increases and decreases as the electron moves farther from the nucleus.

Understanding the attraction between the electron and the nucleus in a hydrogen atom is straightforward because we have only one electron and one proton. In a many-electron atom, however, the situation is more complicated. In addition to the attraction of each electron to the nucleus, each electron experiences the repulsion due to other electrons. These electron–electron repulsions cancel some of the attraction of the electron to the nucleus so that the electron experiences less attraction than it would if the other electrons weren't there. In essence, each electron in a many-electron atom is *screened* from the nucleus by the other electrons. It therefore experiences a net attraction that is smaller than it would experience in the absence of other electrons.

How can we account for the combination of nuclear attraction and electron repulsions for our electron of interest? The simplest way to do so is to imagine that the electron

experiences a net attraction that is the result of the nuclear attraction decreased by the electron–electron repulsions. We call this partially screened nuclear charge the **effective nuclear charge**, Z_{eff}. Because the full attractive force of the nucleus has been decreased by the electron repulsions, we see that the effective nuclear charge is always less than the *actual* nuclear charge ($Z_{eff} < Z$). We can define the amount of screening of the nuclear charge quantitatively by using a *screening constant*, S, such that

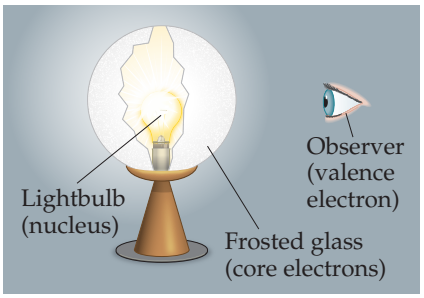
$$Z_{eff} = Z - S \qquad [7.1]$$

where S is a positive number. For a valence electron, most of the shielding is due to the core electrons, which are much closer to the nucleus. As a result, for the valence electrons in an atom *the value of S is usually close to the number of core electrons in the atom*. (Electrons in the same valence shell do not screen one another very effectively, but they do affect the value of S slightly; see "A Closer Look: Effective Nuclear Charge.")

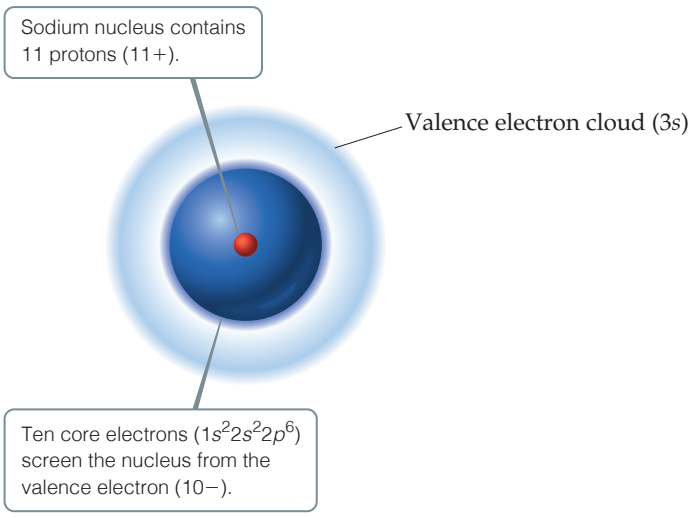
To understand better the notion of effective nuclear charge, we can use an analogy of a light bulb with a frosted glass shade (**Figure 7.2**). The light bulb represents the nucleus, and the observer is the electron of interest, which is usually a valence electron. The amount of light that the electron "sees" is analogous to the amount of net nuclear attraction experienced by the electron. The other electrons in the atom, especially the core electrons, act like a frosted glass lampshade, decreasing the amount of light that gets to the observer. If the light bulb gets brighter while the lampshade stays the same (Z increases), more light is observed. Likewise, if the lampshade gets thicker (S increases), less light is observed. We will find it helpful to keep this analogy in mind as we discuss trends in effective nuclear charge.

Let's consider what we would expect for the magnitude of Z_{eff} for the sodium atom. Sodium has the electron configuration $[Ne]3s^1$. The nuclear charge is $Z = 11+$, and there are 10 core electrons ($1s^2 2s^2 2p^6$), which serve as a "lampshade" to screen the nuclear charge "seen" by the 3*s* electron. Therefore, in the simplest approach, we expect S to equal 10 and the 3*s* electron to experience an effective nuclear charge of $Z_{eff} = 11 - 10 = 1+$ (**Figure 7.3**). The situation is more complicated, however, because the 3*s* electron has a small probability of being very close to the nucleus, in the region occupied by the core electrons. Thus, this electron experiences a greater net attraction than our simple $S = 10$ model suggests: The actual value of Z_{eff} for the 3*s* electron in Na is $Z_{eff} = 2.5+$. In other words, because there is a small probability that the 3*s* electron is close to the nucleus, the value of S in Equation 7.1 changes from 10 to 8.5.

The notion of effective nuclear charge also explains an important effect we noted in Section 6.7: For a many-electron atom, the energies of orbitals with the same n value increase with increasing l value. For example, in the carbon atom, whose electron

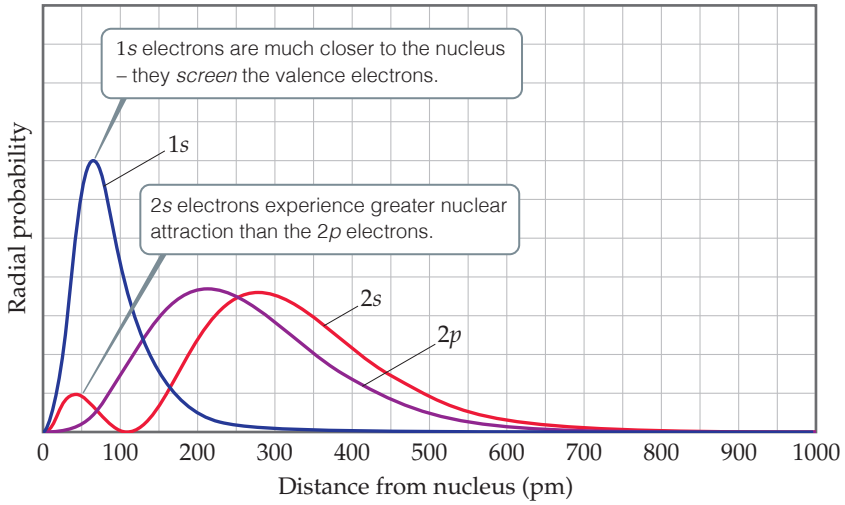


▲ **Figure 7.2 An analogy for effective nuclear charge.** We envision the nucleus as a light bulb, the core electrons as a frosted glass lampshade, and a valence electron as an observer. The amount of light seen by the observer depends on the intensity of the light bulb and the screening by the frosted glass lampshade.



◀ **Figure 7.3 Effective nuclear charge.** The effective nuclear charge experienced by the 3*s* electron in a sodium atom depends on the 11+ charge of the nucleus and the 10− charge of the core electrons.

Go Figure Which electron has a higher probability of being found within 50 pm of the nucleus, one in a 2*s* orbital or one in a 2*p* orbital? Which orbital, 2*s* or 2*p*, will be lower in energy in a multielectron atom?



▲ **Figure 7.4 Comparison of 1*s*, 2*s*, and 2*p* radial probability functions.**

configuration is $1s^2 2s^2 2p^2$, the energy of the 2*p* orbital ($l = 1$) is higher than that of the 2*s* orbital ($l = 0$), even though both orbitals are in the $n = 2$ shell (Figure 6.24). This difference in energies is due to the radial probability functions for the orbitals (**Figure 7.4**). We see first that the 1*s* electrons are much closer to the nucleus—they serve as an effective "lampshade" for the 2*s* and 2*p* electrons. Notice next that the 2*s* probability function has a small peak fairly close to the nucleus, whereas the 2*p* probability function does not. As a result, a 2*s* electron is not screened as much by the core orbitals as is a 2*p* electron. The greater attraction between the 2*s* electron and the nucleus leads to a lower energy for the 2*s* orbital than for the 2*p* orbital. The same reasoning explains the general trend in orbital energies ($ns < np < nd$) in many-electron atoms.

Finally, let's examine trends in valence-electron Z_{eff} values.

The effective nuclear charge increases from left to right across any period of the periodic table.

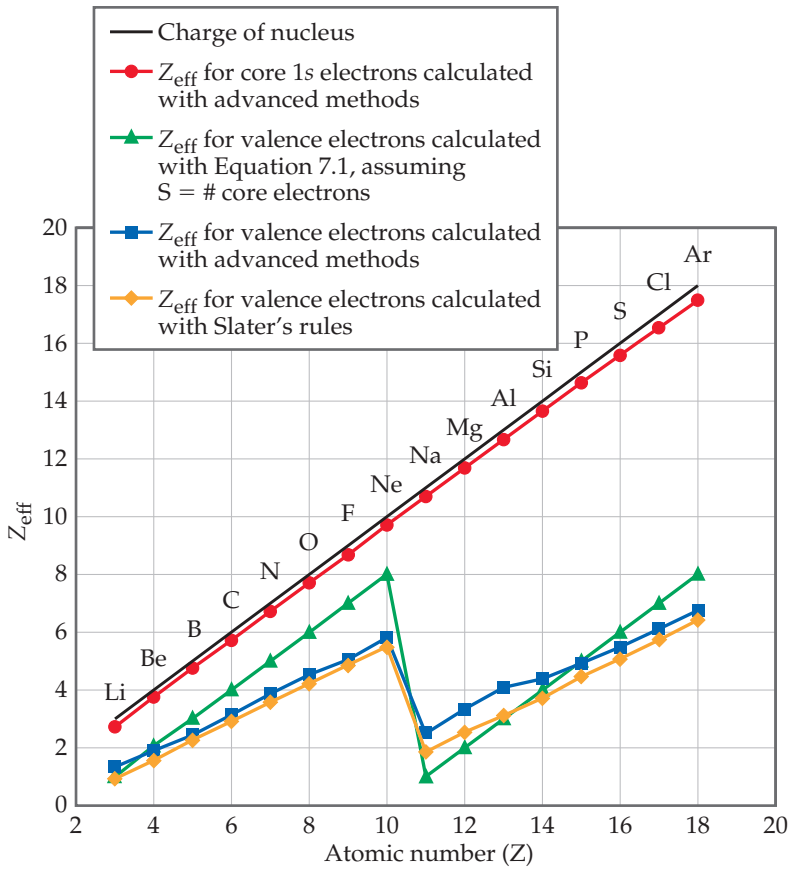
Although the number of core electrons stays the same across the period, the number of protons increases—in our analogy, we are increasing the brightness of the light bulb while keeping the shade the same. The valence electrons added to counterbalance the increasing nuclear charge screen one another ineffectively. Thus, Z_{eff} increases steadily. For example, the two core electrons of lithium ($1s^2 2s^1$) screen the 2*s* valence electron from the 3+ nucleus fairly efficiently. Consequently, the valence electron experiences an effective nuclear charge of roughly $3 - 2 = 1+$. For beryllium ($1s^2 2s^2$) the effective nuclear charge experienced by each valence electron is larger because here the two core 1*s* electrons screen a 4+ nucleus, and each 2*s* electron only partially screens the other. Consequently, the effective nuclear charge experienced by each 2*s* electron is about $4 - 2 = 2+$.

Going down a column, the effective nuclear charge experienced by valence electrons changes far less than it does across a period. For example, using our simple estimate for *S*, we would expect the effective nuclear charge experienced by the valence electrons in lithium and sodium to be about the same, roughly $3 - 2 = 1+$ for lithium and $11 - 10 = 1+$ for sodium. In fact, however, *effective nuclear charge increases slightly as we go down a column* because the more diffuse core electron cloud is less able to screen the valence electrons from the nuclear charge. In the case of the alkali metals, Z_{eff} increases from 1.3+ for lithium, to 2.5+ for sodium, to 3.5+ for potassium.

A CLOSER LOOK Effective Nuclear Charge

To get a sense of how effective nuclear charge varies as both nuclear charge and number of electrons increase, consider Figure 7.5. Although the details of how the Z_{eff} values in the graph were calculated are beyond the scope of our discussion, the trends are instructive.

The effective nuclear charge felt by the outermost electrons is smaller than that felt by inner electrons because of screening by the inner electrons. In addition, the effective nuclear charge felt by the outermost electrons does not increase as steeply with increasing atomic number because the valence electrons make a small but nonnegligible contribution to the screening constant *S*. The most striking feature associated with the Z_{eff} value for the outermost electrons is the sharp drop between the last Period 2 element (Ne) and the first Period 3 element (Na). This drop reflects the fact that the core electrons are much more effective than the valence electrons at screening the nuclear charge.



▲ **Figure 7.5 Variations in effective nuclear charge for Period 2 and Period 3 elements.** Moving from one element to the next in the periodic table, the increase in Z_{eff} felt by the innermost (1*s*) electrons (red circles) closely tracks the increase in nuclear charge *Z* (black line) because these electrons are not screened much. The results of several methods to calculate Z_{eff} for valence electrons are shown in other colors.

Because Z_{eff} can be used to understand many physically measurable quantities, it is desirable to have a simple method for estimating it. The value of *Z* in Equation 7.1 is known exactly, so the challenge boils down to estimating the value of *S*. In the text, we estimated *S* very simply by assuming that each core electron contributes 1.00 to *S* and the outer electrons contribute nothing. A more accurate approach was developed by John Slater (1900–1976), however, and we can use his approach if we limit ourselves to elements that do not have electrons in *d* or *f* subshells.

Electrons for which the principal quantum number *n* is larger than the value of *n* for the electron of interest contribute 0 to the value of *S*. Electrons with the same value of *n* as the electron of interest contribute 0.35 to the value of *S*. Electrons that have principal quantum number $n - 1$ contribute 0.85, while those with even smaller values of *n* contribute 1.00. For example, consider fluorine, which has the ground-state electron configuration $1s^2 2s^2 2p^5$. For a valence electron in fluorine, Slater's rules tell us that $S = (0.35 \times 6) + (0.85 \times 2) = 3.8$. (Slater's rules ignore the contribution of an electron to itself in screening; therefore, we consider only six $n = 2$ electrons, not all seven). Thus, $Z_{eff} = Z - S = 9 - 3.8 = 5.2+$, a little lower than the simple estimate of $9 - 2 = 7+$.

Values of Z_{eff} estimated using the simple method outlined in the text, as well as those estimated with Slater's rules, are plotted in Figure 7.5. While neither of these methods exactly replicates the values of Z_{eff} obtained from more sophisticated calculations, both methods effectively capture the periodic variation in Z_{eff}. While Slater's approach is more accurate, the method outlined in the text does a reasonably good job of estimating Z_{eff} despite its simplicity. For our purposes, therefore, we can assume that the screening constant *S* in Equation 7.1 is roughly equal to the number of core electrons.

Related Exercises: 7.6, 7.16, 7.54, 7.62, 7.89, 7.90, 7.119

Self-Assessment Exercise

7.4 Which would you expect to experience a greater effective nuclear charge?

(a) A 3*p* electron of an Ar atom

(b) A 4*s* electron of a Ca atom

Exercises

7.5 Among the elements N, O, P, and S, which element or elements have the smallest effect nuclear charge if we use Equation 7.1 to calculate Z_{eff}? Which element or elements have the largest effective nuclear charge?

7.6 Detailed calculations show that the value of Z_{eff} for the outermost electrons in Na and K atoms is 2.51+ and 3.49+, respectively. (**a**) What value do you estimate for Z_{eff} experienced by the outermost electron in both Na and K by

assuming core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant? (**b**) What values do you estimate for Z_{eff} using Slater's rules? (**c**) Which approach gives a more accurate estimate of Z_{eff}? (**d**) Does either method of approximation account for the gradual increase in Z_{eff} that occurs upon moving down a group? (**e**) Predict Z_{eff} for the outermost electrons in the Rb atom based on the calculations for Na and K.

7.7 Which will experience the greater effect nuclear charge, the electrons in the $n = 2$ shell in F or the $n = 2$ shell in B? Which will be closer to the nucleus?

Answers to Self-Assessment Exercises

7.4 (a)

7.3 Sizes of Atoms and Ions



Hydrogen offers considerable promise as a clean fuel to power vehicles. However, finding an effective means of storage is currently a barrier to its widespread adoption. The very low boiling point (−253 °C) makes cryogenic storage expensive, and compressing hydrogen in tanks adds an unacceptable amount of weight to any vehicle. The very small size of the hydrogen molecule could be the key to its storage. A class of new materials called MOFs (metal organic frameworks) have been engineered by chemists to have a porous structure with cavities large enough to accommodate hydrogen molecules. Rather like water in a sponge, the absorption of hydrogen into the MOF structure is reversible and storage capacities greater than that in a compressed gas tank can be achieved.

By the end of this section, you should be able to

- Use the periodic table to predict the trends in atomic radii
- Explain how the radius of an atom changes upon losing electrons to form a cation or gaining electrons to form an anion

It is tempting to think of atoms as hard, spherical objects. According to the quantum-mechanical model, however, atoms do not have sharply defined boundaries at which the electron distribution becomes zero. Nevertheless, we can define atomic size in several ways, based on the distances between atoms in various situations.

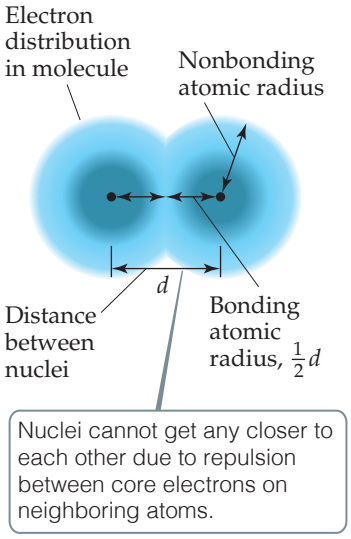
Imagine a collection of argon atoms in the gas phase. When two of these atoms collide, they ricochet apart like colliding billiard balls. This ricocheting happens because

the electron clouds of the colliding atoms cannot penetrate each other to any significant extent. The shortest distance separating the two nuclei during such collisions is twice the radii of the atoms. We call this radius the *nonbonding atomic radius* or the *van der Waals* radius (**Figure 7.6**).

In molecules, the attractive interaction between any two adjacent atoms is what we recognize as a chemical bond. We discuss bonding in Chapters 8 and 9. For now, we need to realize that two bonded atoms are closer together than they would be in a nonbonding collision where the atoms ricochet apart. We can therefore define an atomic radius based on the distance between the nuclei when two atoms are bonded to each other, shown as distance d in Figure 7.6. The **bonding atomic radius** for any atom in a molecule is equal to half of the bond distance d. Note from Figure 7.6 that the bonding atomic radius (also known as the *covalent radius*) is smaller than the nonbonding atomic radius. Unless otherwise noted, we mean the bonding atomic radius when we speak of the "size" of an atom.

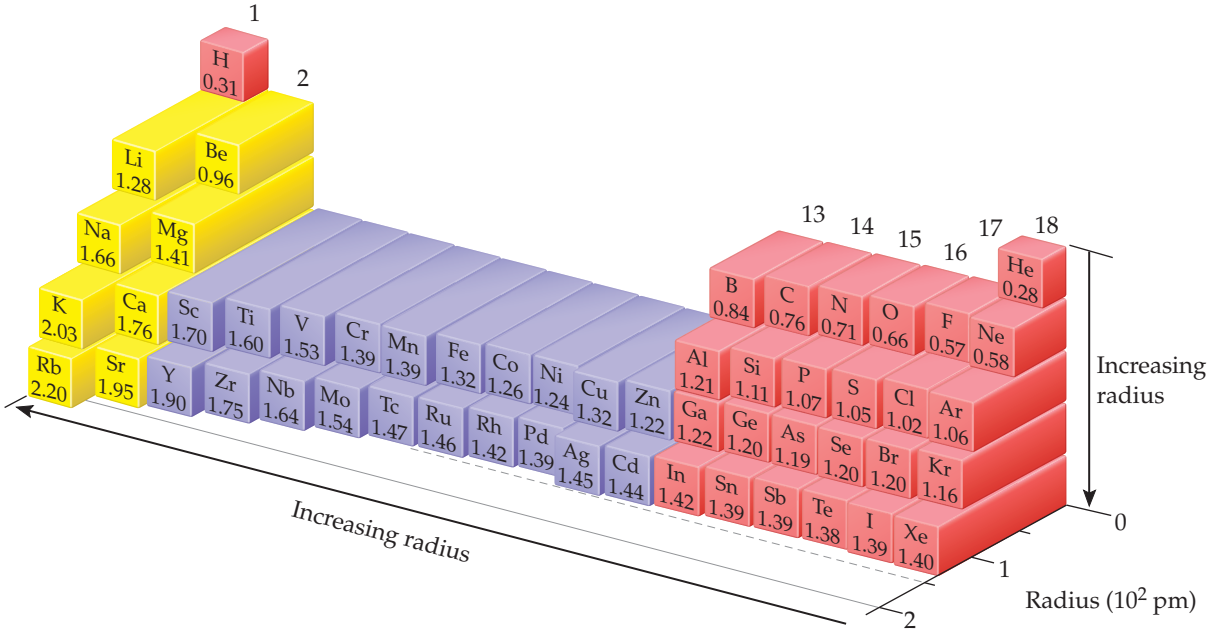
Although it is very difficult to measure the nonbonding atomic radius of an atom, scientists have developed a variety of techniques for measuring the distances separating nuclei in molecules. From observations of these distances in many molecules, each element can be assigned a bonding atomic radius. For example, in the I_2 molecule, the distance separating the nuclei is observed to be 266 pm, which means the bonding atomic radius of an iodine atom in I_2 is $(266\text{ pm})/2 = 133\text{ pm}$. Similarly, the distance separating adjacent carbon nuclei in diamond (a three-dimensional solid network of carbon atoms) is 154 pm; thus, the bonding atomic radius of carbon in diamond is 77 pm. By using structural information on more than 30,000 substances, a consistent set of bonding atomic radii of the elements can be defined (**Figure 7.7**). Note that for the lighter noble gases, the bonding atomic radii must be estimated because there are no known compounds of these elements.

The atomic radii in Figure 7.7 allows us to estimate bond lengths in molecules. For example, the bonding atomic radii for C and Cl are 76 pm and 102 pm, respectively. In CCl_4 the measured length of the C—Cl bond is 177 pm, very close to the sum $(76 + 102\text{ pm})$ of the bonding atomic radii of Cl and C.



▲ **Figure 7.6** **Distinction between nonbonding and bonding atomic radii within a molecule.**

Go Figure Which part of the periodic table (top/bottom, left/right) has the elements with the largest atoms?

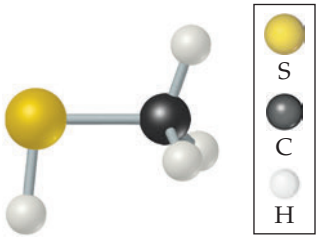


▲ **Figure 7.7** **Trends in bonding atomic radii for Periods 1 through 5.**

Sample Exercise 7.1

Bond Lengths in a Molecule

Natural gas used in home heating and cooking is odorless. Because natural gas leaks pose the danger of explosion or suffocation, various smelly substances are added to the gas to allow detection of a leak. One such substance is methyl mercaptan, CH_3SH. Use Figure 7.7 to predict the lengths of the C—S, C—H, and S—H bonds in this molecule.



Methyl mercaptan

SOLUTION

Analyze and Plan We are given three bonds and told to use Figure 7.7 for bonding atomic radii. We will assume that each bond length is the sum of the bonding atomic radii of the two atoms involved.

Solve

$$\begin{aligned} \text{C—S bond length} &= \text{bonding atomic radius of C} \\ &\quad + \text{bonding atomic radius of S} \\ &= 76\ \text{pm} + 105\ \text{pm} = 181\ \text{pm} \\ \text{C—H bond length} &= 76\ \text{pm} + 31\ \text{pm} = 107\ \text{pm} \\ \text{S—H bond length} &= 105\ \text{pm} + 31\ \text{pm} = 136\ \text{pm} \end{aligned}$$

Check The experimentally determined bond lengths are C—S = 182 pm, C—H = 110 pm, and S—H = 133 pm. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted from bonding atomic radii than do bonds involving larger atoms.)

Comment Notice that our estimated bond lengths are close but not exact matches to the measured bond lengths. Bonding atomic radii must be used with some caution in estimating bond lengths.

Practice Exercise

Using Figure 7.7, predict which is longer, the P—Br bond in PBr_3 or the As—Cl bond in $AsCl_3$.

Periodic Trends in Atomic Radii

Figure 7.7 shows two interesting trends:

1. *Within each group, bonding atomic radius tends to increase from top to bottom.* This trend results primarily from the increase in the principal quantum number (n) of the outer electrons. As we go down a column, the outer electrons have a greater probability of being farther from the nucleus, causing the atomic radius to increase.
2. *Within each period, bonding atomic radius tends to decrease from left to right* (although there are some minor exceptions, such as for Cl to Ar or As to Se). The major factor influencing this trend is the increase in effective nuclear charge Z_{eff} across a period. The increasing effective nuclear charge steadily draws the valence electrons closer to the nucleus, causing the bonding atomic radius to decrease.

Periodic Trends in Ionic Radii

Just as bonding atomic radii can be determined from interatomic distances in molecules, ionic radii can be determined from interatomic distances in ionic compounds. Like the size of an atom, the size of an ion depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the valence electrons reside. When a cation is formed from a neutral atom, electrons are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus. Also, when a cation is formed the number of electron–electron repulsions is reduced. Therefore, *cations are smaller than their parent atoms* (**Figure 7.8**). The opposite is true of anions. When electrons are added to an atom to form an anion, the increased electron–electron repulsions cause the electrons to spread out more in space. Thus, *anions are larger than their parent atoms.*

For ions carrying the same charge, ionic radius increases as we move down a column in the periodic table (Figure 7.8). In other words, as the principal quantum number of the outermost occupied orbital of an ion increases, the radius of the ion increases.

An **isoelectronic series** is a group of ions all containing the same number of electrons. For example, each ion in the isoelectronic series O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+} has

Sample Exercise 7.2

Predicting Relative Sizes of Atomic Radii

Referring to the periodic table, arrange (as much as possible) the atoms B, C, Al, and Si in order of increasing size.

SOLUTION

Analyze and Plan We are given the chemical symbols for four elements and told to use their relative positions in the periodic table to predict the relative size of their atomic radii. We can use the two periodic trends described in the text to help with this problem.

Solve

B and C are in the same period, with C to the right of B. Therefore, we expect the radius of C to be smaller than that of B because radii usually decrease as we move across a period.	radius C $<$ radius B
Al and Si are in the same period, with Si to the right of Al.	radius Si $<$ radius Al
The radius increases as we move down a group with Al and B belonging to the same group, as do C and Si.	radius B $<$ radius Al radius C $<$ radius Si
Combining these comparisons, we can conclude that C has the smallest radius and Al the largest. Unfortunately, the two periodic trends available to us do not supply enough information to determine the relative sizes of B and Si.	radius C $<$ radius B $\sim$ radius Si $<$ radius Al

Check Referring back to Figure 7.7, we can obtain numerical values for each atomic radius that allow us to say that the radius of Si is greater than that of B.

$$\text{C}(76\text{ pm}) < \text{B}\,(84\text{ pm}) < \text{Si}\,(111\text{ pm}) < \text{Al}\,(121\text{ pm})$$

If you examine Figure 7.7 carefully, you will discover that for the *s*- and *p*-block elements the increase in radius moving one element down a column tends to be greater than the increase moving one element left across a row. There are exceptions, however.

Comment Note that the trends we have just discussed are for the *s*- and *p*-block elements. As seen in Figure 7.7, the transition elements do not show a regular decrease moving across a period.

Practice Exercise

Arrange Be, C, K, and Ca in order of increasing atomic radius.

Sample Exercise 7.3

Predicting Relative Sizes of Atomic and Ionic Radii

Arrange Mg^{2+}, Ca^{2+}, and Ca in order of decreasing radius.

SOLUTION

Cations are smaller than their parent atoms, and so $Ca^{2+} < Ca$. Because Ca is below Mg in Group 2, Ca^{2+} is larger than Mg^{2+}. Consequently, $Ca > Ca^{2+} > Mg^{2+}$.

Practice Exercise

Arrange the following atoms and ions in order of increasing ionic radius: F, S^{2-}, Cl, and Se^{2-}.

(**a**) $F < S^{2-} < Cl < Se^{2-}$
(**b**) $F < Cl < S^{2-} < Se^{2-}$
(**c**) $F < S^{2-} < Se^{2-} < Cl$
(**d**) $Cl < F < Se^{2-} < S^{2-}$
(**e**) $S^{2-} < F < Se^{2-} < Cl$

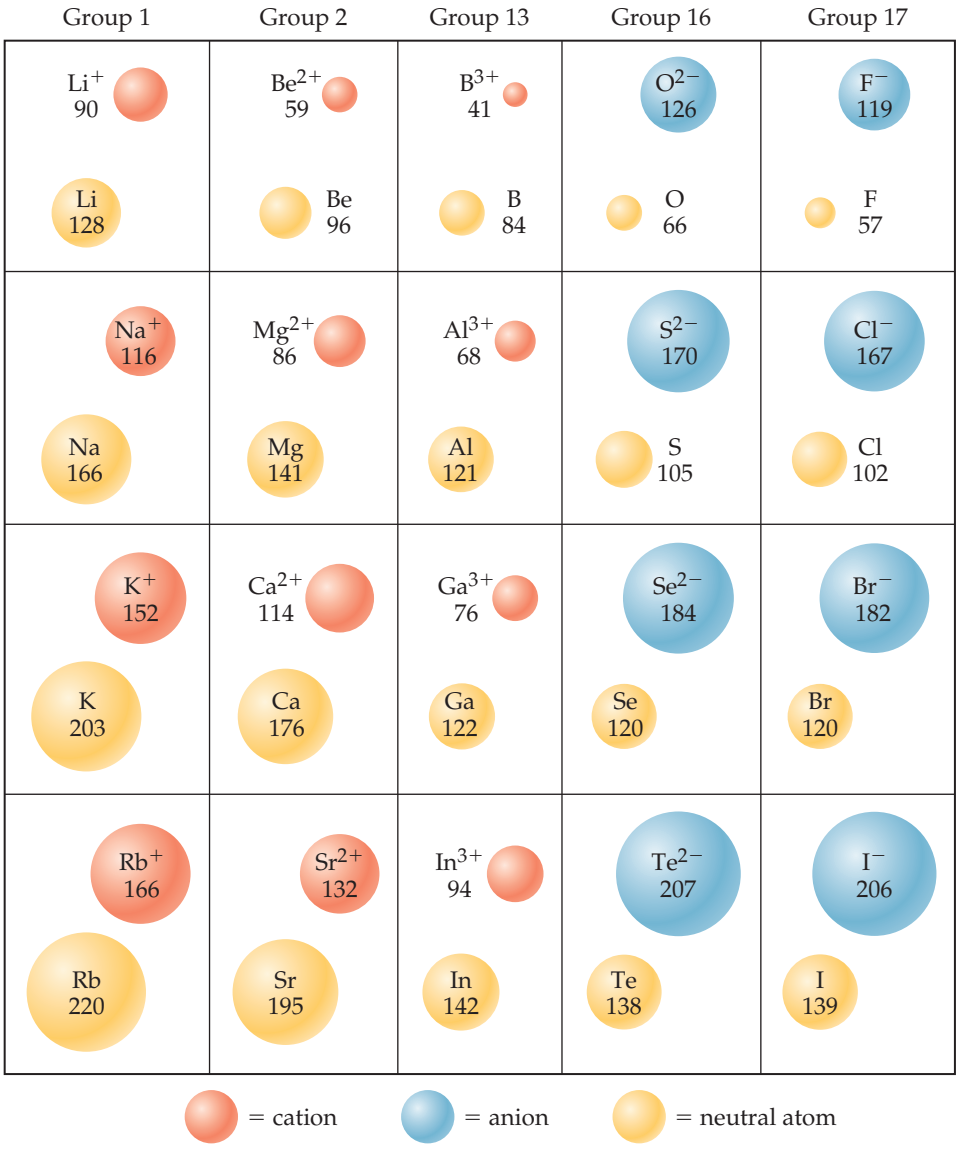
10 electrons. In any isoelectronic series, we can list the members in order of increasing atomic number; therefore, the nuclear charge increases as we move through the series. Because the number of electrons remains constant, ionic radius decreases with increasing nuclear charge as the electrons are more strongly attracted to the nucleus:

Increasing nuclear charge $\longrightarrow$

8 protons 10 electrons	9 protons 10 electrons	11 protons 10 electrons	12 protons 10 electrons	13 protons 10 electrons
O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
126 pm	119 pm	116 pm	86 pm	68 pm

Decreasing ionic radius $\longrightarrow$

Go Figure How do cations of the same charge change in radius as you move down a column in the periodic table?



▲ **Figure 7.8 Cation and anion size.** Radii, in picometers, of atoms and their ions for five groups of representative elements.

Sample Exercise 7.4

Ionic Radii in an Isoelectronic Series

Arrange the ions K^+, Cl^-, Ca^{2+}, and S^{2-} in order of decreasing size.

SOLUTION

This is an isoelectronic series, with all ions having 18 electrons. In such a series, size decreases as nuclear charge (atomic number) increases. The atomic numbers of the ions are S 16, Cl 17, K 19, Ca 20. Thus, the ions decrease in size in the order $S^{2-} > Cl^- > K^+ > Ca^{2+}$.

Practice Exercise

Arrange the following ions in order of increasing ionic radius: Br^-, Rb^+, Se^{2-}, Sr^{2+}, Te^{2-}.

(**a**) $Sr^{2+} < Rb^+ < Br^- < Se^{2-} < Te^{2-}$
(**b**) $Br^- < Sr^{2+} < Se^{2-} < Te^{2-} < Rb^+$
(**c**) $Rb^+ < Sr^{2+} < Se^{2-} < Te^{2-} < Br^-$
(**d**) $Rb^+ < Br^- < Sr^{2+} < Se^{2-} < Te^{2-}$
(**e**) $Sr^{2+} < Rb^+ < Br^- < Te^{2-} < Se^{2-}$

CHEMISTRY PUT TO WORK Ionic Size and Lithium-Ion Batteries

Ionic size plays a major role in determining the properties of devices that rely on movement of ions, such as batteries. "Lithium-ion" batteries, which have become common energy sources for electronic devices such as cell phones, iPads, laptop computers, and electric vehicles rely in part on the small size of the lithium ion for their operation.

A fully charged battery spontaneously produces an electric current and, therefore, power when its positive and negative electrodes are connected to an electrical load, such as a device to be powered. The positive electrode is called the anode, and the negative electrode is called the cathode. The materials used for the electrodes in lithium-ion batteries are under intense development. Currently, the anode material is graphite, a form of carbon, and the cathode is a transition metal oxide, often lithium cobalt oxide, $LiCoO_2$ (**Figure 7.9**). Between anode and cathode is a *separator,* a porous solid material that allows the passage of lithium ions but not electrons.

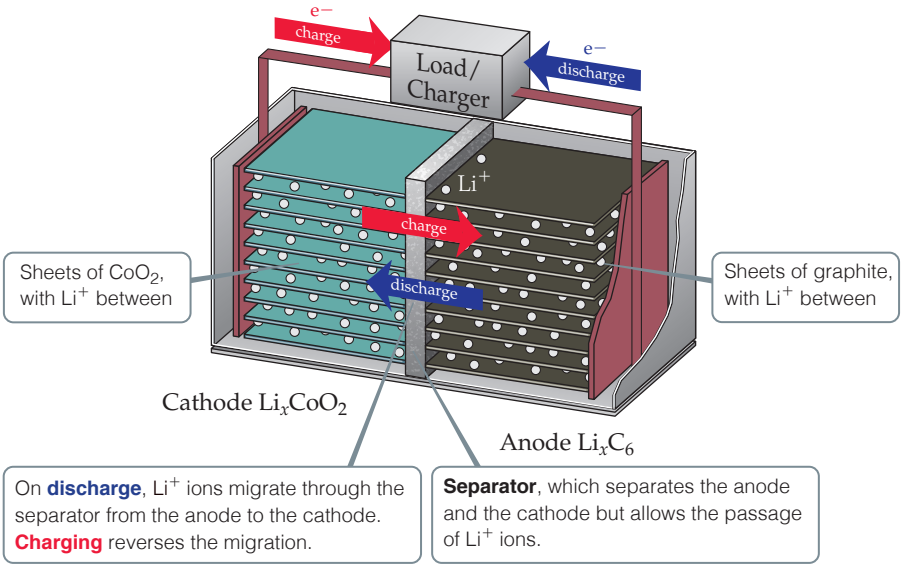
When the battery is being charged by an external source, lithium ions migrate through the separator from the cathode to the anode where they insert between the layers of carbon atoms. The ability of an ion to move through a solid increases as the size of the ion decreases and as the charge on the ion decreases. Lithium ions are smaller than most other cations, and they carry only a 1+ charge, which allows them to migrate more readily than other ions can. As an added bonus, lithium is one of the lightest elements, which is attractive for use in electric vehicles. When the battery discharges, the lithium ions move from anode to cathode. To maintain charge balance, electrons simultaneously migrate from anode to cathode through an external circuit, thereby producing electricity.

At the cathode, lithium ions then insert in the oxide material. Again, the small size of lithium ions is an advantage. For every lithium ion that inserts into the lithium cobalt oxide cathode, a Co^{4+} ion is reduced to a Co^{3+} ion by an electron that has traveled through the external circuit.

The ion migration and the changes in structure that result when lithium ions enter and leave the electrode materials are complicated. Furthermore, the operation of all batteries generate heat because they are not perfectly efficient. In the case of Li-ion batteries, the heating of the separator material (typically a polymer) has led to problems as the size of the batteries has been scaled larger to increase energy capacity. In a very small number of cases, overheating of Li-ion batteries has caused the batteries to catch fire.

Teams worldwide are trying to discover new cathode and anode materials that will easily accept and release lithium ions without falling apart over many repeated cycles. New separator materials that allow for faster passage of lithium ions with less heat generation are also under development. Some research groups are looking at using sodium ions instead of lithium ions because sodium is far more abundant than lithium, although the larger size of sodium ions poses additional challenges. In the coming years, look for continued advances in battery technology based on alkali metal ions.

Related Exercise: 7.98



▲ **Figure 7.9** **Schematic of a lithium-ion battery.**

Self-Assessment Exercise

7.8 The decrease is atomic size left to right across a period is due to:

(a) Atoms of higher atomic number having more electrons

(b) An increase in Z_{eff} across a period

(c) An increase in the principle quantum number of the outer electrons across a period

7.9 When an atom forms a cation, does the radius of the species increase or decrease?

(a) Increase

(b) Decrease

Exercises

7.10 Which quantity must be determined experimentally in order to determine the bonding atomic radius of an atom? (**a**) The distance from the nucleus where the probability of finding an electron goes to zero. (**b**) The distance between the nuclei of two atoms that are bonded together. (**c**) The effective nuclear charge of an atom.

7.11 Tungsten has the highest melting point of any metal in the periodic table: 3422 °C. The distance between W atoms in tungsten metal is 274 pm. (**a**) What is the atomic radius of a tungsten atom in this environment? (This radius is called the *metallic radius*.) (**b**) If you put tungsten metal under high pressure, predict what would happen to the distance between W atoms.

7.12 Estimate the P—Cl bond length from the data in Figure 7.7 and compare your value to the experimental P—Cl bond length in phosphorus tetrachloride PCl_3, 204 pm.

7.13 Using only the periodic table, arrange each set of atoms in order from largest to smallest: (**a**) Ar, As, Kr; (**b**) Cd, Rb, Te; (**c**) C, Cl, Cu.

7.14 Identify each statement as true or false: (**a**) Cations are larger than their corresponding neutral atoms. (**b**) Li^+ is smaller than Li. (**c**) Cl^- is bigger than I^-.

7.15 Which neutral atom is isoelectronic with each of the following ions? H^-, Ca^{2+}, In^{3+}, Ge^{2+}.

7.16 Consider the isoelectronic ions F^- and Na^+. (**a**) Which ion is smaller? (**b**) Using Equation 7.1 and assuming that core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant, S, calculate Z_{eff} for the $2p$ electrons in both ions. (**c**) Repeat this calculation using Slater's rules to estimate the screening constant, S. (**d**) For isoelectronic ions, how are effective nuclear charge and ionic radius related?

Answers to Self-Assessment Exercises

7.8 (b) 7.9 (b)

7.4 | Ionization Energy



Solar wind is a stream of charged particles, mostly electrons, protons, and alpha particles, that is constantly emitted by the sun. The magnetosphere of the earth protects us from this radiation. However, there are times when the magnetic shield and solar wind do interact and give rise to excited atoms, molecules, and ions, which are observed as a beautiful play of lights, the aurora, in the sky near the poles.

By the end of this section, you should be able to

- Predict the trends in ionization energy as successive electrons are removed from an atom.

The ease with which electrons can be removed from an atom or ion has a major impact on chemical behavior. The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. We first encountered ionization in our discussion of the Bohr model of the hydrogen atom. If the electron in an H atom is excited from $n = 1$ (the ground state) to $n = \infty$, the electron is completely removed from the atom; the atom is *ionized*.

In general, the *first ionization energy*, I_1, is the energy needed to remove the first electron from a neutral atom. For example, the first ionization energy for the sodium atom is the energy required for the process

$$Na(g) \longrightarrow Na^+(g) + e^- \qquad [7.2]$$

The *second ionization energy*, I_2, is the energy needed to remove the second electron, and so forth, for successive removals of additional electrons. Thus, I_2 for the sodium atom is the energy associated with the process

$$Na^+(g) \longrightarrow Na^{2+}(g) + e^- \qquad [7.3]$$

Variations in Successive Ionization Energies

The magnitude of the ionization energy tells us how much energy is required to remove an electron; the greater the ionization energy, the more difficult it is to remove an electron. Notice in **Table 7.2** that ionization energies for a given element increase as successive electrons are removed: $I_1 < I_2 < I_3$, and so forth. This trend makes sense because with each successive removal, an electron is being pulled away from an increasingly positive ion, requiring increasingly more energy.

A second important feature shown in Table 7.2 is the sharp increase in ionization energy that occurs when an inner-shell electron is removed. For example, consider silicon, $1s^2 2s^2 2p^6 3s^2 3p^2$. The ionization energies increase steadily from 786 to 4356 kJ/mol for the four electrons in the 3*s* and 3*p* subshells. Removal of the fifth electron, which comes from the 2*p* subshell, requires a great deal more energy: 16 091 kJ/mol. The large increase occurs because the 2*p* electron is much more likely to be found close to the nucleus than are the four $n = 3$ electrons, and, therefore, the 2*p* electron experiences a much greater effective nuclear charge than do the 3*s* and 3*p* electrons.

Every element exhibits a large increase in ionization energy when the first of its inner-shell electrons is removed. This observation supports the idea that only the outermost electrons are involved in the sharing and transfer of electrons that give rise to chemical bonding and reactions. As we will see when we talk about chemical bonds in Chapters 8 and 9, the inner electrons are too tightly bound to the nucleus to be lost from the atom or even shared with another atom.

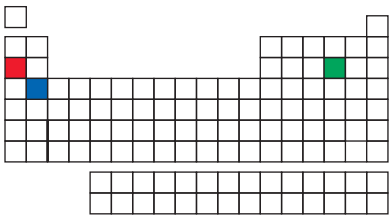
TABLE 7.2 Successive Values of Ionization Energies, *I*, for the Elements Sodium to Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(inner-shell electrons)		
Al	578	1817	2745	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2914	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3822	5159	6542	9362	11018
Ar	1521	2666	3931	5771	7238	8781	11995

Sample Exercise 7.5

Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin. Which one has the largest second ionization energy?



SOLUTION

Analyze and Plan The locations of the elements in the periodic table allow us to predict the electron configurations. The greatest ionization energies involve removal of core electrons. Thus, we should look first for an element with only one electron in the outermost occupied shell.

Solve The red box represents Na, which has one valence electron. The second ionization energy of this element is associated, therefore, with the removal of a core electron. The other elements indicated, S (green) and Ca (blue), have two or more valence electrons. Thus, Na should have the largest second ionization energy.

Check A chemistry handbook gives these I_2 values: Ca, 1145 kJ/mol; S, 2252 kJ/mol; Na, 4562 kJ/mol.

Practice Exercise

The third ionization energy of bromine is the energy required for which of the following processes?

(**a**) $Br(g) \longrightarrow Br^+(g) + e^-$ (**b**) $Br^+(g) \longrightarrow Br^{2+}(g) + e^-$
(**c**) $Br(g) \longrightarrow Br^{2+}(g) + 2\,e^-$ (**d**) $Br(g) \longrightarrow Br^{3+}(g) + 3\,e^-$
(**e**) $Br^{2+}(g) \longrightarrow Br^{3+}(g) + e^-$

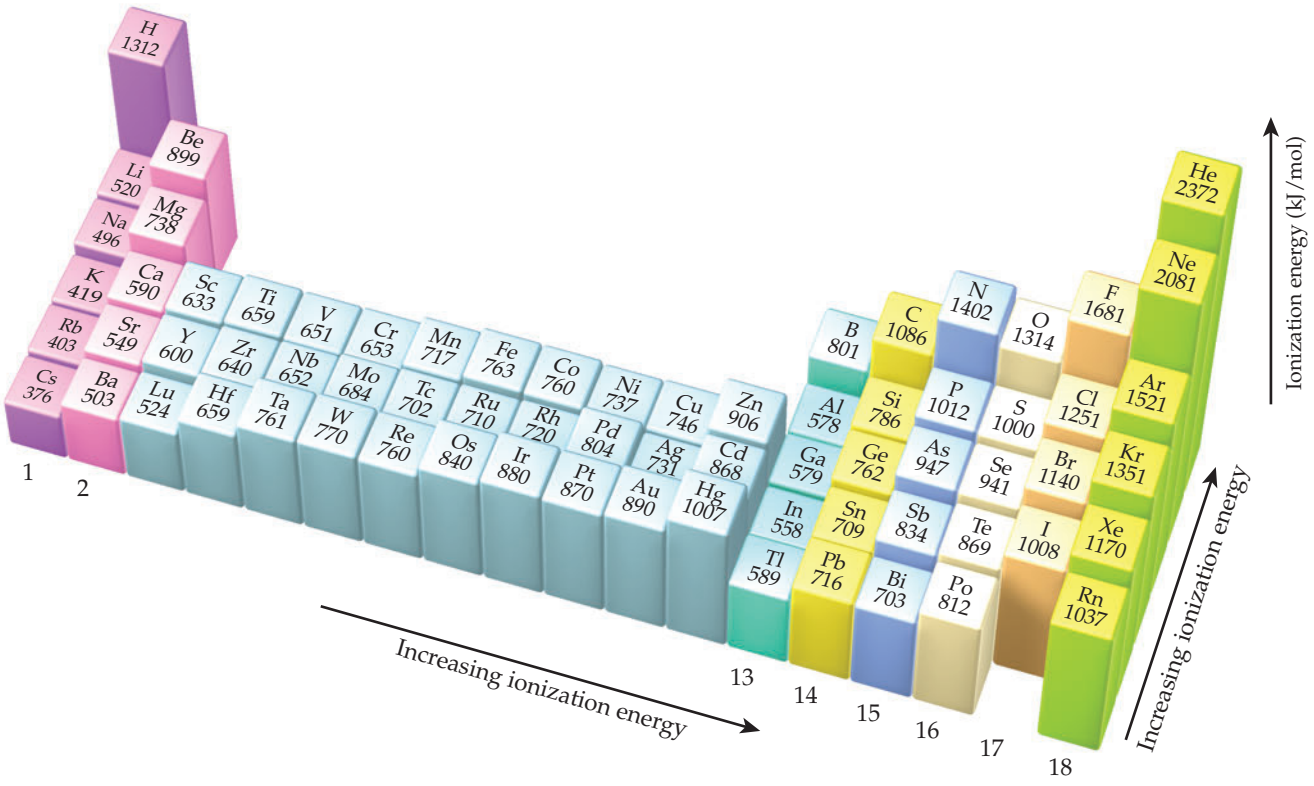
Periodic Trends in First Ionization Energies

Figure 7.10 shows, for the first 54 elements, the trends we observe in first ionization energies as we move from one element to another in the periodic table. The important trends are as follows:

1. I_1 *generally increases as we move left to right across a period.* The alkali metals show the lowest ionization energy in each period, and the noble gases show the highest. There are slight irregularities in this trend that we will discuss shortly.
2. I_1 *generally decreases as we move down any column in the periodic table.* For example, the ionization energies of the noble gases follow the order He > Ne > Ar > Kr > Xe.
3. *The* s- *and* p-*block elements show a larger range of* I_1 *values than do the transition metal elements*. Generally, the ionization energies of the transition metals increase slowly from left to right in a period. The *f*-block metals (not shown in Figure 7.10) also show only a small variation in the values of I_1.

In general, smaller atoms have higher ionization energies. The same factors that influence atomic size also influence ionization energies. The energy needed to remove an electron from the outermost occupied shell depends on both the effective nuclear charge and the average distance of the electron from the nucleus. Either increasing the effective nuclear charge or decreasing the distance from the nucleus increases the attraction between the electron and the nucleus. As this attraction increases, it becomes more difficult to remove the electron, and, thus, the ionization energy increases. As we move across a period, there is both an increase in effective nuclear charge and a decrease in atomic radius, causing the ionization energy to increase. As we move down a column, the atomic radius increases, while the effective nuclear charge increases only gradually. The increase in radius dominates, so the attraction between the nucleus and the electron decreases, causing the ionization energy to decrease.

Go Figure The value for astatine, At, is missing in this figure. To the nearest 100 kJ/mol, what estimate would you make for the first ionization energy of At?

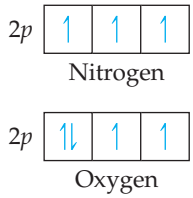


▲ **Figure 7.10** The first ionization energies of the elements in kJ/mol.

The irregularities in a given period are subtle but still readily explained. For example, the decrease in ionization energy from beryllium ($[He]2s^2$) to boron ($[He]2s^22p^1$), shown in Figure 7.10, occurs because the third valence electron of B must occupy the 2*p* subshell, which is empty for Be. Recall that the 2*p* subshell is at a higher energy than the 2*s* subshell (Figure 6.24). The slight decrease in ionization energy when moving from nitrogen ($[He]2s^22p^3$) to oxygen ($[He]2s^22p^4$) is the result of the repulsion of paired electrons in the p^4 configuration (**Figure 7.11**). Remember that according to Hund's rule, each electron in the p^3 configuration resides in a different *p* orbital, which minimizes the electron–electron repulsion among the three 2*p* electrons.

Go Figure

Why is it easier to remove a 2*p* electron from an oxygen atom than from a nitrogen atom?



▲ **Figure 7.11** **2*p* orbital filling in nitrogen and oxygen.**

Electron Configurations of Ions

When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the largest principal quantum number, *n*. For example, when one electron is removed from a lithium atom ($1s^22s^1$), it is the $2s^1$ electron:

$$Li(1s^22s^1) \Rightarrow Li^+(1s^2) + e^-$$

Likewise, when two electrons are removed from Fe ($[Ar]4s^23d^6$), the $4s^2$ electrons are the ones removed:

$$Fe([Ar]4s^23d^6) \Rightarrow Fe^{2+}([Ar]3d^6) + 2\,e^-$$

If an additional electron is removed, forming Fe^{3+}, it comes from a 3*d* orbital because all the orbitals with $n = 4$ are empty:

$$Fe^{2+}([Ar]3d^6) \Rightarrow Fe^{3+}([Ar]3d^5) + e^-$$

Sample Exercise 7.6

Periodic Trends in Ionization Energy

Referring to the periodic table, arrange the atoms Ne, Na, P, Ar, K in order of increasing first ionization energy.

SOLUTION

Analyze and Plan We are given the chemical symbols for five elements. To rank them according to increasing first ionization energy, we need to locate each element in the periodic table. We can then use their relative positions and the trends in first ionization energies to predict their order.

Solve Ionization energy increases as we move left to right across a period and decreases as we move down a group. Because Na, P, and Ar are in the same period, we expect I_1 to vary in the order Na < P < Ar. Because Ne is above Ar in Group 18, we expect Ar < Ne. Similarly, K is directly below Na in Group 1, and so we expect K < Na.

From these observations, we conclude that the ionization energies follow the order

$$K < Na < P < Ar < Ne$$

Check The values shown in Figure 7.10 confirm this prediction.

Practice Exercise

Consider the following statements about first ionization energies:

(i) Because the effective nuclear charge for Mg is greater than that for Be, the first ionization energy of Mg is greater than that of Be.

(ii) The first ionization energy of O is less than that of N because in O we must pair electrons in one of the 2*p* orbitals.

(iii) The first ionization energy of Ar is less than that of Ne because a 3*p* electron in Ar is farther from the nucleus than a 2*p* electron in Ne.

Which of the statements (i), (ii), and (iii) is or are true?

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

It may seem odd that 4*s* electrons are removed before 3*d* electrons in forming transition-metal cations. After all, in writing electron configurations, we added the 4*s* electrons before the 3*d* ones. In writing electron configurations for atoms, however, we are going through an imaginary process in which we move through the periodic table from one element to another. In doing so, we are adding both an electron to an orbital and a proton to the nucleus to change the identity of the element. In ionization, we *do not* reverse this process because no protons are being removed. For example, both Ca and Ti^{2+} have 20 electrons, but a Ti^{2+} ion has more protons than a Ca atom (22 vs. 20).

That changes the relative energy levels of the orbitals enough that the two species have different electron configurations: Ca([Ar]$4s^2$) and Ti^{2+} ([Ar]$3d^2$).

If there is more than one occupied subshell for a given value of n, the electrons are first removed from the orbital with the highest value of l. For example, a tin atom loses its $5p$ electrons before it loses its $5s$ electrons:

$$Sn([Kr]5s^2 4d^{10} 5p^2) \Rightarrow Sn^{2+}([Kr]5s^2 4d^{10}) + 2\,e^- \Rightarrow Sn^{4+}([Kr]4d^{10}) + 4\,e^-$$

Electrons added to an atom to form an anion are added to the empty or partially filled orbital having the lowest value of n. For example, an electron added to a fluorine atom to form the F^- ion goes into the one remaining vacancy in the $2p$ subshell:

$$F(1s^2 2s^2 2p^5) + e^- \Rightarrow F^-(1s^2 2s^2 2p^6)$$

Sample Exercise 7.7

Electron Configurations of Ions

Write the electron configurations for (**a**) Ca^{2+}, (**b**) Co^{3+}, and (**c**) S^{2-}.

SOLUTION

Analyze and Plan We are asked to write electron configurations for three ions. To do so, we first write the electron configuration of each parent atom and then remove or add electrons to form the ions. Electrons are first removed from the orbitals having the highest value of n. They are added to the empty or partially filled orbitals having the lowest value of n.

Solve

(**a**) Calcium (atomic number 20) has the electron configuration [Ar]$4s^2$. To form a 2+ ion, the two outer $4s$ electrons must be removed, giving an ion that is isoelectronic with Ar:

$$Ca^{2+}: [Ar]$$

(**b**) Cobalt (atomic number 27) has the electron configuration [Ar]$4s^2 3d^7$. To form a 3+ ion, three electrons must be removed. As discussed in the text, the $4s$ electrons are removed before the $3d$ electrons. Consequently, we remove the two $4s$ electrons and one of the $3d$ electrons, and the electron configuration for Co^{3+} is

$$Co^{3+}: [Ar]3d^6$$

(**c**) Sulfur (atomic number 16) has the electron configuration [Ne]$3s^2 3p^4$. To form a 2− ion, two electrons must be added. There is room for two additional electrons in the $3p$ orbitals. Thus, the S^{2-} electron configuration is

$$S^{2-}: [Ne]3s^2 3p^6 = [Ar]$$

Comment Remember that many of the common ions of the s- and p-block elements, such as Ca^{2+} and S^{2-}, have the same number of electrons as the closest noble gas. (Section 2.7)

Practice Exercise

The ground-state electron configuration of a Tc atom is [Kr]$5s^2 4d^5$. What is the electron configuration of a Tc^{3+} ion?
(**a**) [Kr]$4d^4$ (**b**) [Kr]$5s^2 4d^2$ (**c**) [Kr]$5s^1 4d^3$ (**d**) [Kr]$5s^2 4d^8$
(**e**) [Kr]$4d^{10}$

Self-Assessment Exercise

7.17 Which would you expect to be greater: I_1 for a sulfur atom or I_2 for an aluminum atom?

(a) I_1 for a sulfur atom
(b) I_2 for an aluminum atom

Exercises

7.18 Write equations that show the processes that describe the first, second, and third ionization energies of a chlorine atom. Which process would require the least amount of energy?

7.19 Which element has the highest second ionization energy: Li, K, or Be?

7.20 (**a**) What is the general relationship between the size of an atom and its first ionization energy? (**b**) Which element in the periodic table has the largest ionization energy? Which has the smallest?

7.21 Based on their positions in the periodic table, predict which atom of the following pairs will have the smaller first ionization energy: (**a**) Br, Kr; (**b**) C, Ca; (**c**) Li, Rb; (**d**) Pb, Si; (**e**) Al, B.

7.22 Write the electron configurations for the following ions, and determine which have noble-gas configurations: (**a**) Cu^{2+}, (**b**) Ca^{2+}, (**c**) N^{3-}, (**d**) Ru^{2+}, (**e**) H^-.

7.23 Give three examples of +2 ions that have an electron configuration of nd^{10} ($n = 3, 4, 5 \ldots$).

Answers to Self-Assessment Exercises

7.17 (b)

7.5 | Electron Affinity



Plastic food wrap has a low permeability to oxygen and water vapor. It may be used to keep food fresh and is a convenient means to cover plates, bowls, and jugs of different shapes and sizes. Its stretchiness allows it to wrap easily around objects and static electricity helps it stick. When the food wrap is pulled off its roll, electrons can be removed from the molecules on one surface and added to another. This builds up a small charge that helps it stick to the object you are covering.

We have looked at the ionization of atoms in the previous section. Here, we look at the addition of electrons to atoms to form anions, a process called electron affinity. By the end of this section, you should be able to

- Explain how electron affinity and ionization energy are related and how irregularities in the periodic trends for electron affinity can be related to electron configuration.

The first ionization energy of an atom is a measure of the energy change associated with removing an electron from the atom to form a cation. For example, the first ionization energy of Cl(g), 1251 kJ/mol, is the energy change associated with the process

$$\textit{Ionization energy}: \quad \underset{[\mathrm{Ne}]3s^2 3p^5}{\mathrm{Cl}(g)} \longrightarrow \underset{[\mathrm{Ne}]3s^2 3p^4}{\mathrm{Cl}^+(g)} + \mathrm{e}^- \qquad \Delta E = 1251\ \mathrm{kJ/mol} \qquad [7.4]$$

The positive value of the ionization energy means that energy must be put into the atom to remove the electron. *All ionization energies for atoms are positive: Energy must be absorbed to remove an electron.*

Most atoms can also gain electrons to form anions. The energy change that occurs when an electron is added to a gaseous atom is called the **electron affinity** because it measures the attraction, or *affinity,* of the atom for the added electron. For most atoms, energy is *released* when an electron is added. For example, the addition of an electron to a chlorine atom is accompanied by an energy change of −349 kJ/mol, the negative sign indicating that energy is released during the process. We therefore say that the electron affinity of Cl is −349 kJ/mol.*

*Two sign conventions are used for electron affinity. In most introductory texts, including this one, the thermodynamic sign convention is used: A negative sign indicates that addition of an electron is an exothermic process, as in the electron affinity for chlorine, −349 kJ/mol. Historically, however, electron affinity has been defined as the energy released when an electron is added to a gaseous atom or ion. Because 349 kJ/mol is released when an electron is added to Cl(g), the electron affinity by this convention would be +349 kJ/mol.

Electron affinity: $Cl(g) + e^- \longrightarrow Cl^-(g)$ $EA = -349\ kJ/mol$ [7.5]

$[Ne]3s^23p^5$ $[Ne]3s^23p^6$

It is important to understand the difference between ionization energy and electron affinity:

- Ionization energy measures the energy change when an atom *loses* an electron.
- Electron affinity measures the energy change when an atom *gains* an electron.

The greater the attraction between an atom and an added electron, the more negative the atom's electron affinity. For some elements, such as the noble gases, the electron affinity has a positive value, meaning that the anion is higher in energy than are the separated atom and electron:

$$Ar(g) + e^- \longrightarrow Ar^-(g) \qquad EA > 0 \qquad [7.6]$$

$[Ne]3s^23p^6$ $[Ne]3s^23p^64s^1$

The fact that the electron affinity is positive means that an electron will not attach itself to an Ar atom; in other words the Ar^- ion is unstable and does not form.

Periodic Trends in Electron Affinity

The electron affinities for the *s*- and *p*-block elements of the first five periods are shown in **Figure 7.12**. Notice that the trends are not as evident as they are for ionization energy. The halogens, which are one electron shy of a filled *p* subshell, have the most negative electron affinities. By gaining an electron, a halogen atom forms a stable anion that has a noble-gas configuration (Equation 7.5). The addition of an electron to a noble gas, however, requires that the electron reside in a higher-energy subshell that is empty in the atom (Equation 7.6). Because occupying a higher-energy subshell is energetically unfavorable, the electron affinity is highly positive. The electron affinities of Be and Mg are positive for the same reason; the added electron would reside in a previously empty *p* subshell that is higher in energy.

The electron affinities of the Group 15 elements are also interesting. Because these elements have half-filled *p* subshells, the added electron must be put in an orbital that is already occupied, resulting in larger electron–electron repulsions. Consequently, these elements have electron affinities that are either positive (N) or less negative than those of their neighbors to the left (P, As, Sb). Recall that in Section 7.4 we saw a discontinuity in the trends in first ionization energy for the same reason.

Electron affinities do not change greatly as we move down a group (Figure 7.12). With F, for instance, the added electron goes into a 2*p* orbital, for Cl a 3*p* orbital, for Br a 4*p* orbital, and so forth. As we proceed from F to I, therefore, the average distance between the added electron and the nucleus steadily increases, causing the electron–nucleus attraction to decrease. However, the orbital that holds the outermost electron is increasingly spread out, so that as we proceed from F to I, the electron–electron repulsions are also reduced. As a result, the reduction in the electron–nucleus attraction is counterbalanced by the reduction in electron–electron repulsions.

Go Figure

Why are the electron affinities of the Group 14 elements more negative than those of the Group 15 elements?

1												18
H −73	2											He > 0
Li −60	Be > 0											Ne > 0
Na −53	Mg > 0											Ar > 0
K −48	Ca −2											Kr > 0
Rb −7	Sr −5											Xe > 0

13	14	15	16	17
B −27	C −122	N > 0	O −141	F −328
Al −43	Si −134	P −72	S −200	Cl −349
Ga −30	Ge −119	As −78	Se −195	Br −325
In −30	Sn −107	Sb −103	Te −190	I −295

▲ **Figure 7.12** Electron affinity in kJ/mol for selected *s*- and *p*-block elements.

Self-Assessment Exercise

7.24 What is the relationship between the value for the first ionization energy of a $Cl^-(g)$ ion and the electron affinity of $Cl(g)$?

(a) The values are the same magnitude but of opposite sign
(b) EA for $Cl(g) > I_1$ for $Cl^-(g)$

Exercises

7.25 Write an equation for the first electron affinity of helium. Would you predict a positive or a negative energy value for this process? Is it possible to directly measure the first electron affinity of helium?

7.26 Which of the following, I or I^-, will have a negative electron affinity?

7.27 Consider the first ionization energy of neon and the electron affinity of fluorine. (**a**) Write equations, including electron configurations, for each process. (**b**) These two quantities have opposite signs. Which will be positive, and which will be negative? (**c**) Would you expect the magnitudes of these two quantities to be equal? If not, which one would you expect to be larger?

Answers to Self-Assessment Exercises

7.24 (a)

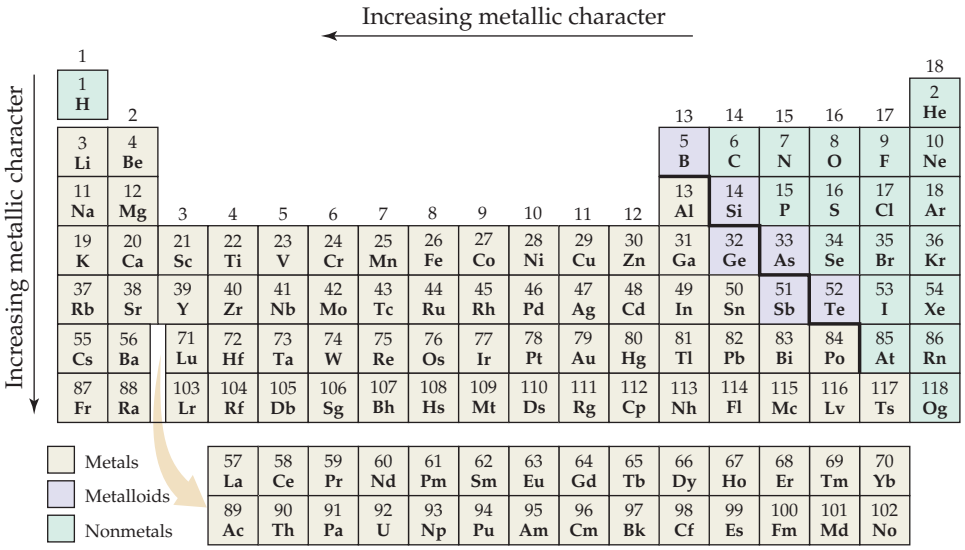
7.6 Metals, Nonmetals, and Metalloids



Atomic radii, ionization energies, and electron affinities are properties of individual atoms. With the exception of the noble gases, however, none of the elements exist in nature as individual atoms. To get a broader understanding of the properties of elements, we must also examine periodic trends in properties of samples that involve large collections of atoms.

Nowhere are the differences between elements belonging to the same column more apparent than amongst the Group 14 elements: carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). The lightest element in Group 14, carbon, comes in many different forms from the very hard diamond to charcoal, whose rough texture, ability to draw light or intensely dark lines, and easy removability give it a wide range of applications. Moving to the bottom of Group 14, we find lead, which is a relatively soft metal. Our bodies, and those of nearly every living thing on planet Earth, are made from molecules that contain carbon, while the toxicity of lead is well documented. In between, we find silicon and germanium, both of which have the same arrangement of atoms as diamond

Go Figure How do the periodic trends in metallic character compare to those for ionization energy?



▲ **Figure 7.13** Metals, metalloids, and nonmetals.

TABLE 7.3 Characteristic Properties of Metals and Nonmetals

Metals	Nonmetals
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, and some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

and are semiconductors used extensively in integrated circuits and computers. Tin shows dual behavior in the sense that it behaves as a metal at temperatures above 13 °C (β-Sn or white tin) and as a semiconductor below 13 °C (α-Sn or gray tin).

By the end of this section, you should be able to

- Recognize the general properties of the elements and their oxides

The elements can be broadly grouped as metals, nonmetals, and metalloids (Figure 7.13). Some of the distinguishing properties of metals and nonmetals are summarized in Table 7.3.

In the following sections, we explore some common patterns of reactivity across the periodic table. We will examine reactivity for selected nonmetals and metals in more depth in later chapters.

The more an element exhibits the physical and chemical properties of metals, the greater its **metallic character**. As indicated in Figure 7.13, metallic character generally increases as we proceed down a group of the periodic table and decreases as we proceed right across a period. Let's now examine the close relationships that exist between electron configurations and the properties of metals, nonmetals, and metalloids.

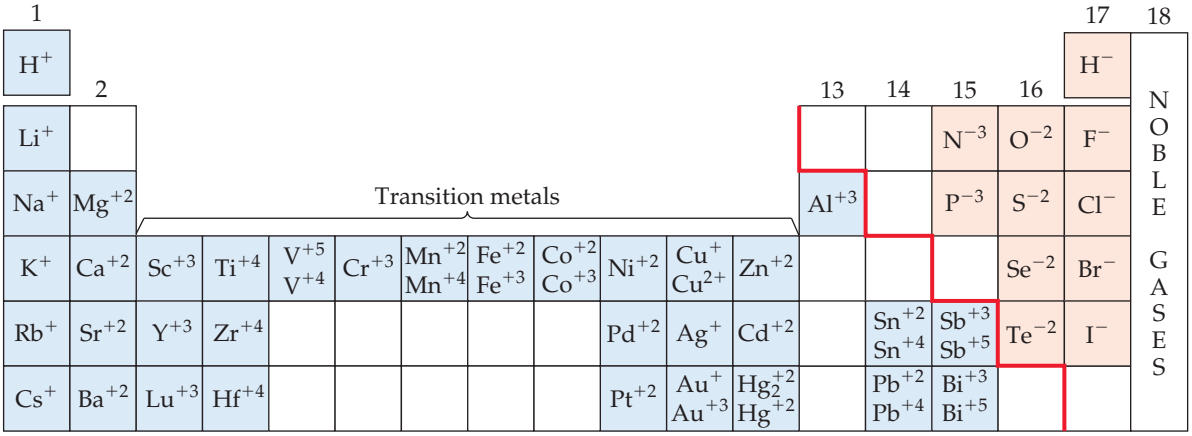


▲ **Figure 7.14** Metals are shiny, malleable, and ductile.

Metals

Most metallic elements exhibit the shiny luster we associate with metals (Figure 7.14). Metals conduct heat and electricity. In general, they are malleable (can be pounded into

Go Figure The red stepped line divides metals from nonmetals. How are common oxidation states divided by this line?



▲ **Figure 7.15 Representative oxidation states of the elements.** Note that hydrogen exhibits both positive and negative oxidation numbers, +1 and −1.

thin sheets) and ductile (can be drawn into wires). All are solids at room temperature except mercury (melting point = −39 °C), which is a liquid at room temperature. Two metals melt at slightly above room temperature, cesium at 28.4 °C and gallium at 29.8 °C. At the other extreme, many metals melt at very high temperatures. For example, tungsten, which is used for the filaments of incandescent light bulbs, melts at 3422 °C.

Metals tend to have low ionization energies (Figure 7.10) *and, therefore, can form cations relatively easily.* As a result, metals are oxidized (lose electrons) when they undergo chemical reactions. Among the fundamental atomic properties (radius, electron configuration, electron affinity, and so forth), first ionization energy is the best indicator of whether an element behaves as a metal or a nonmetal.

Figure 7.15 shows the oxidation states of representative ions of metals and nonmetals. As noted in Section 2.7, the charge on any alkali metal ion in a compound is always 1+, and that on any alkaline earth metal is always 2+. For atoms belonging to either of these groups, the outer *s* electrons are easily lost, yielding a noble-gas electron configuration. For metals belonging to groups with partially occupied *p* orbitals (Groups 13–17), cations are formed either by losing only the outer *p* electrons (such as Sn^{2+}) or the outer *s* and *p* electrons (such as Sn^{4+}). The charge on transition-metal ions does not follow an obvious pattern. One characteristic of the transition metals is their ability to form more than one cation. For example, compounds of Fe^{2+} and Fe^{3+} are both very common.

Compounds made up of a metal and a nonmetal tend to be ionic substances. For example, most metal oxides and halides are ionic solids. To illustrate, the reaction between nickel metal and oxygen produces nickel oxide, an ionic solid containing Ni^{2+} and O^{2-} ions:

$$2\,Ni(s) + O_2(g) \longrightarrow 2\,NiO(s) \qquad [7.7]$$

The oxides are particularly important because of the great abundance of oxygen in our environment.

Most metal oxides are basic. Those that dissolve in water react to form metal hydroxides, as in the following examples:

$$\text{Metal oxide} + \text{water} \longrightarrow \text{metal hydroxide}$$

$$Na_2O(s) + H_2O(l) \longrightarrow 2\,NaOH(aq) \qquad [7.8]$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) \qquad [7.9]$$

The basicity of metal oxides is due to the oxide ion, which reacts with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq) \qquad [7.10]$$

Sample Exercise 7.8

Properties of Metal Oxides

(**a**) Would you expect scandium oxide to be a solid, liquid, or gas at room temperature?
(**b**) Write the balanced chemical equation for the reaction of scandium oxide with nitric acid.

SOLUTION

Analyze and Plan We are asked about one physical property of scandium oxide—its state at room temperature—and one chemical property—how it reacts with nitric acid.

Solve

(**a**) Because scandium oxide is the oxide of a metal, we expect it to be an ionic solid. Indeed it is, with the very high melting point of 2485 °C.

(**b**) In compounds, scandium has a 3+ charge, Sc^{3+}, and the oxide ion is O^{2-}. Consequently, the formula of scandium oxide is Sc_2O_3. Metal oxides tend to be basic and, therefore, to react with acids to form a salt plus water. In this case, the salt is scandium nitrate, $Sc(NO_3)_3$:

$$Sc_2O_3(s) + 6\,HNO_3(aq) \longrightarrow 2\,Sc(NO_3)_3(aq) + 3\,H_2O(l)$$

Practice Exercise

Suppose that a metal oxide of formula M_2O_3 were soluble in water. What would be the major product or products of dissolving the substance in water?

(**a**) $MH_3(aq) + O_2(g)$
(**b**) $M(s) + H_2(g) + O_2(g)$
(**c**) $M^{3+}(aq) + H_2O_2(aq)$
(**d**) $M(OH)_2(aq)$
(**e**) $M(OH)_3(aq)$

Go Figure Would you expect NiO to dissolve in an aqueous solution of $NaNO_3$?



Nickel oxide (NiO), nitric acid (HNO_3), and water

NiO is insoluble in water but reacts with HNO_3 to give a green solution of the salt $Ni(NO_3)_2$.

▲ **Figure 7.16 Metal oxides react with acids.** NiO does not dissolve in water but does react with nitric acid (HNO_3) to give a green solution of $Ni(NO_3)_2$.

Go Figure

Do you think sulfur is malleable?



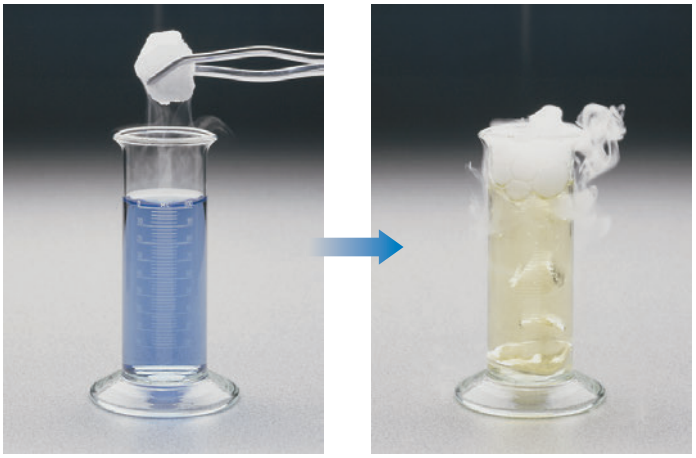
▲ **Figure 7.17 Sulfur, known to the medieval world as "brimstone," is a nonmetal.**

Even metal oxides that are insoluble in water demonstrate their basicity by reacting with acids to form a salt plus water, as illustrated in **Figure 7.16**:

$$\text{Metal oxide} + \text{acid} \longrightarrow \text{salt} + \text{water}$$
$$NiO(s) + 2\,HNO_3(aq) \longrightarrow Ni(NO_3)_2(aq) + H_2O(l) \qquad [7.11]$$

Nonmetals

Nonmetals can be solid, liquid, or gas. They are not lustrous and generally are poor conductors of heat and electricity. Their melting points are generally lower than those of metals (although diamond, a form of carbon, is an exception and melts at 3570 °C). Under ordinary conditions, seven nonmetals exist as diatomic molecules. Five of these are gases (H_2, N_2, O_2, F_2, and Cl_2), one is a liquid (Br_2), and one is a volatile solid (I_2). Excluding the noble gases, the remaining nonmetals are solids that can be either hard, such as diamond, or soft, such as sulfur (**Figure 7.17**).



▲ **Figure 7.18 The reaction of CO_2 with water containing a bromothymol blue indicator.** Initially, the blue color tells us the water is slightly basic. When a piece of solid carbon dioxide ("dry ice") is added, the color changes to yellow, indicating an acidic solution. The mist is water droplets condensed from the air by cold CO_2 gas that sublimes off before reacting.

Because of their relatively large, negative electron affinities, nonmetals tend to gain electrons when they react with metals. For example, the reaction of aluminum with bromine produces the ionic compound aluminum bromide:

$$2\,Al(s) + 3\,Br_2(l) \longrightarrow 2\,AlBr_3(s) \qquad [7.12]$$

A nonmetal will typically gain enough electrons to fill its outermost occupied *p* subshell, giving a noble-gas electron configuration. For example, the bromine atom gains one electron to fill its 4*p* subshell:

$$Br([Ar]4s^2 3d^{10} 4p^5) + e^- \Rightarrow Br^-([Ar]4s^2 3d^{10} 4p^6)$$

Compounds composed entirely of nonmetals are typically molecular substances that tend to be gases, liquids, or low melting point solids at room temperature. Examples include the common hydrocarbons we use for fuel (methane, CH_4; propane, C_3H_8; octane, C_8H_{18}) and the gases HCl, NH_3, and H_2S. Many pharmaceuticals are molecules composed of C, H, N, O, and other nonmetals. For example, the molecular formula for the drug Celebrex® is $C_{17}H_{14}F_3N_3O_2S$.

Most nonmetal oxides are acidic, which means that those that dissolve in water form acids:

$$\text{Nonmetal oxide} + \text{water} \longrightarrow \text{acid}$$

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq) \qquad [7.13]$$

$$P_4O_{10}(s) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(aq) \qquad [7.14]$$

The reaction of carbon dioxide with water (**Figure 7.18**) accounts for the acidity of carbonated water and, to some extent, rainwater. Because sulfur is present in oil and coal, combustion of these common fuels produces sulfur dioxide and sulfur trioxide. These substances dissolve in water to produce *acid rain*, a major pollutant in many parts of the world. Like acids, most nonmetal oxides dissolve in basic solutions to form a salt plus water:

$$\text{Nonmetal oxide} + \text{base} \longrightarrow \text{salt} + \text{water}$$

$$CO_2(g) + 2\,NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l) \qquad [7.15]$$

Metalloids

Metalloids have properties intermediate between those of metals and those of nonmetals. They may have some characteristic metallic properties but lack others. For example, the metalloid silicon *looks* like a metal (**Figure 7.19**), but it is brittle rather than malleable and does not conduct heat or electricity nearly as well as metals do.



▲ **Figure 7.19 Elemental silicon.**

Sample Exercise 7.9

Reactions of Nonmetal Oxides

Write a balanced chemical equation for the reaction of solid selenium dioxide, $SeO_2(s)$, with (**a**) water, (**b**) aqueous sodium hydroxide.

SOLUTION

Analyze and Plan We note that selenium is a nonmetal. We therefore need to write chemical equations for the reaction of a nonmetal oxide with water and with a base, NaOH. Nonmetal oxides are acidic, reacting with water to form an acid and with bases to form a salt and water.

Solve

(**a**) The reaction between selenium dioxide and water is like that between carbon dioxide and water (Equation 7.13):

$$SeO_2(s) + H_2O(l) \longrightarrow H_2SeO_3(aq)$$

(It does not matter that SeO_2 is a solid and CO_2 is a gas under ambient conditions; the point is that both are water-soluble nonmetal oxides.)

The reaction with sodium hydroxide is like that in Equation 7.15:

$$SeO_2(s) + 2\,NaOH(aq) \longrightarrow Na_2SeO_3(aq) + H_2O(l)$$

Practice Exercise

Consider the following oxides: SO_2, Y_2O_3, MgO, Cl_2O, N_2O_5. How many are expected to form acidic solutions in water?
(**a**) 1 (**b**) 2 (**c**) 3 (**d**) 4 (**e**) 5

Several metalloids, most notably silicon, are electrical semiconductors and are the principal elements used in integrated circuits and computer chips. One of the reasons metalloids can be used for integrated circuits is that their electrical conductivity is intermediate between that of metals and that of nonmetals. Very pure silicon is an electrical insulator, but its conductivity can be dramatically increased with the addition of specific impurities called *dopants*. This modification provides a mechanism for controlling the electrical conductivity by controlling the chemical composition. We will return to this point in Chapter 12.

Self-Assessment Exercise

7.28 A compound XCl_2, where X is an element, has a melting point of −121 °C. Would you expect the compound to be ionic or molecular?

(a) Ionic

(b) Molecular

Exercises

7.29 (**a**) Does metallic character increase, decrease, or remain unchanged as one goes from left to right across a row of the periodic table? (**b**) Does metallic character increase, decrease, or remain unchanged as one goes down a column of the periodic table? (**c**) Are the periodic trends in (a) and (b) the same as or different from those for first ionization energy?

7.30 Discussing this chapter, a classmate says, "An element that commonly forms a cation is a metal." Do you agree or disagree?

7.31 Predict whether each of the following oxides is ionic or molecular: ZnO, K_2O, SO_2, OF_2, TiO_2.

7.32 Would you expect zirconium(II) oxide, ZrO, to react more readily with HCl(*aq*) or NaOH(*aq*)?

7.33 Chlorine reacts with oxygen to form Cl_2O_7. (**a**) What is the name of this product (see Table 2.6)? (**b**) Write a balanced equation for the formation of $Cl_2O_7(l)$ from the elements. (**c**) Would you expect Cl_2O_7 to be more reactive toward $H^+(aq)$ or $OH^-(aq)$? (**d**) If the oxygen in Cl_2O_7 is considered to have the −2 oxidation state, what is the oxidation state of the Cl? What is the electron configuration of Cl in this oxidation state?

7.34 Write balanced equations for the following reactions: (**a**) boron trichloride with water, (**b**) cobalt (II) oxide with nitric acid, (**c**) phosphorus pentoxide with water, (**d**) carbon dioxide with aqueous barium hydroxide.

Answers to Self-Assessment Exercises

7.28 (b)

7.7 Trends for Group 1 and Group 2 Metals





▲ **Figure 7.20** Sodium, like the other alkali metals, is soft enough to be cut with a knife.

In the 1820's, Goldsworthy Gurney found that a sample of calcium oxide heated with a hydrogen-oxygen blowpipe glowed with an intense white light. This was adopted by theatres in the 1830's and 1840's, and the expression 'in the limelight' was born. While effective, the lights needed constant attention and were a fire hazard. Consequently, they were replaced by electric lighting soon after its invention by Thomas Edison in 1789.

By the end of this section, you should have

- Acquired an overview of the chemistry of Group 1 and 2 metals

As we have seen, elements in a given group possess general similarities. However, trends also exist within each group. In this section, we use the periodic table and our knowledge of electron configurations to examine the chemistry of the **alkali metals** and **alkaline earth metals**.

Group 1: The Alkali Metals

The alkali metals are soft metallic solids (**Figure 7.20**). All have characteristic metallic properties, such as a silvery, metallic luster, and high thermal and electrical conductivity. The name *alkali* comes from an Arabic word meaning "ashes." Many compounds of sodium and potassium, two alkali metals, were isolated from wood ashes by early chemists.

As **Table 7.4** shows, the alkali metals have low densities and melting points, and these properties vary in a fairly regular way with increasing atomic number. We see

TABLE 7.4 Some Properties of the Alkali Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (pm)	I_1 (kJ/mol)
Lithium	$[He]2s^1$	181	0.53	128	520
Sodium	$[Ne]3s^1$	98	0.97	166	496
Potassium	$[Ar]4s^1$	63	0.86	203	419
Rubidium	$[Kr]5s^1$	39	1.53	220	403
Cesium	$[Xe]6s^1$	28	1.88	244	376

the usual trends as we move down the group, such as increasing atomic radius and decreasing first ionization energy. The alkali metal of any given period has the lowest I_1 value in the period (Figure 7.10), which reflects the relative ease with which its outer *s* electron can be removed. As a result, the alkali metals are all very reactive, losing one electron to form ions carrying a 1+ charge.

The alkali metals exist in nature only as compounds. Sodium and potassium are relatively abundant in Earth's crust, in seawater, and in biological systems, always as the cations of ionic compounds. All alkali metals combine directly with most nonmetals. For example, they react with hydrogen to form hydrides and with sulfur to form sulfides:

$$2\,M(s) + H_2(g) \longrightarrow 2\,MH(s) \qquad [7.16]$$

$$2\,M(s) + S(s) \longrightarrow M_2S(s) \qquad [7.17]$$

where M represents any alkali metal. In hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as H^-, the **hydride ion**. A hydrogen atom that has *gained* an electron, this ion is distinct from the hydrogen ion, H^+, formed when a hydrogen atom *loses* its electron.

The alkali metals react vigorously with water, producing hydrogen gas and a solution of an alkali metal hydroxide:

$$2\,M(s) + 2\,H_2O(l) \longrightarrow 2\,MOH(aq) + H_2(g) \qquad [7.18]$$

These reactions are very exothermic (**Figure 7.21**). In many cases, enough heat is generated to ignite the H_2, producing a fire or sometimes even an explosion, as in the case of K reacting with water. The reaction is even more violent for Rb and, especially, Cs, because their ionization energies are even lower than that of K.

Recall that the most common ion of oxygen is the oxide ion, O^{2-}. We would therefore expect that the reaction of an alkali metal with oxygen would produce the corresponding metal oxide. Indeed, reaction of Li metal with oxygen does form lithium oxide:

$$4\,Li(s) + O_2(g) \longrightarrow \underset{\text{lithium oxide}}{2\,Li_2O(s)} \qquad [7.19]$$

When dissolved in water, Li_2O and other soluble metal oxides form hydroxide ions from the reaction of O^{2-} ions with H_2O (Equation 7.10).

The reactions of the other alkali metals with oxygen are more complex than we would anticipate. For example, when sodium reacts with oxygen, the main product is sodium *peroxide*, which contains the O_2^{2-} ion:

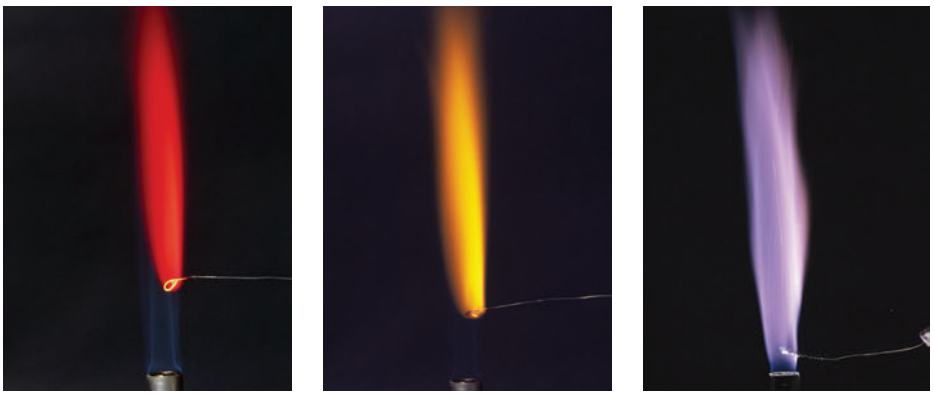
$$2\,Na(s) + O_2(g) \longrightarrow \underset{\text{sodium peroxide}}{Na_2O_2(s)} \qquad [7.20]$$

Go Figure Would you expect rubidium metal to be more or less reactive with water than potassium metal?



Li Na K

▲ **Figure 7.21** **The alkali metals react vigorously with water.**



Li Na K

▲ **Figure 7.22** **Placed in a flame, ions of each alkali metal emit light of a characteristic wavelength.**

Potassium, rubidium, and cesium react with oxygen to form compounds that contain the O_2^- ion, which we call the *superoxide ion*. For example, potassium forms potassium superoxide, KO_2:

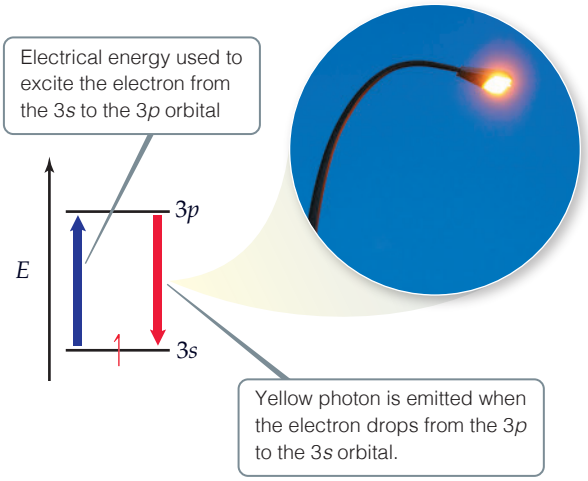
$$K(s) + O_2(g) \longrightarrow \underset{\text{potassium superoxide}}{KO_2(s)} \qquad [7.21]$$

Be aware that the reactions in Equations 7.20 and 7.21 are somewhat unexpected; in most cases, the reaction of oxygen with a metal forms the metal oxide.

As seen from Equations 7.18 through 7.21, the alkali metals are extremely reactive toward water and oxygen. Because of this reactivity, the metals are usually stored submerged in a liquid hydrocarbon, such as mineral oil or kerosene.

Although alkali metal ions are colorless, each emits a characteristic color when placed in a flame (**Figure 7.22**). The ions are reduced to gaseous metal atoms in the flame. The high temperature excites the valence electron from the ground state to a higher-energy orbital, causing the atom to be in an excited state. The atom then emits energy in the form of visible light as the electron falls back into the lower-energy orbital and the atom returns to its ground state. The light emitted is at a specific wavelength for each element, just as we saw earlier for line spectra of hydrogen and sodium. The characteristic yellow emission of sodium at 589 nm is the basis for sodium vapor lamps (**Figure 7.23**).

Go Figure If we had potassium vapor lamps, what color would they be?



▲ **Figure 7.23** **The characteristic yellow light in a sodium lamp results from excited electrons in the high-energy 3*p* orbital falling back to the lower-energy 3*s* orbital.**

Sample Exercise 7.10

Reactions of an Alkali Metal

Write a balanced equation for the reaction of cesium metal with (**a**) $Cl_2(g)$, (**b**) $H_2O(l)$, (**c**) $H_2(g)$.

SOLUTION

Analyze and Plan Because cesium is an alkali metal, we expect its chemistry to be dominated by oxidation of the metal to Cs^+ ions. Further, we recognize that Cs is far down the periodic table, which means it is among the most active of all metals and probably reacts with all three substances.

Solve The reaction between Cs and Cl_2 is a simple combination reaction between a metal and a nonmetal, forming the ionic compound CsCl:

$$2\,Cs(s) + Cl_2(g) \longrightarrow 2\,CsCl(s)$$

From Equations 7.18 and 7.16, we predict the reactions of cesium with water and hydrogen to proceed as follows:

$$2\,Cs(s) + 2\,H_2O(l) \longrightarrow 2\,CsOH(aq) + H_2(g)$$
$$2\,Cs(s) + H_2(g) \longrightarrow 2\,CsH(s)$$

All three reactions are redox reactions where cesium forms a Cs^+ ion. The Cl^-, OH^-, and H^- are all 1– ions, which means the products have 1:1 stoichiometry with Cs^+.

Practice Exercise

Consider the following three statements about the reactivity of an alkali metal M with oxygen gas:

(i) Based on their positions in the periodic table, the expected product is the ionic oxide M_2O.
(ii) Some of the alkali metals produce metal peroxides or metal superoxides when they react with oxygen.
(iii) When dissolved in water, an alkali metal oxide produces a basic solution.

Which of the statements (i), (ii), and (iii) is or are true?

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

CHEMISTRY AND LIFE The Improbable Development of Lithium Drugs

Alkali metal ions tend to play an unexciting role in most chemical reactions. As noted in Section 4.2, all salts of the alkali metal ions are soluble in water, and the ions are spectators in most aqueous reactions (except for those involving the alkali metals in their elemental form, such as those in Equations 7.16 through 7.21). However, these ions play an important role in human physiology. Sodium and potassium ions, for example, are major components of blood plasma and intracellular fluid, respectively, with average concentrations of 0.1 *M*. These electrolytes serve as vital charge carriers in normal cellular function. In contrast, the lithium ion has no known function in normal human physiology. Since the discovery of lithium in 1817, however, people have believed that salts of the element possessed almost mystical healing powers. There were even claims that lithium ions were an ingredient in ancient "fountain of youth" formulas. In 1927, C. L. Grigg began marketing a soft drink that contained lithium. The original unwieldy name of the beverage was "Bib-Label Lithiated Lemon-Lime Soda," which was soon changed to the simpler and more familiar name 7UP® (**Figure 7.24**).

Because of concerns of the US Food and Drug Administration, lithium was removed from 7UP® during the early 1950s. At nearly the same time, psychiatrists discovered that lithium ions have a remarkable therapeutic effect on the mental condition called *bipolar disorder*. Individuals that suffer from this psychosis, undergo severe mood swings from deep depression to a manic euphoria. The lithium ion smoothes these mood swings, allowing the bipolar patient to function more effectively in daily life.

The antipsychotic action of Li^+ was discovered by accident in the 1940s by Australian psychiatrist John Cade (1912–1980) as he was researching the use of uric acid—a component of urine—to treat manic-depressive illness. He administered the acid to manic laboratory animals in the form of its most soluble salt, lithium urate, and found that many of the manic symptoms seemed to disappear. Later studies showed that uric acid has no role in the therapeutic effects observed; rather, the Li^+ ions were responsible. Because lithium overdose can cause severe side effects in humans, including kidney failure and death, lithium salts were not approved as antipsychotic drugs for humans until 1970. Today Li^+ is usually administered orally in the form of Li_2CO_3, which is the active ingredient in prescription drugs such as Eskalith®. Lithium drugs are effective for about 70% of bipolar patients who take it.



▲ **Figure 7.24** **Lithium no more.** The soft drink 7UP® originally contained a lithium salt that was claimed to give the beverage healthful benefits, including "an abundance of energy, enthusiasm, a clear complexion, lustrous hair, and shining eyes!" The lithium was removed from the beverage in the early 1950s, about the time that the antipsychotic action of Li^+ was discovered.

In this age of sophisticated drug design and biotechnology, the simple lithium ion is still the most effective treatment of this destructive psychiatric disorder. Remarkably, despite intensive research, scientists still do not fully understand the biochemical action of lithium that leads to its therapeutic effects. Because of its similarity to Na^+, Li^+ is incorporated into blood plasma, where it can affect the behavior of nerve and muscle cells. Because Li^+ has a smaller radius than Na^+ (Figure 7.8), the way Li^+ interacts with molecules in human cells is different from the way Na^+ interacts with the molecules. Other studies indicate that Li^+ alters the function of certain neurotransmitters, which might lead to its effectiveness as an antipsychotic drug.

Group 2: The Alkaline Earth Metals

Like the alkali metals, the alkaline earth metals are all solids at room temperature and have typical metallic properties (**Table 7.5**). Compared with the alkali metals, the alkaline earth metals are harder and denser, and melt at higher temperatures.

The first ionization energies of the alkaline earth metals are low but not as low as those of the alkali metals. Consequently, the alkaline earth metals are less reactive than their alkali metal neighbors. As noted in Section 7.4, the ease with which the elements lose electrons decreases as we move across a period and increases as we move down a group. Thus, beryllium and magnesium, the lightest alkaline earth metals, are the least reactive.

The trend of increasing reactivity within the group is shown by the way the alkaline earth metals behave in the presence of water. Beryllium does not react with either water or steam, even when heated red-hot. Magnesium reacts slowly with liquid water and more readily with steam:

$$Mg(s) + H_2O(g) \longrightarrow MgO(s) + H_2(g) \qquad [7.22]$$

Calcium and the elements below it react readily with water at room temperature (although more slowly than the alkali metals adjacent to them in the periodic table). The reaction between calcium and water (**Figure 7.25**), for example, is

$$Ca(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g) \qquad [7.23]$$

Equations 7.22 and 7.23 illustrate the dominant pattern in the reactivity of the alkaline earth elements: They tend to lose their two outer *s* electrons and form 2+ ions. For example, magnesium reacts with chlorine at room temperature to form $MgCl_2$ and burns with dazzling brilliance in air to give MgO:

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s) \qquad [7.24]$$

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s) \qquad [7.25]$$

In the presence of O_2, magnesium metal is protected by a thin coating of water-insoluble MgO. Thus, even though Mg is high in the activity series, it can be incorporated into lightweight structural alloys used in, for example, automobile wheels. The heavier alkaline earth metals (Ca, Sr, and Ba) are even more reactive toward nonmetals than is magnesium.

The heavier alkaline earth ions give off characteristic colors when heated in a hot flame. Strontium salts produce the brilliant red color in fireworks, and barium salts produce the green color.

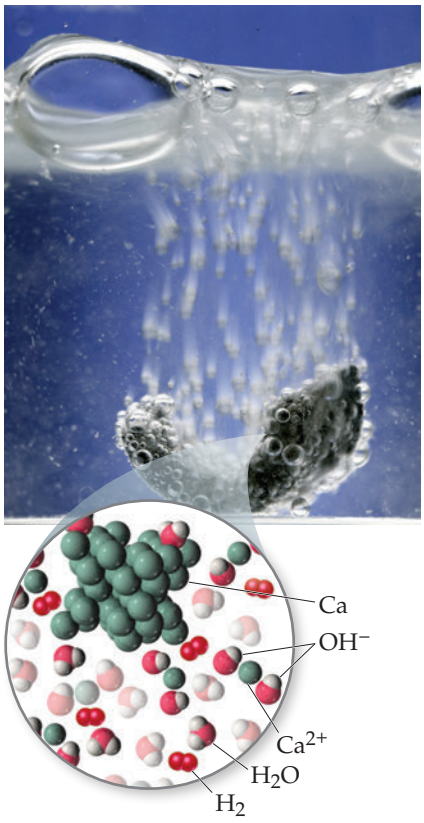
Like their neighbors sodium and potassium, magnesium and calcium are relatively abundant on Earth and in seawater and are essential for living organisms as cations in ionic compounds. Calcium is particularly important for growth and maintenance of bones and teeth.

TABLE 7.5 Some Properties of the Alkaline Earth Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (pm)	I_1 (kJ/mol)
Beryllium	$[He]2s^2$	1287	1.85	96	899
Magnesium	$[Ne]3s^2$	650	1.74	141	738
Calcium	$[Ar]4s^2$	842	1.55	176	590
Strontium	$[Kr]5s^2$	777	2.63	195	549
Barium	$[Xe]6s^2$	727	3.51	215	503

Go Figure

What is the cause of the bubbles that are formed? How could you test your answer?



▲ **Figure 7.25** **Elemental calcium reacts with water.**

Self-Assessment Exercise

7.35 Which ion do you expect to have the smallest radius?

(a) K^+

(b) Ca^{2+}

Exercises

7.36 (**a**) Why is calcium generally more reactive than beryllium? (**b**) Why is calcium generally less reactive than rubidium?

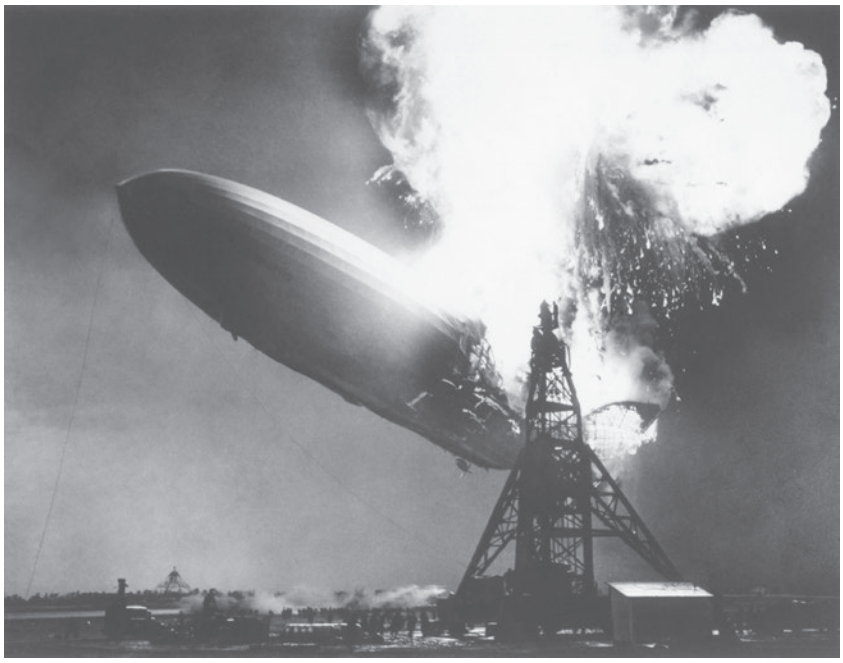
7.37 Write a balanced equation for the reaction that occurs in each of the following cases: (**a**) Potassium metal is exposed to an atmosphere of chlorine gas. (**b**) Strontium oxide is added to water. (**c**) A fresh surface of lithium metal is exposed to oxygen gas. (**d**) Sodium metal reacts with molten sulfur.

7.38 (**a**) As described in Section 7.7, the alkali metals react with hydrogen to form hydrides and react with halogens to form halides. Compare the roles of hydrogen and halogens in these reactions. Write balanced equations for the reaction of fluorine with calcium and for the reaction of hydrogen with calcium. (**b**) What is the oxidation number and electron configuration of calcium in each product?

Answers to Self-Assessment Exercises

7.35 (b)

7.8 Trends for Selected Nonmetals



Hydrogen, generated from the reaction of dilute acid on iron filings, was first reported by Robert Boyle in 1671. The gas was recognized as a new substance ninety years later by Henry Cavendish who called it 'flammable air' but this was changed to hydrogen by Antoine Lavoisier in 1783 upon observing that the gas burnt in air to give water. The name is derived from the Greek *hydro* for water and *genes* for creator.

As the lightest element, it was the obvious choice of gas for the early airships that appeared around 1900. However, the highly flammable nature of hydrogen lead to the disaster of the Hindenburg on 6th May 1937, when the airship burst into flames while attempting to dock at Lakehurst, New Jersey. Air travel was still in its infancy, and there were journalists on hand to report on the arrival of the airship's maiden flight from Europe to the USA. It took just 90 seconds for the hydrogen to burn out and spelt the end to commercial travel by airship.

By the end of this section, you should have

- Acquired an overview of the chemistry of selected non-metals

Hydrogen

We have seen that the chemistry of the alkali metals is dominated by the loss of their outer ns^1 electron to form cations. The $1s^1$ electron configuration of hydrogen suggests that its chemistry should have some resemblance to that of the alkali metals. The chemistry of hydrogen is much richer and more complex than that of the alkali metals,

however, mainly because the ionization energy of hydrogen, 1312 kJ/mol, is higher than any metal and comparable to that of oxygen. As a result, hydrogen is a nonmetal that occurs as a colorless diatomic gas, $H_2(g)$, under most conditions.

The reactivity of hydrogen with nonmetals reflects its much greater tendency to hold on to its electron relative to the alkali metals. Unlike the alkali metals, hydrogen reacts with most nonmetals to form molecular compounds in which its electron is shared with, rather than completely transferred to, the other nonmetal. For example, we have seen that sodium metal reacts vigorously with chlorine gas to produce the ionic compound sodium chloride, in which the outermost sodium electron is completely transferred to a chlorine atom (Figure 2.19):

$$\mathrm{Na}(s) + \tfrac{1}{2}\,\mathrm{Cl_2}(g) \longrightarrow \underset{\text{ionic}}{\mathrm{NaCl}(s)} \qquad \Delta H^\circ = -410.9\ \mathrm{kJ} \qquad [7.26]$$

By contrast, molecular hydrogen reacts with chlorine gas to form hydrogen chloride gas, which consists of HCl molecules:

$$\tfrac{1}{2}\mathrm{H_2}(g) + \tfrac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \underset{\text{molecular}}{\mathrm{HCl}(g)} \qquad \Delta H^\circ = -92.3\ \mathrm{kJ} \qquad [7.27]$$

Hydrogen readily forms molecular compounds with other nonmetals, such as the formation of water, $H_2O(l)$; ammonia, $NH_3(g)$; and methane, $CH_4(g)$. The ability of hydrogen to form bonds with carbon is one of the most important aspects of organic chemistry, as will see in later chapters.

We have seen that, particularly in the presence of water, hydrogen does readily form H^+ ions in which the hydrogen atom has lost its electron. For example, $HCl(g)$ dissolves in H_2O to form a solution of hydrochloric acid, $HCl(aq)$, in which the electron of the hydrogen atom *is* transferred to the chlorine atom—a solution of hydrochloric acid consists largely of $H^+(aq)$ and $Cl^-(aq)$ ions stabilized by the H_2O solvent.* Indeed, the ability of molecular compounds of hydrogen with nonmetals to form acids in water is one of the most important aspects of aqueous chemistry. We will discuss the chemistry of acids and bases in detail later in the text, particularly in Chapter 16.

Finally, as is typical for nonmetals, hydrogen also has the ability to gain an electron from a metal with a low ionization energy. For example, we saw in Equation 7.16 that hydrogen reacts with active metals to form solid metal hydrides that contain the hydride ion, H^-. The fact that hydrogen can gain an electron further illustrates that it behaves much more like a nonmetal than an alkali metal.

Group 16: The Oxygen Group

As we proceed down Group 16, there is a change from nonmetallic to metallic character (Figure 7.13). Oxygen, sulfur, and selenium are typical nonmetals. Tellurium is a metalloid, and polonium, which is radioactive and quite rare, is a metal. Oxygen is a colorless gas at room temperature; all of the other members of Group 16 are solids. Some of the physical properties of the Group 16 elements are given in **Table 7.6**.

As we saw in Section 2.6, oxygen exists in two molecular forms, O_2 and O_3. Because O_2 is the more common form, people generally mean it when they say "oxygen,"

TABLE 7.6 Some Properties of the Group 16 Elements

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (pm)	I_1 (kJ/mol)
Oxygen	$[He]2s^22p^4$	−218	1.43 g/L	66	1314
Sulfur	$[Ne]3s^23p^4$	115	1.96 g/cm^3	105	1000
Selenium	$[Ar]3d^{10}4s^24p^4$	221	4.82 g/cm^3	120	941
Tellurium	$[Kr]4d^{10}5s^25p^4$	450	6.24 g/cm^3	138	869
Polonium	$[Xe]4f^{14}5d^{10}6s^26p^4$	254	9.20 g/cm^3	140	812

*A more realistic description is one where an H^+ ion is transferred from HCl to H_2O forming Cl^- and H_3O^+. We will explore this chemistry in detail in Chapter 16.

although the name *dioxygen* is more descriptive. The O_3 form is **ozone**. The two forms of oxygen are examples of *allotropes,* defined as different forms of the same element. About 21% of dry air consists of O_2 molecules. Ozone is present in very small amounts in the upper atmosphere and in polluted air. It is also formed from O_2 in electrical discharges, such as in lightning storms:

$$3\,O_2(g) \longrightarrow 2\,O_3(g) \qquad \Delta H^\circ = 284.6\ \text{kJ} \qquad [7.28]$$

This reaction is strongly endothermic, telling us that O_3 is less stable than O_2.

Although both O_2 and O_3 are colorless and therefore do not absorb visible light, O_3 absorbs certain wavelengths of ultraviolet light that O_2 does not. Because of this difference, the presence of ozone in the upper atmosphere is beneficial, filtering out harmful UV light. Ozone and oxygen also have different chemical properties. Ozone, which has a pungent odor, is a powerful oxidizing agent. Because of this property, ozone is sometimes added to water to kill bacteria or used in low levels to help to purify air. However, the reactivity of ozone also makes its presence in polluted air near Earth's surface detrimental to human health.

Oxygen has a great tendency to attract electrons from other elements (to *oxidize* them). Oxygen in combination with a metal is almost always present as the oxide ion, O^{2-}. This ion has a noble-gas configuration and is particularly stable. As shown in Figure 5.14, the formation of nonmetal oxides is also often very exothermic and thus energetically favorable.

In our discussion of the alkali metals, we noted two less common oxygen anions—the peroxide (O_2^{2-}) ion and the superoxide (O_2^-) ion. Compounds of these ions often react to produce an oxide and O_2:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g) \quad \Delta H^\circ = -196.1\ \text{kJ} \qquad [7.29]$$

After oxygen, the most important member of Group 16 is sulfur. This element exists in several allotropic forms, the most common and stable of which is the yellow solid having the molecular formula S_8. This molecule consists of an eight-membered ring of sulfur atoms (**Figure 7.26**). Even though solid sulfur consists of S_8 rings, we usually write it simply as S(*s*) in chemical equations to simplify the stoichiometric coefficients.

Like oxygen, sulfur has a tendency to gain electrons from other elements to form sulfides, which contain the S^{2-} ion. In fact, most sulfur in nature is present as metal sulfides. Sulfur is below oxygen in the periodic table, and the tendency of sulfur to form sulfide anions is not as great as that of oxygen to form oxide ions. As a result, the chemistry of sulfur is more complex than that of oxygen. In fact, sulfur and its compounds (including those in coal and petroleum) can be burned in oxygen. The main product is sulfur dioxide, a major air pollutant:

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad [7.30]$$

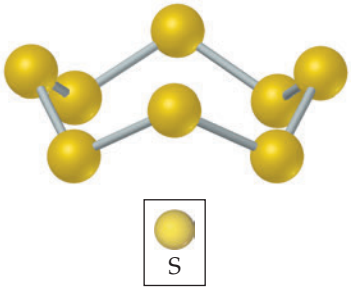
Below sulfur in Group 16 is selenium, Se. This relatively rare element is essential for life in trace quantities, although it is toxic at high doses. There are many allotropes of Se, including several eight-membered ring structures that resemble the S_8 ring.

The next element in the group is tellurium, Te. Its elemental structure is even more complex than that of Se, consisting of long, twisted chains of Te—Te bonds. Both Se and Te favor the −2 oxidation state, as do O and S.

From O to S to Se to Te, the elements form larger and larger molecules and become increasingly metallic. The thermal stability of Group 16 compounds with hydrogen decreases down the column: $H_2O > H_2S > H_2Se > H_2Te$, with H_2O, water, being the most stable of the series.

Go Figure

Suppose it were possible to flatten the S_8 ring. What shape would you expect the flattened ring to have?



▲ **Figure 7.26 Elemental sulfur exists as the S_8 molecule.** At room temperature, this is the most common allotropic form of sulfur.

Group 17: The Halogens

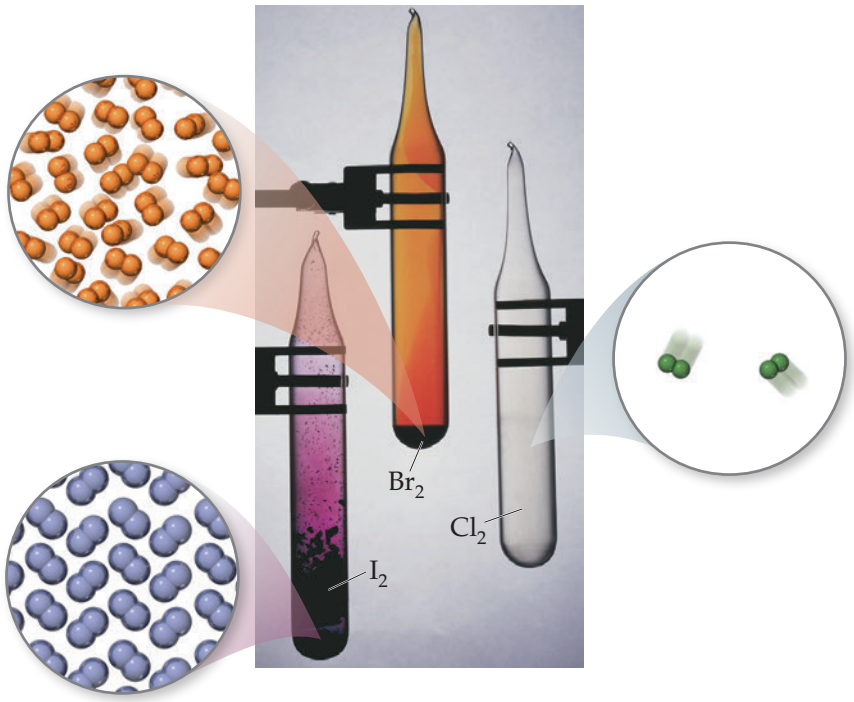
Some of the properties of the Group 17 elements, the **halogens**, are given in **Table 7.7**. Astatine, which is both extremely rare and radioactive, is omitted because many of its properties are not yet known. Even less is known about the recently discovered Tennessine.

Unlike the Group 16 elements, all of the halogens that have been characterized are nonmetals. Their melting and boiling points increase with increasing atomic number. Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. Each element consists of diatomic molecules: F_2, Cl_2, Br_2, and I_2 (**Figure 7.27**).

TABLE 7.7 Some Properties of the Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (pm)	I_1 (kJ/mol)
Fluorine	$[He]2s^2 2p^5$	−220	1.69 g/L	57	1681
Chlorine	$[Ne]3s^2 3p^5$	−102	3.12 g/L	102	1251
Bromine	$[Ar]4s^2 3d^{10} 4p^5$	−7.3	3.12 g/cm^3	120	1140
Iodine	$[Kr]5s^2 4d^{10} 5p^5$	114	4.94 g/cm^3	139	1008

Go Figure Why are more molecules of I_2 seen in the molecular view relative to the number of Cl_2 molecules?



▲ **Figure 7.27** The elemental halogens exist as diatomic molecules.

The halogens have highly negative electron affinities (Figure 7.12). Thus, it is not surprising that the chemistry of the halogens is dominated by their tendency to gain electrons from other elements to form halide ions, X^-. (In many equations, X is used to indicate any one of the halogen elements.) Fluorine and chlorine are more reactive than bromine and iodine. In fact, fluorine removes electrons from almost any substance with which it comes into contact, including water, and usually does so very exothermically, as in the following examples:

$$2\,H_2O(l) + 2\,F_2(g) \longrightarrow 4\,HF(aq) + O_2(g) \quad \Delta H = -758.9\ kJ \qquad [7.31]$$

$$SiO_2(s) + 2\,F_2(g) \longrightarrow SiF_4(g) + O_2(g) \quad \Delta H = -704.0\ kJ \qquad [7.32]$$

As a result, fluorine gas is difficult and dangerous to use in the laboratory, requiring specialized equipment.

Chlorine is the most industrially useful of the halogens. It is produced by a process called electrolysis, where an electrical current is used to oxidize chloride anions to molecular chlorine, Cl_2. Unlike fluorine, chlorine reacts slowly with water to form relatively stable aqueous solutions of HCl and HOCl (hypochlorous acid):

$$Cl_2(g) + H_2O(l) \longrightarrow HCl(aq) + HOCl(aq) \qquad [7.33]$$

Chlorine is often added to drinking water and swimming pools because the HOCl(*aq*) that is generated serves as a disinfectant.

The halogens react directly with most metals to form ionic halides. The halogens also react with hydrogen to form gaseous hydrogen halide compounds:

$$H_2(g) + X_2 \longrightarrow 2\,HX(g) \qquad [7.34]$$

These compounds are all very soluble in water and dissolve to form the hydrohalic acids. As we discussed in Section 4.3, HCl(*aq*), HBr(*aq*), and HI(*aq*) are strong acids, whereas HF(*aq*) is a weak acid.

Group 18: The Noble Gases

The Group 18 elements, known as the **noble gases**, are all nonmetals that are gases at room temperature. They are all *monatomic* (that is, they consist of single atoms rather than molecules). Some physical properties of the noble-gas elements are listed in Table 7.8. The high radioactivity of radon (Rn, atomic number 86) has limited the study of its reaction chemistry and some of its properties.

The noble gases have completely filled *s* and *p* subshells. All elements of Group 18 have large first ionization energies, and we see the expected decrease as we move down the column. Because the noble gases possess such stable electron configurations, they are exceptionally unreactive. In fact, until the early 1960s the elements were called the *inert gases* because they were thought to be incapable of forming chemical compounds. In 1962, Neil Bartlett (1932–2008) at the University of British Columbia reasoned that the ionization energy of Xe might be low enough to allow it to form compounds. For this to happen, Xe would have to react with a substance with an extremely high ability to remove electrons from other substances, such as fluorine. Bartlett synthesized the first noble-gas compound by combining Xe with the fluorine-containing compound PtF_6. Xenon also reacts directly with $F_2(g)$ to form the molecular compounds XeF_2, XeF_4, and XeF_6. Krypton has a higher I_1 value than xenon and is therefore less reactive. In fact, only a single stable compound of krypton is known, KrF_2. In 2000, Finnish scientists reported the first neutral molecule that contains argon, the HArF molecule, which is stable only at low temperatures.

TABLE 7.8 Some Properties of the Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (pm)	I_1 (kJ/mol)
Helium	$1s^2$	4.2	0.18	28	2372
Neon	$[He]2s^22p^6$	27.1	0.90	58	2081
Argon	$[Ne]3s^23p^6$	87.3	1.78	106	1521
Krypton	$[Ar]4s^23d^{10}4p^6$	120	3.75	116	1351
Xenon	$[Kr]5s^24d^{10}5p^6$	165	5.90	140	1170
Radon	$[Xe]6s^24f^{14}5d^{10}6p^6$	211	9.73	150	1037

*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

Self-Assessment Exercise

7.39 The density of bromine is 1000 times larger than chlorine. What factor do you think plays the biggest role in this dramatic change?

(a) The increased mass of a bromine atom.

(b) The fact that bromine is a liquid and chlorine a gas.

(c) The larger atomic radius of bromine.

Exercises

7.40 Compare the elements bromine and chlorine with respect to the following properties: (**a**) electron configuration, (**b**) most common ionic charge, (**c**) first ionization energy, (**d**) reactivity toward water, (**e**) electron affinity, (**f**) atomic radius. Account for the differences between the two elements.

7.41 Until the early 1960s, the Group 18 elements were called the inert gases. (**a**) Why was the term *inert gases* dropped? (**b**) What discovery triggered this change in name? (**c**) What name is applied to the group now?

7.42 Write a balanced equation for the reaction that occurs in each of the following cases: (**a**) White phorphrous, $P_4(s)$, reacts with chlorine gas. (**b**) Sodium metal reacts with water. (**c**) Hydrogen bromide gas reacts with chlorine gas. (**d**) Aluminum trichloride reacts with aqueous sodium hydroxide.

Answers to Self-Assessment Exercises

7.39 (b)

Sample Integrative Exercise

Putting Concepts Together

The element bismuth (Bi, atomic number 83) is the heaviest member of Group 15. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

(**a**) Based on values presented in Figure 7.7 and Tables 7.5 and 7.6, what might you expect for the bonding atomic radius of bismuth?

(**b**) What accounts for the general increase in atomic radius going down the Group 15 elements?

(**c**) Another major use of bismuth has been as an ingredient in low-melting metal alloys, such as those used in fire sprinkler systems and in typesetting. The element itself is a brittle white crystalline solid. How do these characteristics fit with the fact that bismuth is in the same periodic group with such nonmetallic elements as nitrogen and phosphorus?

(**d**) Bi_2O_3 is a basic oxide. Write a balanced chemical equation for its reaction with dilute nitric acid. If 6.77 g of Bi_2O_3 is dissolved in dilute acidic solution to make 0.500 L of solution, what is the molarity of the solution of Bi^{3+} ion?

(**e**) ^{209}Bi is the heaviest stable isotope of any element. How many protons and neutrons are present in this nucleus?

(**f**) The density of Bi at 25 °C is 9.808 g/cm^3. How many Bi atoms are present in a cube of the element that is 5.00 cm on each edge? How many moles of the element are present?

SOLUTION

(**a**) Bismuth is directly below antimony, Sb, in Group 15. Based on the observation that atomic radii increase as we go down a column, we would expect the radius of Bi to be greater than that of Sb, which is 139 pm. We also know that atomic radii generally decrease as we proceed from left to right in a period. Tables 7.5 and 7.6 each give an element in the same period, namely, Ba and Po. We would therefore expect that the radius of Bi is smaller than that of Ba (215 pm) and larger than that of Po (140 pm). We also see that in other periods, the difference in radius between the neighboring Group 15 and Group 16 elements is relatively small. We might therefore expect that the radius of Bi is slightly larger than that of Po—much closer to the radius of Po than to the radius of Ba. The tabulated value for the atomic radius on Bi is 148 pm, in accord with our expectations.

(**b**) The general increase in radius with increasing atomic number in the Group 15 elements occurs because additional shells of electrons are being added, with corresponding increases in nuclear charge. The core electrons in each case largely screen the outermost electrons from the nucleus, so the effective nuclear charge does not vary greatly as we go to higher atomic numbers. However, the principal quantum number, n, of the outermost electrons steadily increases, with a corresponding increase in orbital radius.

(**c**) The contrast between the properties of bismuth and those of nitrogen and phosphorus illustrates the general rule that there is a trend toward increased metallic character as we move down in a given group. Bismuth, in fact, is a metal. The increased metallic character occurs because the outermost electrons are more readily lost in bonding, a trend that is consistent with its lower ionization energy.

(**d**) Following the procedures described in Section 4.2 for writing molecular and net ionic equations, we have the following:

Molecular equation:

$$Bi_2O_3(s) + 6\,HNO_3(aq) \longrightarrow 2\,Bi(NO_3)_3(aq) + 3\,H_2O(l)$$

Net ionic equation:

$$Bi_2O_3(s) + 6\,H^+(aq) \longrightarrow 2\,Bi^{3+}(aq) + 3\,H_2O(l)$$

In the net ionic equation, nitric acid is a strong acid and $Bi(NO_3)_3$ is a soluble salt, so we need to show only the reaction of the solid with the hydrogen ion forming the $Bi^{3+}(aq)$ ion

Continued

and water. To calculate the concentration of the solution, we proceed as follows (Section 4.5):

$$\frac{6.77\ \text{g}\ Bi_2O_3}{0.500\ \text{L soln}} \times \frac{1\ \text{mol}\ Bi_2O_3}{466.0\ \text{g}\ Bi_2O_3} \times \frac{2\ \text{mol}\ Bi^{3+}}{1\ \text{mol}\ Bi_2O_3}$$

$$= \frac{0.0581\ \text{mol}\ Bi^{3+}}{\text{L soln}} = 0.0581\ M$$

(**e**) Recall that the atomic number of any element is the number of protons and electrons in a neutral atom of the element. Bismuth is element 83; there are therefore 83 protons in the nucleus. Because the atomic mass number is 209, there are $209 - 83 = 126$ neutrons in the nucleus.

(**f**) We can use the density and the atomic weight to determine the number of moles of Bi, and then use Avogadro's number to convert the result to the number of atoms. The volume of the cube is $(5.00)^3\ \text{cm}^3 = 125\ \text{cm}^3$. Then we have

$$125\ \text{cm}^3\ \text{Bi} \times \frac{9.808\ \text{g Bi}}{1\ \text{cm}^3} \times \frac{1\ \text{mol Bi}}{209.0\ \text{g Bi}} = 5.87\ \text{mol Bi}$$

$$5.87\ \text{mol Bi} \times \frac{6.022 \times 10^{23}\ \text{atom Bi}}{1\ \text{mol Bi}} = 3.53 \times 10^{24}\ \text{atoms Bi}$$

Chapter Summary and Key Terms

DEVELOPMENT OF THE PERIODIC TABLE (INTRODUCTION AND SECTION 7.1) The periodic table was first developed by Mendeleev and Meyer on the basis of the similarity in chemical and physical properties exhibited by certain elements. Moseley established that each element has a unique atomic number, which added more order to the periodic table.

We now know that elements in the same column of the periodic table have the same number of electrons in their **valence orbitals**. This similarity in valence electronic structure leads to the similarities among elements in the same group. Differences among elements in the same group arise because their valence orbitals are in different shells.

EFFECTIVE NUCLEAR CHARGE (SECTION 7.2) Many properties of atoms depend on the **effective nuclear charge**, which is the portion of the nuclear charge that an outer electron experiences after accounting for repulsions by other electrons in the atom. The core electrons are very effective in screening the outer electrons from the full charge of the nucleus, whereas electrons in the same shell do not screen each other very effectively. Because the actual nuclear charge increases as we progress through a period, the effective nuclear charge experienced by valence electrons increases as we move left to right across a period.

SIZES OF ATOMS AND IONS (SECTION 7.3) The size of an atom can be gauged by its **bonding atomic radius**, which is based on measurements of the distances separating atoms in their chemical compounds. In general, atomic radii increase down a column in the periodic table and decrease left to right across a row.

Cations are smaller than their parent atoms; anions are larger than their parent atoms. For ions of the same charge, size increases going down a column of the periodic table. An **isoelectronic series** is a series of ions that has the same number of electrons. For such a series, size decreases with increasing atomic number as the electrons are attracted more strongly to the nucleus as its positive charge increases.

IONIZATION ENERGY (SECTION 7.4) The first **ionization energy** of an atom is the minimum energy needed to remove an electron from the atom in the gas phase, forming a cation. The second ionization energy is the energy needed to remove a second electron, and so forth. Ionization energies show a sharp increase after all the valence electrons have been removed because of the much higher effective nuclear charge experienced by the core electrons. The first ionization energies of the elements show periodic trends that are opposite those seen for atomic radii, with smaller atoms having higher first ionization energies. Thus, first ionization energies decrease as we go down a column and increase as we proceed left to right across a row.

We can write electron configurations for ions by first writing the electron configuration of the neutral atom and then removing or adding the appropriate number of electrons. For cations, electrons are removed first from the orbitals of the neutral atom with the largest value of n. If there are two valence orbitals with the same value of n (such as 4s and 4p), then the electrons are lost first from the orbital with a higher value of l (in this case, 4p). For anions, electrons are added to orbitals in the reverse order.

ELECTRON AFFINITY (SECTION 7.5) The **electron affinity** of an element is the energy change upon adding an electron to an atom in the gas phase, forming an anion. A negative electron affinity means that energy is released when the electron is added; hence, when the electron affinity is negative the anion is stable. By contrast, a positive electron affinity means that the anion is not stable relative to the separated atom and electron. In general, electron affinities become more negative as we proceed from left to right across the periodic table. The halogens have the most negative electron affinities. The electron affinities of the noble gases are positive because the added electron would have to occupy a new, higher-energy subshell.

METALS, NONMETALS, AND METALLOIDS (SECTION 7.6) The elements can be categorized as metals, nonmetals, and metalloids. Most elements are metals; they occupy the left side and the middle of the periodic table. Nonmetals appear in the upper-right section of the table. Metalloids occupy a narrow band between the metals and nonmetals. The tendency of an element to exhibit the properties of metals, called the **metallic character**, increases as we proceed down a column and decreases as we proceed from left to right across a row.

Metals have a characteristic luster, and they are good conductors of heat and electricity. When metals react with nonmetals, the metal atoms are oxidized to cations and ionic substances are generally formed. Most metal oxides are basic; they react with acids to form salts and water.

Nonmetals lack metallic luster and are generally poor conductors of heat and electricity. Several are gases at room temperature. Compounds composed entirely of nonmetals are generally molecular. Nonmetals usually form anions in their reactions with metals. Nonmetal oxides are acidic; they react with bases to form salts and water. Metalloids have properties that are intermediate between those of metals and nonmetals.

TRENDS FOR GROUP 1 AND 2 METALS (SECTION 7.7) The periodic properties of the elements can help us understand the properties of groups of the representative elements. The **alkali metals** (Group 1) are soft metals with low densities and low melting points. They have the lowest ionization energies of the elements. As a result, they are very reactive toward nonmetals, easily losing their outer s electron to form 1+ ions.

The **alkaline earth metals** (Group 2) are harder and denser, and have higher melting points than the alkali metals. They are also very

reactive toward nonmetals, although not as reactive as the alkali metals. The alkaline earth metals readily lose their two outer *s* electrons to form 2+ ions. Both alkali and alkaline earth metals react with hydrogen to form ionic substances that contain the **hydride ion**, H^-.

TRENDS FOR SELECTED NONMETALS (SECTION 7.8) Hydrogen is a nonmetal with properties that are distinct from any of the groups of the periodic table. It forms molecular compounds with other nonmetals, such as oxygen and the halogens.

Oxygen and sulfur are the most important elements in Group 16. Oxygen is usually found as a diatomic molecule, O_2. **Ozone**, O_3, is an important allotrope of oxygen. Oxygen has a strong tendency to gain electrons from other elements, thus oxidizing them. In combination with metals, oxygen is usually found as the oxide ion, O^{2-}, although salts of the peroxide ion, O_2^{2-}, and superoxide ion, O_2^-, are sometimes formed. Elemental sulfur is most commonly found as S_8 molecules. In combination with metals, it is most often found as the sulfide ion, S^{2-}.

The **halogens** (Group 17) exist as diatomic molecules. The halogens have the most negative electron affinities of the elements. Thus, their chemistry is dominated by a tendency to form 1− ions, especially in reactions with metals.

The **noble gases** (Group 18) exist as monatomic gases. They are very unreactive because they have completely filled *s* and *p* subshells. Only the heaviest noble gases are known to form compounds, and they do so only with very active nonmetals, such as fluorine.

Learning Outcomes After studying this chapter, you should be able to:

- Explain the meaning of effective nuclear charge, Z_{eff}, and how Z_{eff} depends on nuclear charge and electron configuration. (Section 7.2) *Related Exercises: 7.5–7.7, 7.53*
- Use the periodic table to predict the trends in atomic radii, ionic radii, ionization energy, and electron affinity. (Sections 7.2, 7.3, 7.4, and 7.5) *Related Exercises*: *7.27, 7.59, 7.69, 7.70*
- Explain how the radius of an atom changes upon losing electrons to form a cation or gaining electrons to form an anion. (Section 7.3) *Related Exercises*: *7.60, 7.63–7.65*
- Use the periodic table to determine the electron configurations of ions. (Section 7.3) *Related Exercises: 7.15, 7.22, 7.61, 7.71*
- Predict the trends in ionization energy as successive electrons are removed, including the discontinuous increase that occurs when the ionization corresponds to removing a core electron. (Section 7.4) *Related Exercises*: *7.18, 7.19, 7.67, 7.69*
- Explain how electron affinity and ionization energy are related, and how irregularities in the periodic trends for electron affinity can be related to electron configuration. (Section 7.5) *Related Exercises*: *7.27, 7.75, 7.101, 7.104*
- Explain the differences in chemical and physical properties of metals and nonmetals, including the basicity of metal oxides and the acidity of nonmetal oxides. (Section 7.6) *Related Exercises*: *7.31, 7.76, 7.78, 7.79*
- Explain how atomic properties, such as ionization energy and electron affinity, relate to the chemical reactivity and physical properties of the alkali and alkaline earth metals (Groups 1 and 2). (Section 7.7) *Related Exercises*: *7.36, 7.82*
- Write balanced equations for the reactions of the Group 1 and 2 metals with water, oxygen, hydrogen, and the halogens. (Sections 7.7 and 7.8) *Related Exercises: 7.37, 7.83*
- List and explain the unique characteristics of hydrogen. (Section 7.8) *Related Exercises: 7.38, 7.84, 7.108*
- Explain how the atomic properties, such as ionization energy and electron affinity, of Group 16, 17, and 18 elements relate to their chemical reactivity and physical properties. (Section 7.8) *Related Exercises: 7.40, 7.85, 7.86*

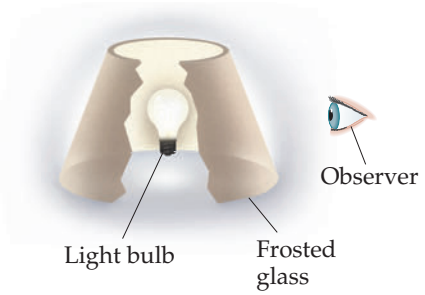
Key Equations

- $Z_{eff} = Z - S$ [7.1] Estimating effective nuclear charge

Exercises

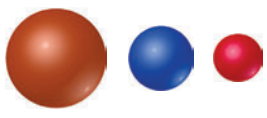
Visualizing Concepts

7.43 As discussed in the text, we can draw an analogy between the attraction of an electron to a nucleus and the act of perceiving light from a light bulb through a frosted glass shade, as shown in the illustration.



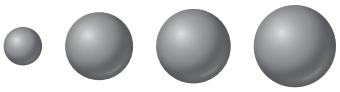
Using the simple method of estimating effective nuclear charge, Equation 7.1, how does the intensity of the light bulb and/or the thickness of the frosting change in the following cases: (**a**) Moving from boron to carbon? (**b**) Moving from boron to aluminum? [Section 7.2]

7.44 Which of these spheres represents F, which represents Br, and which represents Br^-? [Section 7.3]

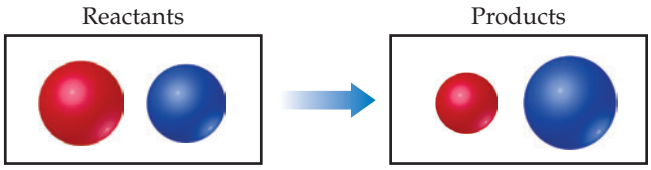


7.45 Consider the Mg^{2+}, Cl^-, K^+, and Se^{2-} ions. The four spheres below represent these four ions, scaled according to ionic size. (**a**) Without referring to Figure 7.8, match each ion to its

appropriate sphere. (**b**) In terms of size, between which of the spheres would you find the (i) Ca^{2+} and (ii) S^{2-} ions? [Section 7.3]

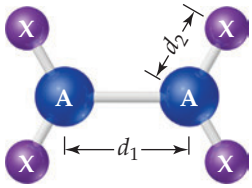


7.46 In the following reaction

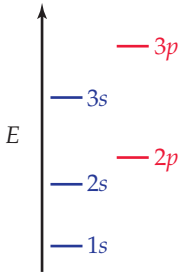


which sphere represents a metal and which represents a nonmetal? [Section 7.3]

7.47 Consider the A_2X_4 molecule depicted here, where A and X are elements. The A—A bond length in this molecule is d_1, and the four A—X bond lengths are each d_2. (**a**) In terms of d_1 and d_2, how could you define the bonding atomic radii of atoms A and X? (**b**) In terms of d_1 and d_2, what would you predict for the X—X bond length of an X_2 molecule? [Section 7.3]



7.48 A qualitative diagram of the atomic orbital energies for an Na atom is shown here. The number of orbitals in each subshell is not shown.



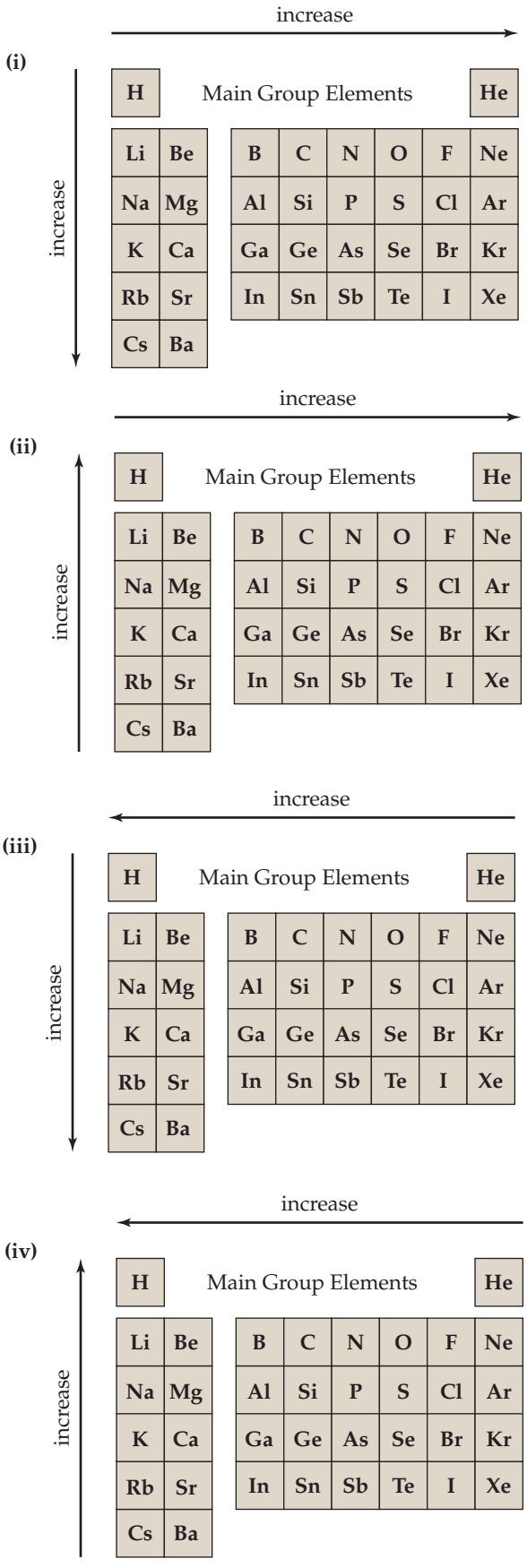
(**a**) Are all of the subshells for $n = 1$, $n = 2$, and $n = 3$ shown? If not, what is missing?

(**b**) The 2*s* and 2*p* energy levels are different. Which of the following is the best explanation for why this is the case? (**i**) The 2*s* and 2*p* energy levels have different energies in the hydrogen atom, so of course they will have different energies in the sodium atom, (**ii**) The energy of the 2*p* orbital is higher than that of the 2*s* in all many-electron atoms. (**iii**) The 2*s* level in Na has electrons in it, whereas the 2*p* does not.

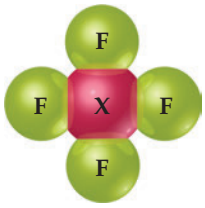
(**c**) Which of the energy levels holds the highest-energy electron in a sodium atom?

(**d**) A sodium vapor lamp (Figure 7.23) operates by using electricity to excite the highest-energy electron to the next highest-energy level. Light is produced when the excited electron drops back to the lower level. Which two energy levels are involved in this process for the Na atom? [Section 7.7]

7.49 Which of the following charts shows the general periodic trends for each of the following properties of the main-group elements (you can neglect small deviations going either across a row or down a column of the periodic table)? (**1**) Bonding atomic radius, (**2**) first ionization energy, (**3**) effective nuclear charge. [Sections 7.2–7.6]



7.50 An element X reacts with $F_2(g)$ to form the molecular product shown here. (**a**) Write a balanced equation for this reaction (do not worry about the phases for X and the product). (**b**) Do you think that X is a metal or nonmetal? [Section 7.6]



Periodic Table; Effective Nuclear Charge (Sections 7.1 and 7.2)

7.51 (**a**) Evaluate the expressions 2×1, $2 \times (1 + 3)$, $2 \times (1 + 3 + 5)$, and $2 \times (1 + 3 + 5 + 7)$. (**b**) How do the atomic numbers of the noble gases relate to the numbers from part (a)? (**c**) What topic discussed in Chapter 6 is the source of the number "2" in the expressions in part (a)?

7.52 Moseley's experiments on X rays emitted from atoms led to the concept of atomic numbers. (**a**) If arranged in order of increasing atomic mass, which element would come after chlorine? (**b**) Describe two ways in which the properties of this element differ from the other elements in Group 18.

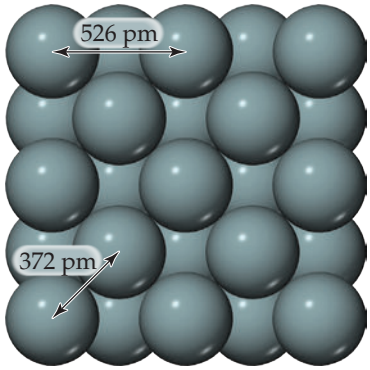
7.53 Which of the following statements about effective nuclear charge for the outermost valence electron of an atom is *incorrect*? (**i**) The effective nuclear charge can be thought of as the true nuclear charge minus a screening constant due to the other electrons in the atom. (**ii**) Effective nuclear charge increases going left to right across a row of the periodic table. (**iii**) Valence electrons screen the nuclear charge more effectively than do core electrons. (**iv**) The effective nuclear charge shows a sudden decrease when we go from the end of one row to the beginning of the next row of the periodic table. (**v**) The change in effective nuclear charge going down a column of the periodic table is generally less than that going across a row of the periodic table.

7.54 Detailed calculations show that the value of Z_{eff} for the outermost electrons in Si and Cl atoms is 4.29+ and 6.12+, respectively. (**a**) What value do you estimate for Z_{eff} experienced by the outermost electron in both Si and Cl by assuming core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant? (**b**) What values do you estimate for Z_{eff} using Slater's rules? (**c**) Which approach gives a more accurate estimate of Z_{eff}? (**d**) Which method of approximation more accurately accounts for the steady increase in Z_{eff} that occurs upon moving left to right across a period? (**e**) Predict Z_{eff} for a valence electron in P, phosphorus, based on the calculations for Si and Cl.

7.55 Arrange the following atoms in order of increasing effective nuclear charge experienced by the electrons in the $n = 2$ shell: Be, Br, Na, P, Se.

Atomic and Ionic Radii (Section 7.3)

7.56 With the exception of helium, the noble gases condense to form solids when they are cooled sufficiently. At temperatures below 83 K, argon forms a close-packed solid whose structure is shown here. (**a**) What is the apparent radius of an argon atom in solid argon, assuming the atoms touch as shown in this figure? (**b**) Is this value larger or smaller than the bonding atomic radius estimated for argon in Figure 7.7? (**c**) Based on this comparison would you say that the atoms are held together by chemical bonds in solid argon?



7.57 Which of the following statements about the bonding atomic radii in Figure 7.7 is *incorrect*? (**i**) For a given period, the radii of the representative elements generally decrease from left to right across a period. (**ii**) The radii of the representative elements for the $n = 3$ period are all larger than those of the corresponding elements in the $n = 2$ period. (**iii**) For most of the representative elements, the change in radius from the $n = 2$ to the $n = 3$ period is greater than the change in radius from $n = 3$ to $n = 4$. (**iv**) The radii of the transition elements generally increase moving from left to right within a period. (**v**) The large radii of the Group 1 elements are due to their relatively small effective nuclear charges.

7.58 The experimental Pb—Cl bond length in lead(II)chloride, $PbCl_2$, is 244 pm. Based on this value and data in Figure 7.7, predict the atomic radius of Pb.

7.59 Using only the periodic table, arrange each set of atoms in order of increasing radius: (**a**) Cs, Se, Te; (**b**) S, Si, Sr; (**c**) P, Po, Pb.

7.60 Explain the following variations in atomic or ionic radii:

(**a**) $I^- > I > I^+$

(**b**) $Ca^{2+} > Mg^{2+} > Be^{2+}$

(**c**) $Fe > Fe^{2+} > Fe^{3+}$

7.61 Some ions do not have a corresponding neutral atom that has the same electron configuration. For each of the following ions, identify the neutral atom that has the same number of electrons and determine if this atom has the same electron configuration. (**a**) Cl^-, (**b**) Sc^{3+}, (**c**) Fe^{2+}, (**d**) Zn^{2+}, (**e**) Sn^{4+}.

7.62 Consider the isoelectronic ions Cl^- and K^+. (**a**) Which ion is smaller? (**b**) Using Equation 7.1 and assuming that core electrons contribute 1.00 and valence electrons contribute nothing to the screening constant, S, calculate Z_{eff} for these two ions. (**c**) Repeat this calculation using Slater's rules to estimate the screening constant, S. (**d**) For isoelectronic ions, how are effective nuclear charge and ionic radius related?

7.63 Consider S, Cl, and K and their most common ions. (**a**) List the atoms in order of increasing size. (**b**) List the ions in order of increasing size. (**c**) Explain any differences in the orders of the atomic and ionic sizes.

7.64 Arrange each of the following sets of atoms and ions, in order of increasing size: (**a**) Pb, Pb^{2+}, Pb^{4+}; (**b**) V^{3+}, Co^{2+},Co^{3+}; (**c**) Se^{2-}, S^{2-}, Sn^{2+}; (**d**) K^+, Rb^+, Br^-.

7.65 Provide a brief explanation for each of the following: (**a**) Cl^- is larger than Ar. (**b**) P^{3-} is larger than S^{2-}. (**c**) K^+ is larger than Na^+. (**d**) F^- is larger than F.

7.66 In the ionic compounds LiF, NaCl, KBr, and RbI, the measured cation–anion distances are 201 pm (Li–F), 282 pm (Na–Cl), 330 pm (K–Br), and 367 pm (Rb–I), respectively. (**a**) Predict the cation–anion distance using the values of ionic radii given in Figure 7.8. (**b**) Calculate the difference between the experimentally measured ion–ion distances and the ones predicted from Figure 7.8. (**c**) What estimates of the cation–anion

distance would you obtain for these four compounds using neutral atom *bonding atomic radii*? Are these estimates as accurate as the estimates using ionic radii?

Ionization Energies; Electron Affinities (Sections 7.4 and 7.5)

7.67 Write equations that show the process for (**a**) the first two ionization energies of zinc and (**b**) the fourth ionization energy of calcium.

7.68 Identify each statement as true or false: (**a**) Ionization energies are always endothermic. (**b**) Potassium has a larger first ionization energy than lithium. (**c**) The second ionization energy of the sodium atom is larger than the second ionization energy of the magnesium atom. (**d**) The third ionization energy is three times the first ionization energy of an atom.

7.69 (**a**) What is the trend in first ionization energies as one proceeds down the Group 17 elements? Explain how this trend relates to the variation in atomic radii. (**b**) What is the trend in first ionization energies as one moves across the fourth period from K to Kr? How does this trend compare with the trend in atomic radii?

7.70 For each of the following pairs, indicate which element has the smaller first ionization energy: (**a**) Cs, Cl; (**b**) Fe, Zn; (**c**) I, Cl; (**d**) Se, Sn.

7.71 Write the electron configurations for the following ions, and determine which have noble-gas configurations: (**a**) Ti^{2+}, (**b**) Br^-, (**c**) Mg^{2+}, (**d**) Po^{2-}, (**e**) Pt^{2+}, (**f**) V^{3+}.

7.72 Give examples of transition metal ions with +3 charge that have an electron configuration of nd^5 ($n = 3, 4, 5 \ldots$).

7.73 If the electron affinity for an element is a negative number, does it mean that the anion of the element is more stable than the neutral atom? Explain.

7.74 What is the relationship between the ionization energy of an anion with a 1− charge such as F^- and the electron affinity of the neutral atom, F?

7.75 Consider the following equation:

$$Al^{3+}(g) + e^- \longrightarrow Al^{2+}(g)$$

Which of the following statements are true? (**i**) The energy change for this process is the second electron affinity of Al atom since $Al^{2+}(g)$ is formed. (**ii**) The energy change for this process is the negative of the third ionization energy of the Al atom. (**iii**) The energy change for this process is the electron affinity of the Al^{2+} ion.

Properties of Metals and Nonmetals (Section 7.6)

7.76 You read the following statement about two elements X and Y: One of the elements is a good conductor of electricity, and the other is a semiconductor. Experiments show that the first ionization energy of X is twice as great as that of Y. Which element has the greater metallic character?

7.77 Discussing this chapter, a classmate says, "Since elements that form cations are metals and elements that form anions are nonmetals, elements that do not form ions are metalloids." Do you agree or disagree?

7.78 Some metal oxides, such as Sc_2O_3, do not react with pure water, but they do react when the solution becomes either acidic or basic. Do you expect Sc_2O_3 to react when the solution becomes acidic or when it becomes basic? Write a balanced chemical equation to support your answer.

7.79 Arrange the following oxides in order of increasing acidity: K_2O, BaO, ZnO, H_2O, CO_2, SO_2.

7.80 An element X reacts with oxygen to form XO_2 and with chlorine to form XCl_4. XO_2 is a white solid that melts at high temperatures (above 1000 °C). Under usual conditions, XCl_4 is a colorless liquid with a boiling point of 58 °C. (**a**) XCl_4 reacts with water to form XO_2 and another product. What is the likely identity of the other product? (**b**) Do you think that element X is a metal, nonmetal, or metalloid? (**c**) By using a sourcebook such as the *CRC Handbook of Chemistry and Physics,* try to determine the identity of element X.

7.81 Write balanced equations for the following reactions: (**a**) sulfur dioxide with water, (**b**) lithium oxide in water, (**c**) zinc oxide with dilute hydrochloric acid, (**d**) arsenic trioxide with aqueous potassium hydroxide.

Group Trends in Metals and Nonmetals (Sections 7.7 and 7.8)

7.82 Copper and calcium both form +2 ions, but copper is far less reactive. Suggest an explanation, taking into account the ground-state electron configurations of these elements and their atomic radii.

7.83 Write a balanced equation for the reaction that occurs in each of the following cases: (**a**) Lithium is added to water. (**b**) Calcium is added to water. (**c**) Potassium reacts with chlorine gas. (**d**) Rubidium reacts with oxygen.

7.84 Potassium and hydrogen react to form the ionic compound potassium hydride. (**a**) Write a balanced equation for this reaction. (**b**) Use data in Figures 7.10 and 7.12 to determine the energy change in kJ/mol for the following two reactions:

$$K(g) + H(g) \longrightarrow K^+(g) + H^-(g)$$
$$K(g) + H(g) \longrightarrow K^-(g) + H^+(g)$$

(**c**) Based on your calculated energy changes in (b), which of these reactions is energetically more favorable (or less unfavorable)? (**d**) Is your answer to (c) consistent with the description of potassium hydride as containing hydride ions?

7.85 Little is known about the properties of astatine, At, because of its rarity and high radioactivity. Nevertheless, it is possible for us to make many predictions about its properties. (**a**) Do you expect the element to be a gas, liquid, or solid at room temperature? Explain. (**b**) Would you expect At to be a metal, nonmetal, or metalloid? Explain. (**c**) What is the chemical formula of the compound it forms with Na?

7.86 (**a**) Why does xenon react with fluorine, whereas neon does not? (**b**) Using appropriate reference sources, look up the bond lengths of Xe—F bonds in several molecules. How do these numbers compare to the bond lengths calculated from the atomic radii of the elements?

7.87 Write a balanced equation for the reaction that occurs in each of the following cases: (**a**) Calcium metal is heated in an atmosphere of oxygen gas. (**b**) Copper oxide is heated in an atmosphere of hydrogen gas. (**c**) Chlorine reacts with nitrogen gas.(**d**) Boron tribromide reacts with water.

Additional Exercises

7.88 Consider the stable elements through lead ($Z = 82$). In how many instances are the atomic weights of the elements out of order relative to the atomic numbers of the elements?

7.89 Figure 7.4 shows the radial probability distribution functions for the 2*s* orbitals and 2*p* orbitals. (**a**) Which orbital, 2*s* or 2*p,* has more electron density close to the nucleus? (**b**) How would you modify Slater's rules to adjust for the difference in electronic penetration of the nucleus for the 2*s* and 2*p* orbitals?

7.90 (**a**) If the core electrons were totally effective at screening the valence electrons and the valence electrons provided no screening for each other, what would be the effective nuclear charge acting on the 3*s* and 3*p* valence electrons in P? (**b**) Repeat these calculations using Slater's rules. (**c**) Detailed calculations indicate that the effective nuclear charge is 5.6+ for the 3*s* electrons and 4.9+ for the 3*p* electrons. Why are the values for the 3*s* and 3*p* electrons different? (**d**) If you remove a single electron from a P atom, which orbital will it come from?

7.91 As we move across a period of the periodic table, why do the sizes of the transition elements change more gradually than those of the representative elements?

7.92 In the series of Group 16 hydrides, of general formula MH_2, the measured bond distances are O—H, 96 pm; S—H, 134 pm; Se—H, 146 pm. (**a**) Compare these values with those estimated by use of the atomic radii in Figure 7.7. (**b**) Explain the steady increase in M—H bond distance in this series in terms of the electron configurations of the M atoms.

7.93 In Table 7.8, the bonding atomic radius of neon is listed as 58 pm, whereas that for xenon is listed as 140 pm. A classmate of yours states that the value for Xe is more realistic than the one for Ne. Is she correct? If so, what is the basis for her statement?

7.94 The P—P bond length in white phosphorus is 189 pm. The Cl—Cl bond length in Cl_2 is 199 pm. (**a**) Based on these data, what is the predicted P—Cl bond length in phosphorus trichloride, PCl_3, in which each of the three Cl atoms is bonded to the P atom? (**b**) What bond length is predicted for PCl_3, using the atomic radii in Figure 7.7?

7.95 The following observations are made about two hypothetical elements A and B: The A—A and B—B bond lengths in the elemental forms of A and B are 236 and 194 pm, respectively. A and B react to form the binary compound AB_2, which has a *linear* structure (that is $\angle B{-}A{-}B = 180°$). Based on these statements, predict the separation between the two B nuclei in a molecule of AB_2.

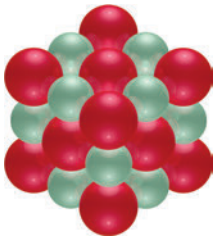
7.96 Elements in Group 17 in the periodic table are called the halogens; elements in Group 16 are called the chalcogens. (**a**) What is the most common oxidation state of the chalcogens compared to the halogens? (**b**) For each of the following periodic properties, state whether the halogens or the chalcogens have larger values: atomic radii, ionic radii of the most common oxidation state, first ionization energy, second ionization energy.

7.97 Note from the following table that there is a significant increase in atomic radius upon moving from Y to La, whereas the radii of Zr to Hf are the same. Suggest an explanation for this effect.

Atomic Radii (pm)			
Sc	170	Ti	160
Y	190	Zr	175
La	207	Hf	175

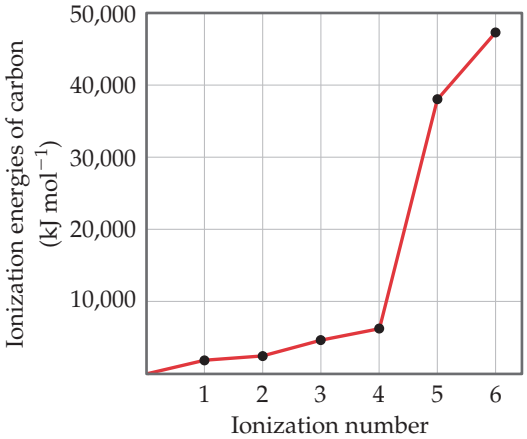
7.98 (**a**) Which ion is smaller, Co^{3+} or Co^{4+}? (**b**) In a lithium-ion battery that is discharging to power a device, for every Li^+ that inserts into the lithium cobalt oxide electrode, a Co^{4+} ion must be reduced to a Co^{3+} ion to balance charge. Using the *CRC Handbook of Chemistry and Physics* or other standard reference, find the ionic radii of Li^+, Co^{3+}, and Co^{4+}. Order these ions from smallest to largest. (**c**) Will the lithium cobalt oxide cathode expand or contract as lithium ions are inserted? (**d**) Lithium is not nearly as abundant as sodium. If sodium ion batteries were developed that function in the same manner as lithium ion batteries, do you think "sodium cobalt oxide" would still work as the electrode material? Explain. (**e**) If you don't think cobalt would work as the redox-active partner ion in the sodium version of the electrode, suggest an alternative metal ion and explain your reasoning.

7.99 The ionic substance strontium oxide, SrO, forms from the reaction of strontium metal with molecular oxygen. The arrangement of the ions in solid SrO is analogous to that in solid NaCl:



(**a**) Write a balanced equation for the formation of SrO(*s*) from its elements. (**b**) Based on the ionic radii in Figure 7.8, predict the length of the side of the cube in the figure (the distance from the center of an atom at one corner to the center of an atom at a neighboring corner). (**c**) The density of SrO is 5.10 g/cm^3. Given your answer to part (b), how many formula units of SrO are contained in the cube shown here?

7.100 Explain the variation in the ionization energies of carbon, as displayed in this graph:



7.101 Group 14 elements have much more negative electron affinities than their neighbors in Groups 13 and 15 (see Figure 7.12). Which of the following statements best explains this observation? (**i**) The Group 14 elements have much higher first ionization energies than their neighbors in Groups 13 and 15. (**ii**) The addition of an electron to a Group 14 element leads to a half-filled np^3 outer electron configuration. (**iii**) The Group 14 elements have unusually large atomic radii. (**iv**) The Group 14 elements are easier to vaporize than are the Group 13 and 15 elements.

7.102 In the chemical process called *electron transfer*, an electron is transferred from one atom or molecule to another. (We will talk about electron transfer extensively in Chapter 20.) A simple electron transfer reaction is

$$A(g) + A(g) \longrightarrow A^+(g) + A^-(g)$$

In terms of the ionization energy and electron affinity of atom A, what is the energy change for this reaction? For a representative nonmetal such as chlorine, is this process exothermic? For a representative metal such as sodium, is this process exothermic?

7.103 (**a**) Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. (**b**) Why does O^{3-} not exist?

7.104 Use electron configurations to explain the following observations: (**a**) The first ionization energy of phosphorus is greater than that of sulfur. (**b**) The electron affinity of nitrogen is lower (less negative) than those of both carbon and oxygen. (**c**) The second ionization energy of oxygen is greater than the first ionization energy of fluorine. (**d**) The third ionization energy of manganese is greater than those of both chromium and iron.

7.105 Identify a +2 cation that has the following ground state electron configurations: (**a**) [Ne] (**b**) $[Ar]3d^9$ (**c**) $[Xe]4f^{14}5d^{10}6s^2$.

7.106 Which of the following chemical equations is connected to the definitions of (**a**) the first ionization energy of oxygen, (**b**) the second ionization energy of ox`ygen, and (**c**) the electron affinity of oxygen?

(**i**) $O(g) + e^- \longrightarrow O^-(g)$ (**ii**) $O(g) \longrightarrow O^+(g) + e^-$

(**iii**) $O(g) + 2\,e^- \longrightarrow O^{2-}(g)$ (**iv**) $O(g) \longrightarrow O^{2+}(g) + 2\,e^-$

(**v**) $O^+(g) \longrightarrow O^{2+}(g) + e^-$

7.107 The electron affinities, in kJ/mol, for the Group 11 and Group 12 metals are as follows:

Cu −119	Zn > 0
Ag −126	Cd > 0
Au −223	Hg > 0

(**a**) Why are the electron affinities of the Group 12 elements greater than zero? (**b**) Why do the electron affinities of the Group 11 elements become more negative as we move down the group? [*Hint:* Examine the trends in the electron affinities of other groups as we proceed down the periodic table.]

7.108 Hydrogen is an unusual element because it behaves in some ways like the alkali metal elements and in other ways like nonmetals. Its properties can be explained in part by its electron configuration and by the values for its ionization energy and electron affinity. (**a**) Explain why the electron affinity of hydrogen is much closer to the values for the alkali elements than for the halogens. (**b**) Is the following statement true? "Hydrogen has the smallest bonding atomic radius of any element that forms chemical compounds." If not, correct it. If it is, explain in terms of electron configurations. (**c**) Explain why the ionization energy of hydrogen is closer to the values for the halogens than for the alkali metals. (**d**) The hydride ion is H^-. Write out the process corresponding to the first ionization energy of the hydride ion. (**e**) How does the process in part (d) compare to the process for the electron affinity of a neutral hydrogen atom?

7.109 The first ionization energy of the oxygen molecule is the energy required for the following process:

$$O_2(g) \longrightarrow O_2^+(g) + e^-$$

The energy needed for this process is 1175 kJ/mol, very similar to the first ionization energy of Xe. Would you expect O_2 to react with F_2? If so, suggest a product or products of this reaction.

7.110 It is possible to define *metallic character* as we do in this book and base it on the reactivity of the element and the ease with which it loses electrons. Alternatively, one could measure how well electricity is conducted by each of the elements to determine how "metallic" the elements are. On the basis of conductivity, there is not much of a trend in the periodic table: Silver is the most conductive metal, and manganese the least. Look up the first ionization energies of silver and manganese; which of these two elements would you call more metallic based on the way we define it in this book?

7.111 Which of the following is the expected product of the reaction of $Mg(s)$ and $N_2(g)$ under heat? (**i**) $Mg_3N(s)$, (**ii**) $MgN_2(s)$, (**iii**) $Mg_3N_2(s)$, (**iv**) $Mg(s)$ and $N_2(g)$ will not react with one another.

7.112 Elemental barium reacts more violently with water than does elemental calcium. Which of the following best explains this difference in reactivity? (**i**) Calcium has greater metallic character than does barium. (**ii**) The electron affinity of calcium is smaller than that of barium. (**iii**) The first and second ionization energies of barium are less than those of calcium. (**iv**) The atomic radius of barium is smaller than that of calcium. (**v**) The ionic radius of the barium ion is larger than that of the calcium ion.

7.113 (**a**) One of the alkali metals reacts with oxygen to form a solid white substance. When this substance is dissolved in water, the solution gives a positive test for hydrogen peroxide, H_2O_2. When the solution is tested in a burner flame, a lilac-purple flame is produced. What is the likely identity of the metal? (**b**) Write a balanced chemical equation for the reaction of the white substance with water.

7.114 Zinc in its 2+ oxidation state is an essential metal ion for life. Zn^{2+} is found bound to many proteins that are involved in biological processes, but unfortunately Zn^{2+} is hard to detect by common chemical methods. Therefore, scientists who are interested in studying Zn^{2+}-containing proteins frequently substitute Cd^{2+} for Zn^{2+}, since Cd^{2+} is easier to detect. (**a**) On the basis of the properties of the elements and ions discussed in this chapter and their positions in the periodic table, describe the pros and cons of using Cd^{2+} as a Zn^{2+} substitute. (**b**) Proteins that speed up (catalyze) chemical reactions are called *enzymes*. Many enzymes are required for proper metabolic reactions in the body. One problem with using Cd^{2+} to replace Zn^{2+} in enzymes is that Cd^{2+} substitution can decrease or even eliminate enzymatic activity. Can you suggest a different metal ion that might replace Zn^{2+} in enzymes instead of Cd^{2+}? Justify your answer.

7.115 A historian discovers a nineteenth-century notebook in which some observations, dated 1822, were recorded on a substance thought to be a new element. Here are some of the data recorded in the notebook: "Ductile, silver-white, metallic looking. Softer than lead. Unaffected by water. Stable in air. Melting point: 153 °C. Density: 7.3 g/cm^3. Electrical conductivity: 20% that of copper. Hardness: About 1% as hard as iron. When 4.20 g of the unknown is heated in an excess of oxygen, 5.08 g of a white solid is formed. The solid could be

sublimed by heating to over 800 °C." (**a**) Using information in the text and the *CRC Handbook of Chemistry and Physics*, and making allowances for possible variations in numbers from current values, identify the element reported. (**b**) Write a balanced chemical equation for the reaction with oxygen. (**c**) Judging from Figure 7.1, might this nineteenth-century investigator have been the first to discover a new element?

7.116 In April 2010, a research team reported that it had made Element 117. This discovery was confirmed in 2012 by additional experiments. Write the ground-state electron configuration for Element 117 and estimate values for its first ionization energy, electron affinity, atomic size, and common oxidation state based on its position in the periodic table.

7.117 We will see in Chapter 12 that semiconductors are materials that conduct electricity better than nonmetals but not as well as metals. The only two elements in the periodic table that are technologically useful semiconductors are silicon and germanium. Integrated circuits in computer chips today are based on silicon. Compound semiconductors are also used in the electronics industry. Examples are gallium arsenide, GaAs; gallium phosphide, GaP; cadmium sulfide, CdS; and cadmium selenide, CdSe. (**a**) What is the relationship between the compound semiconductors' compositions and the positions of their elements on the periodic table relative to Si and Ge? (**b**) Workers in the semiconductor industry refer to "II–VI" and "III–V" materials, using Roman numerals. Can you identify which compound semiconductors are II–VI and which are III–V? (**c**) Suggest other compositions of compound semiconductors based on the positions of their elements in the periodic table.

Integrative Exercises

7.118 Moseley established the concept of atomic number by studying X rays emitted by the elements. The X rays emitted by some of the elements have the following wavelengths:

Element	Wavelength (pm)
Ne	1461
Ca	335.8
Zn	143.5
Zr	78.6
Sn	49.1

(**a**) Calculate the frequency, ν, of the X rays emitted by each of the elements, in Hz. (**b**) Plot the square root of versus the atomic number of the element. What do you observe about the plot? (**c**) Explain how the plot in part (b) allowed Moseley to predict the existence of undiscovered elements. (**d**) Use the result from part (b) to predict the X-ray wavelength emitted by iron. (**e**) A particular element emits X rays with a wavelength of 98.0 pm. What element do you think it is?

7.119 (**a**) Write the electron configuration for Li and estimate the effective nuclear charge experienced by the valence electron. (**b**) The energy of an electron in a one-electron atom or ion equals $(-2.18 \times 10^{-18}\,\text{J})\left(\frac{Z^2}{n^2}\right)$, where Z is the nuclear charge and n is the principal quantum number of the electron. Estimate the first ionization energy of Li. (**c**) Compare the result of your calculation with the value reported in Table 7.4 and explain the difference. (**d**) What value of the effective nuclear charge gives the proper value for the ionization energy? Does this agree with your explanation in part (c)?

7.120 One way to measure ionization energies is ultraviolet photoelectron spectroscopy (PES), a technique based on the photoelectric effect. In PES, monochromatic light is directed onto a sample, causing electrons to be emitted. The kinetic energy of the emitted electrons is measured. The difference between the energy of the photons and the kinetic energy of the electrons corresponds to the energy needed to remove the electrons (that is, the ionization energy). Suppose that a PES experiment is performed in which mercury vapor is irradiated with ultraviolet light of wavelength 58.4 nm. (**a**) What is the energy of a photon of this light, in joules? (**b**) Write an equation that shows the process corresponding to the first ionization energy of Hg. (**c**) The kinetic energy of the emitted electrons is measured to be 1.72×10^{-18} J. What is the first ionization energy of Hg, in kJ/mol? (**d**) Using Figure 7.10, determine which of the halogen elements has a first ionization energy closest to that of mercury.

7.121 Mercury in the environment can exist in oxidation states 0, +1, and +2. One major question in environmental chemistry research is how to best measure the oxidation state of mercury in natural systems; this is made more complicated by the fact that mercury can be reduced or oxidized on surfaces differently than it would be if it were free in solution. XPS, X-ray photoelectron spectroscopy, is a technique related to PES (see Exercise 7.120), but instead of using ultraviolet light to eject valence electrons, X rays are used to eject core electrons. The energies of the core electrons are different for different oxidation states of the element. In one set of experiments, researchers examined mercury contamination of minerals in water. They measured the XPS signals that corresponded to electrons ejected from mercury's 4*f* orbitals at 105 eV, from an X-ray source that provided 1253.6 eV of energy ($1\,\text{ev} = 1.602 \times 10^{-19}\text{J}$). The oxygen on the mineral surface gave emitted electron energies at 531 eV, corresponding to the 1*s* orbital of oxygen. Overall the researchers concluded that oxidation states were +2 for Hg and −2 for O. (**a**) Calculate the wavelength of the X rays used in this experiment. (**b**) Compare the energies of the 4*f* electrons in mercury and the 1*s* electrons in oxygen from these data to the first ionization energies of mercury and oxygen from the data in this chapter. (**c**) Write out the ground-state electron configurations for Hg^{2+} and O^{2-}; which electrons are the valence electrons in each case?

7.122 When magnesium metal is burned in air (Figure 3.5), two products are produced. One is magnesium oxide, MgO. The other is the product of the reaction of Mg with molecular nitrogen, magnesium nitride. When water is added to magnesium nitride, it reacts to form magnesium oxide and ammonia gas. (**a**) Based on the charge of the nitride ion (Table 2.5), predict the formula of magnesium nitride. (**b**) Write a balanced equation for the reaction of magnesium nitride with water. What is the driving force for this reaction? (**c**) In an experiment, a piece of magnesium ribbon is burned in air in a crucible. The mass of the mixture of MgO and magnesium nitride after burning is 0.470 g. Water is added to the crucible, further reaction occurs, and the crucible is heated to dryness until the final product is 0.486 g of MgO. What was the mass percentage of magnesium nitride in the mixture obtained after the initial burning? (**d**) Magnesium nitride can also be formed by reaction of the metal with ammonia at high temperature. Write a balanced equation for this reaction. If a 6.3 g Mg ribbon reacts with 2.57 g $NH_3(g)$ and the reaction goes to completion, which component

is the limiting reactant? What mass of $H_2(g)$ is formed in the reaction? (**e**) The standard enthalpy of formation of solid magnesium nitride is −461.08 kJ/mol. Calculate the standard enthalpy change for the reaction between magnesium metal and ammonia gas.

7.123 (**a**) The measured Bi—Br bond length in bismuth tribromide, $BiBr_3$, is 263 pm. Based on this value and the data in Figure 7.8, predict the atomic radius of Bi. (**b**) Bismuth tribromide is soluble in acidic solution. It is formed by treating solid bismuth(III) oxide with aqueous hydrobromic acid. Write a balanced chemical equation for this reaction. (**c**) While bismuth(III) oxide is soluble in acidic solutions, it is insoluble in basic solutions such as NaOH(*aq*). Based on these properties, is bismuth characterized as a metallic, metalloid, or nonmetallic element? (**d**) Treating bismuth with fluorine gas forms BiF_5. Use the electron configuration of Bi to explain the formation of a compound with this formulation. (**e**) While it is possible to form BiF_5 in the manner just described, pentahalides of bismuth are not known for the other halogens. Explain why the pentahalide might form with fluorine but not with the other halogens. How does the behavior of bismuth relate to the fact that xenon reacts with fluorine to form compounds but not with the other halogens?

7.124 Potassium superoxide, KO_2, is often used in oxygen masks (such as those used by firefighters) because KO_2 reacts with CO_2 to release molecular oxygen. Experiments indicate that 2 mol of $KO_2(s)$ react with each mole of $CO_2(g)$. (**a**) The products of the reaction are $K_2CO_3(s)$ and $O_2(g)$. Write a balanced equation for the reaction between $KO_2(s)$ and $CO_2(g)$. (**b**) Indicate the oxidation number for each atom involved in the reaction in part (a). What elements are being oxidized and reduced? (**c**) What mass of $KO_2(s)$ is needed to consume 18.0 g $CO_2(g)$? What mass of $O_2(g)$ is produced during this reaction?

Design an Experiment

In this chapter we have seen that the reaction of potassium metal with oxygen leads to a product that we might not expect, namely, potassium superoxide, $KO_2(s)$. Let's design some experiments to learn more about this unusual product.

(**a**) One of your team members proposes that the capacity to form a superoxide such as KO_2 is related to a low value for the first ionization energy. How would you go about testing this hypothesis for the metals of Group 1? What other periodic property of the alkali metals might be considered as a factor favoring superoxide formation?

(**b**) $KO_2(s)$ is the active ingredient in many breathing masks used by firefighters because it can be used as a source of $O_2(g)$. In principle, $KO_2(s)$ can react with both major components of human breath, $H_2O(g)$ and $CO_2(g)$, to produce $O_2(g)$ and other products (all of which follow the expected patterns of reactivity we have seen). Predict the other products in these reactions and design experiments to determine whether $KO_2(s)$ does actually react with both $H_2O(g)$ and $CO_2(g)$.

(**c**) Propose an experiment to determine whether either of the reactions in part (b) is more important in the operation of a firefighter's breathing mask.

(**d**) The reaction of K(*s*) and $O_2(g)$ leads to a mixture of $KO_2(s)$ and $K_2O(s)$. Use ideas presented in this exercise to design an experiment to determine the percentages of $KO_2(s)$ and $K_2O(s)$ in the product mixture that results from the reaction of K(*s*) with excess $O_2(g)$.

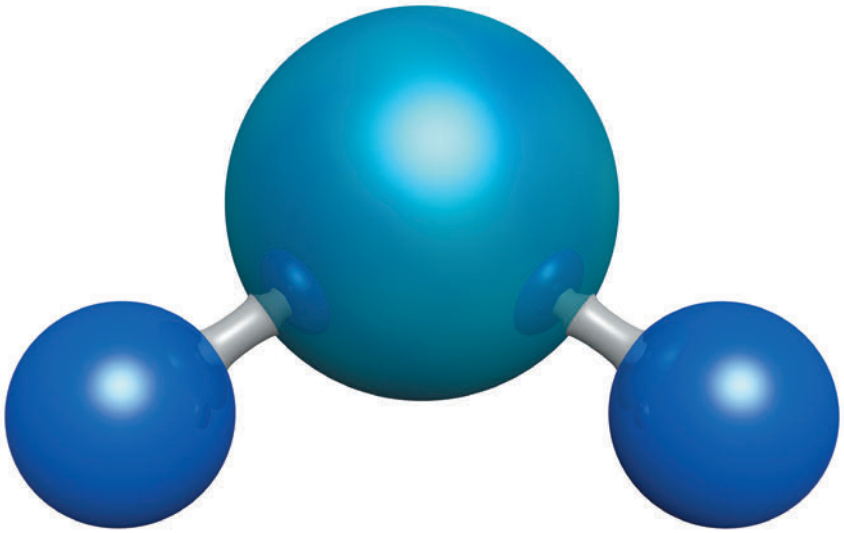
8

BASIC CONCEPTS OF CHEMICAL BONDING

WHAT'S AHEAD

8.1 Lewis Symbols and the Octet Rule
8.2 Ionic Bonding
8.3 Covalent Bonding
8.4 Bond Polarity and Electronegativity
8.5 Drawing Lewis Structures
8.6 Resonance Structures
8.7 Exceptions to the Octet Rule
8.8 Strengths and Lengths of Covalent Bonds

8.1 | Lewis Symbols and the Octet Rule



The electrons involved in chemical bonding are the *valence electrons*, which, for most atoms, are those in the outermost occupied shell. The American chemist G. N. Lewis (1875–1946) suggested a simple way of showing the valence electrons in an atom and tracking them during bond formation, using what are now known as either *Lewis electron-dot symbols* or simply Lewis symbols.

By the end of this section, you should be able to

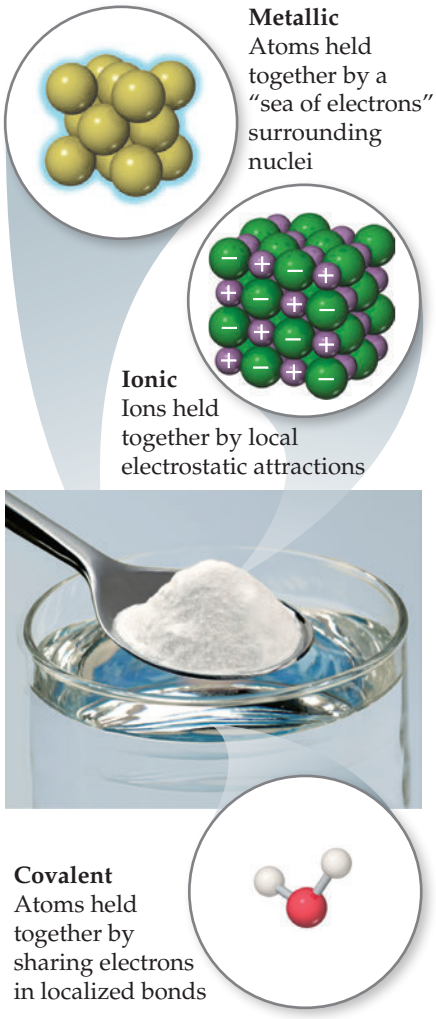
- Draw the Lewis symbol of the elements.

Whenever two atoms or ions are strongly held together, we say there is a **chemical bond** between them. There are three general types of chemical bonds: *ionic*, *covalent*, and *metallic*. These three types of bonds are in the substances illustrated in Figure 8.1: We add table salt to water using a stainless-steel spoon.

Table salt is sodium chloride, NaCl, which consists of sodium ions, Na^+, and chloride ions, Cl^-. The structure is held together by **ionic bonds**, which are formed due to the electrostatic attractions between oppositely charged ions. The water consists mainly of H_2O molecules. The hydrogen and oxygen atoms are bonded to one another through **covalent bonds**, in which molecules are formed by the sharing of electrons between atoms. The spoon consists mainly of iron metal, in which Fe atoms are connected to one another by **metallic bonds**, which are formed by electrons that are relatively free to move from one atom to another. These different substances—NaCl, H_2O, and Fe metal—behave as they do because of the ways in which their constituent atoms are connected to one another. For example, NaCl readily dissolves in water, but Fe metal does not.

Go Figure

If the white powder were sugar, $C_{12}H_{22}O_{11}$, how would we have to change this picture?



▲ **Figure 8.1 Ionic, covalent, and metallic bonds.** The three different substances shown here are held together by different types of chemical bonds.

Lewis Symbols

The **Lewis symbol** for an element consists of the element's chemical symbol plus a dot for each valence electron. Sulfur, for example, has the electron configuration $[Ne]3s^23p^4$ and therefore six valence electrons. Its Lewis symbol is



The dots are placed on the four sides of the symbol—top, bottom, left, and right—and each side can accommodate up to two electrons. All four sides are equivalent, which means that the choice of sides for placement of two electrons rather than one electron is arbitrary. In general, we spread out the dots as much as possible. In the Lewis symbol for S, for instance, we prefer the dot arrangement shown rather than the arrangement having two electrons on three of the sides and none on the fourth.

The electron configurations and Lewis symbols for the main-group elements of Periods 2 and 3 are shown in Figure 8.2. Notice that the number of valence electrons in any representative element is related to the element's group number. For example, the Lewis symbols for oxygen and sulfur, members of Group 16, both show six dots.

The Octet Rule

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table. The noble gases have very stable electron arrangements, as evidenced by their high ionization energies, low affinity for additional electrons, and general lack of chemical reactivity. Because all the noble gases except He have eight valence electrons, many atoms undergoing reactions end up with eight valence electrons. This observation has led to a guideline known as the **octet rule**: *Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons*.

An octet of electrons consists of full *s* and *p* subshells in an atom. In a Lewis symbol, an octet is shown as four pairs of valence electrons arranged around the element symbol, as

Group	1	2	13	14	15	16	17	18
Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Electron Configuration	$[He]2s^1$	$[He]2s^2$	$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Lewis Symbol	Li·	·Be·	·B·	·C·	·N:	:O:	:F:	:Ne:
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
	$[Ne]3s^1$	$[Ne]3s^2$	$[Ne]3s^23p^1$	$[Ne]3s^23p^2$	$[Ne]3s^23p^3$	$[Ne]3s^23p^4$	$[Ne]3s^23p^5$	$[Ne]3s^23p^6$
	Na·	·Mg·	·Al·	·Si·	·P:	:S:	:Cl:	:Ar:

▲ **Figure 8.2 Lewis symbols.**

in the Lewis symbols for Ne and Ar in Figure 8.2. There are exceptions to the octet rule, as we will see in Section 8.7, but it provides a useful framework for introducing many important concepts of bonding. The octet rule mostly applies to atoms that have *s* and *p* valence electrons; compounds of the transition metals, having valence *d* electrons, will be examined in Chapter 23.

Self-Assessment Exercise

8.1 Which is the correct Lewis symbol of As?

(a) Ä̈s

(b) Ä̈s·

(c) ·Ä̈s·

Exercises

8.2 (**a**) True or false: An element's number of valence electrons is the same as its atomic number. (**b**) How many valence electrons does a nitrogen atom possess? (**c**) An atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$. How many valence electrons does the atom have?

8.3 Consider the element silicon, Si. (**a**) Write its electron configuration. (**b**) How many valence electrons does a silicon atom have? (**c**) Which subshells hold the valence electrons?

8.4 Write the Lewis symbol for atoms of each of the following elements: (**a**) Te, (**b**) Si, **(c)** Kr, (**d**) P.

Answers to Self-Assessment Exercises

8.1 (c)

8.2 | Ionic Bonding



These gypsum crystals, found deep in a cave in Ukraine, are composed of $CaSO_4 \cdot 2H_2O$. The ionic bonding between calcium and sulfate ions at the atomic scale leads to the characteristic crystal shape at the human scale.

By the end of this section, you should be able to

- Predict the occurrence of ionic bonding
- Understand the factors affecting the lattice energy of an ionic solid

Ionic substances generally result from the interaction of metals on the left side of the periodic table with nonmetals on the right side (excluding the noble gases, Group 18). For example, when sodium metal, Na(s), is brought into contact with chlorine gas, $Cl_2(g)$, a violent reaction ensues (**Figure 8.3**). The product of this very exothermic reaction is sodium chloride, NaCl(s):

$$Na(s) + \tfrac{1}{2}\,Cl_2(g) \longrightarrow NaCl(s) \qquad \Delta H_f^\circ = -410.9\ \text{kJ} \qquad [8.1]$$

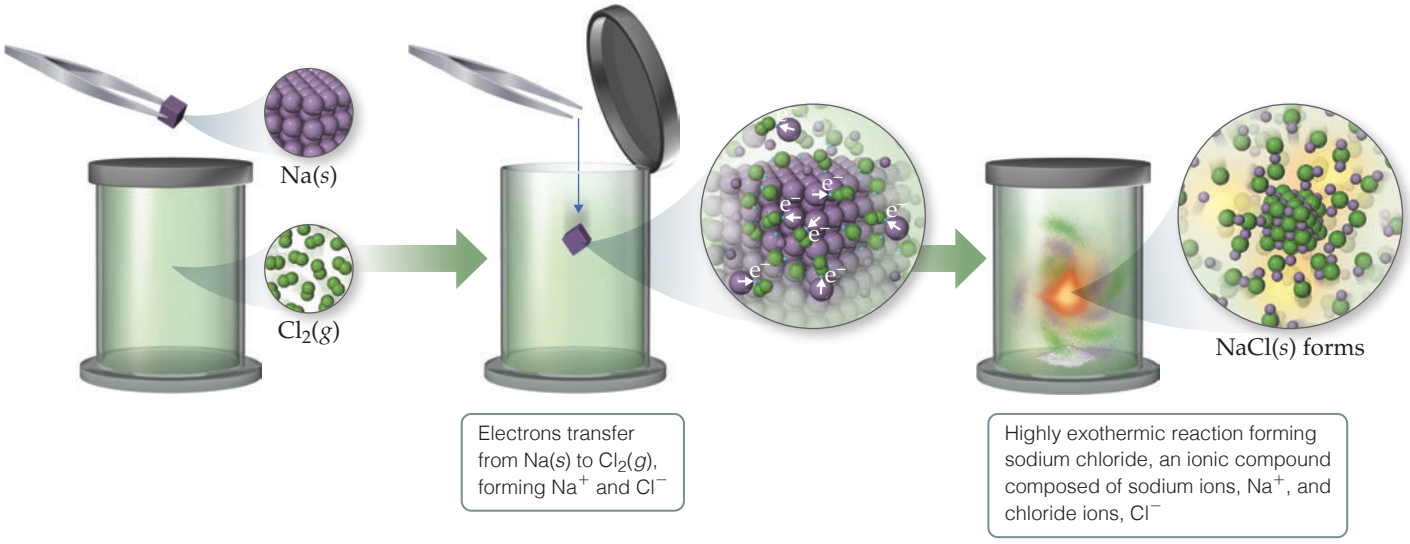
Sodium chloride is composed of Na^+ and Cl^- ions arranged in a three-dimensional array (**Figure 8.4**).

The formation of Na^+ from Na and Cl^- from Cl_2 indicates that an electron has been lost by a sodium atom and gained by a chlorine atom—we say there has been an *electron transfer* from the Na atom to the Cl atom. Two of the atomic properties discussed in Chapter 7 give us an indication of how readily electron transfer occurs: ionization energy, which indicates how easily an electron can be removed from an atom; and electron affinity, which measures how much an atom wants to gain an electron. Electron transfer to form oppositely charged ions occurs when one atom readily gives up an electron (low ionization energy) and another atom readily gains an electron (high electron affinity). Thus, NaCl is a typical ionic compound because it consists of a metal of low ionization energy and a nonmetal of high electron affinity. Using Lewis electron-dot symbols (and showing a chlorine atom rather than the Cl_2 molecule), we can represent this reaction as

$$Na\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}\!: \longrightarrow Na^+ + [:\ddot{\underset{\cdot\cdot}{Cl}}\!:]^- \qquad [8.2]$$

The blue arrow indicates the transfer of an electron from the Na atom to the Cl atom. Each ion has an octet of electrons, the Na^+ octet being the $2s^2 2p^6$ electrons that lie below the single 3s valence electron of the Na atom. We have put a bracket around the chloride ion to emphasize that all eight electrons are located on it.

Go Figure Do you expect a similar reaction between potassium metal and elemental bromine?



▲ **Figure 8.3** **Reaction of sodium metal with chlorine gas to form the ionic compound sodium chloride.**

Ionic substances possess several characteristic properties. They are usually brittle substances with high melting points. They are usually crystalline. Furthermore, ionic crystals often can be cleaved; that is, they break apart along smooth, flat surfaces. These characteristics result from electrostatic forces that maintain the ions in a rigid, well-defined, three-dimensional arrangement such as that shown in Figure 8.4.

Energetics of Ionic Bond Formation

The formation of sodium chloride from sodium and chlorine is *very* exothermic, as indicated by the large negative enthalpy of formation value given in Equation 8.1, $\Delta H_f^\circ = -410.9$ kJ. Appendix C shows that the heat of formation of other ionic substances is also quite negative. What factors make the formation of ionic compounds so exothermic?

In Equation 8.2, we represented the formation of NaCl as the transfer of an electron from Na to Cl. Recall from Section 7.4 that the loss of electrons from an atom is always an endothermic process. Removing an electron from Na(g) to form $Na^+(g)$ for instance, requires 496 kJ/mol. Recall from Section 7.5 that when a nonmetal gains an electron, the process is generally exothermic, as seen from the negative electron affinities of the elements. Adding an electron to Cl(g), for example, releases 349 kJ/mol. From the magnitudes of these energies, we can see that the transfer of an electron from an Na atom to a Cl atom would not be exothermic—the overall process would be an endothermic process that requires 496 − 349 = 147 kJ/mol. This endothermic process corresponds to the formation of sodium and chloride ions that are infinitely far apart—in other words, the positive energy change assumes that the ions do not interact with each other, which is quite different from the situation in ionic solids.

The principal reason ionic compounds are stable is the attraction between ions of opposite charge. This attraction draws the ions together, releasing energy and causing many ions to form a solid array, or lattice, such as that shown in Figure 8.4. A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid is given by the **lattice energy**, which is *the energy required to completely separate one mole of a solid ionic compound into its gaseous ions*.

To envision this process for NaCl, imagine that the structure in Figure 8.4 expands from within, so that the distances between the ions increase until the ions are very far apart. This process requires 788 kJ/mol, which is the value of the lattice energy:

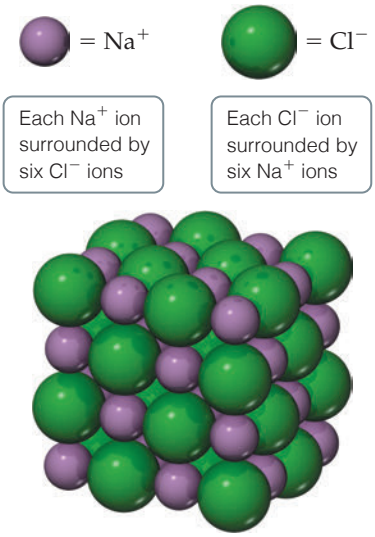
$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{lattice} = +788 \text{ kJ/mol} \qquad [8.3]$$

Notice that this process is highly endothermic. The reverse process—the coming together of $Na^+(g)$ and $Cl^-(g)$ to form NaCl(s)—is therefore highly exothermic ($\Delta H = -788$ kJ/mol).

Table 8.1 lists the lattice energies for a number of ionic compounds. The large positive values indicate that the ions are strongly attracted to one another in ionic solids.

Go Figure

If no color key were provided, how would you know which color ball represented Na^+ and which represented Cl^-?



▲ **Figure 8.4** **The crystal structure of sodium chloride.**

TABLE 8.1 Lattice Energies for Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2526
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

The energy released by the attraction between ions of unlike charge more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process. The strong attractions also cause most ionic materials to be hard and brittle with high melting points—for example, NaCl melts at 801 °C.

The magnitude of the lattice energy of an ionic solid depends on the charges of the ions, their sizes, and their arrangement in the solid. We saw in Section 5.1 that the electrostatic potential energy of two interacting charged particles is given by

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \qquad [8.4]$$

In this equation Q_1 and Q_2 are the charges on the particles in Coulombs, with their signs; d is the distance between their centers in meters; and κ is a constant, 8.99×10^9 J m/C^2. Equation 8.4 indicates that the attractive interaction between two oppositely charged ions increases as the magnitudes of their charges increase and as the distance between their centers decreases. Thus, *for a given arrangement of ions, the lattice energy increases as the charges on the ions increase and as their radii decrease*. The variation in the magnitude of lattice energies depends more on ionic charge than on ionic radius because ionic radii vary over only a limited range compared to charges.

Sample Exercise 8.1

Magnitudes of Lattice Energies

Without consulting Table 8.1, arrange the ionic compounds NaF, CsI, and CaO in order of increasing lattice energy.

SOLUTION

Analyze From the formulas for three ionic compounds, we must determine their relative lattice energies.

Plan We need to determine the charges and relative sizes of the ions in the compounds. We then use Equation 8.4 qualitatively to determine the relative energies, knowing that (**a**) the larger the ionic charges, the greater the energy and (**b**) the farther apart the ions are, the lower the energy.

Solve NaF consists of Na^+ and F^- ions, CsI of Cs^+ and I^- ions, and CaO of Ca^{2+} and O^{2-} ions. Because the product Q_1Q_2 appears in the numerator of Equation 8.4, the lattice energy increases dramatically when the charges increase. Thus, we expect the lattice energy of CaO, which has 2+ and 2− ions, to be the greatest of the three.

The ionic charges are the same in NaF and CsI. The difference in their lattice energies thus depends on the difference in the distance between ions in the lattice. Because ionic size increases as we go down a group in the periodic table, we know that Cs^+ is larger than Na^+ and I^- is larger than F^-. Therefore, the distance between Na^+ and F^- ions in NaF is less than the distance between the Cs^+ and I^- ions in CsI. As a result, the lattice energy of NaF should be greater than that of CsI. In order of increasing energy, therefore, we have CsI < NaF < CaO.

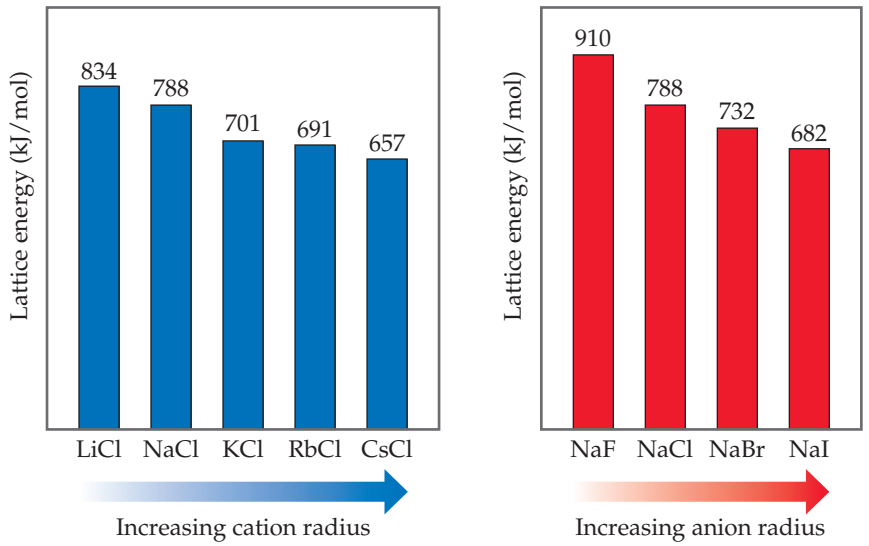
Check Table 8.1 confirms our predicted order is correct.

Practice Exercise

Without looking at Table 8.1, predict which one of the following orderings of lattice energy is correct for these ionic compounds.
(**a**) NaCl > MgO > CsI > ScN (**b**) ScN > MgO > NaCl > CsI
(**c**) NaCl > CsI > ScN > CaO (**d**) MgO > NaCl > ScN > CsI
(**e**) ScN > CsI > NaCl > MgO

Because lattice energy decreases as distance between ions increases, lattice energies follow trends that parallel those in ionic radius shown in Figure 7.8. In particular, because ionic radius increases as we go down a group of the periodic table, we find that, for a given type of ionic compound, lattice energy decreases as we go down a group. **Figure 8.5** illustrates this trend for the alkali chlorides MCl (M = Li, Na, K, Rb, Cs) and the sodium halides NaX (X = F, Cl, Br, I).

Go Figure Using this figure, find the most likely range of values for the lattice energy of KF.



▲ **Figure 8.5** **Periodic trends in lattice energy as a function of cation or anion radius.**

Electron Configurations of Ions of the *s*- and *p*-Block Elements

The energetics of ionic bond formation helps explain why many ions tend to have noble-gas electron configurations. For example, sodium readily loses one electron to form Na^+, which has the same electron configuration as Ne:

$$\text{Na} \quad 1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$$
$$\text{Na}^+ \quad 1s^2 2s^2 2p^6 = [\text{Ne}]$$

Even though lattice energy increases with increasing ionic charge, we never find ionic compounds that contain Na^{2+} ions. The second electron removed would have to come from an inner shell of the sodium atom, and removing electrons from an inner shell requires a very large amount of energy. The increase in lattice energy is not enough to compensate for the energy needed to remove an inner-shell electron. Thus, sodium and the other Group 1 metals are found in ionic substances only as 1+ ions.

Similarly, adding electrons to nonmetals is either exothermic or only slightly endothermic as long as the electrons are added to the valence shell. Thus, a Cl atom easily adds an electron to form Cl^-, which has the same electron configuration as Ar:

$$\text{Cl} \quad 1s^2 2s^2 2p^6 3s^2 3p^5 = [\text{Ne}]3s^2 3p^5$$
$$\text{Cl}^- \quad 1s^2 2s^2 2p^6 3s^2 3p^6 = [\text{Ne}]3s^2 3p^6 = [\text{Ar}]$$

To form a Cl^{2-} ion, the second electron would have to be added to the next higher shell of the Cl atom, an addition that is energetically very unfavorable. Therefore, we never observe Cl^{2-} ions in ionic compounds. We thus expect ionic compounds of the representative metals from Groups 1, 2, and 13 to contain 1+, 2+, and 3+ cations, respectively, and we usually expect ionic compounds of the representative nonmetals of Groups 15, 16, and 17 to contain 3−, 2−, and 1− anions, respectively.

A CLOSER LOOK Calculation of Lattice Energies: The Born–Haber Cycle

Lattice energies cannot be determined directly by experiment. They can, however, be calculated by envisioning the formation of an ionic compound as occurring in a series of well-defined steps. We can then use Hess's law to combine the steps in a way that gives the lattice energy for the compound. By so doing, we construct a **Born–Haber cycle**, a thermochemical cycle named after the German scientists Max Born (1882–1970) and Fritz Haber (1868–1934), who introduced it to analyze the factors contributing to the stability of ionic compounds.

Let's use NaCl as an example. In Equation 8.3, which defines lattice energy, NaCl(*s*) is the reactant, and the gas-phase ions $Na^+(g)$ and $Cl^-(g)$ are the products. This equation is our target as we apply Hess's Law.

In seeking a set of other equations that can be added up to give our target equation, we can use the heat of formation for NaCl:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s) \qquad \Delta H_f^\circ[NaCl(s)] = -411\ kJ \quad [8.5]$$

Of course, we will have to turn this equation around so that we have NaCl(*s*) as the reactant as we do in the equation for the lattice energy. We can use two other equations to arrive at our target, as shown here:

1. $NaCl(s) \longrightarrow Na(s) + \tfrac{1}{2}Cl_2(g)$ $\quad \Delta H_1 = -\Delta H_f^\circ[NaCl(s)] = +411\ kJ$
2. $Na(s) \longrightarrow Na^+(g) + e^-$ $\quad \Delta H_2 = ??$
3. $e^- + \tfrac{1}{2}Cl_2(g) \longrightarrow Cl^-(g)$ $\quad \Delta H_3 = ???$

4. $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ $\quad \Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{lattice}$

Step 2 involves the formation of sodium ion from solid sodium, which is just the heat of formation for sodium gas and the first ionization energy for sodium (Appendix C and Figure 7.10 list numbers for these processes):

$$Na(s) \longrightarrow Na(g) \qquad \Delta H = \Delta H_f^\circ[Na(g)] = 108\ kJ \quad [8.6]$$

$$Na(g) \longrightarrow Na^+(g) + e^- \qquad \Delta H = I_1(Na) = 496\ kJ \quad [8.7]$$

The sum of these two processes gives us the required energy for Step 2, which is 604 kJ.

Similarly, for Step 3, we have to create chlorine atoms, and then anions, from the Cl_2 molecule, in two steps. The enthalpy changes for these two steps are the sum of the enthalpy of formation of Cl(*g*) and the electron affinity of chlorine, *EA*(Cl):

$$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g) \qquad \Delta H = \Delta H_f^\circ[Cl(g)] = 122\ kJ \quad [8.8]$$

$$e^- + Cl(g) \longrightarrow Cl^-(g) \qquad \Delta H = EA(Cl) = -349\ kJ \quad [8.9]$$

The sum of these two processes gives us the required energy for Step 3, which is −227 kJ.

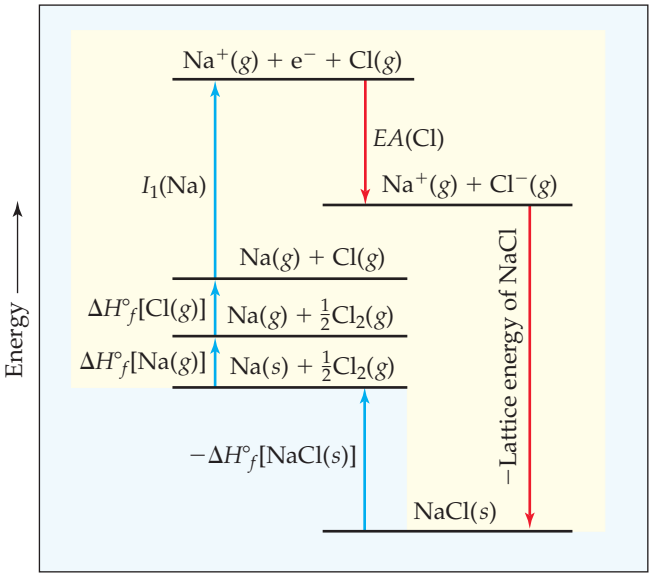
Finally, when we put it all together, we have:

1. $NaCl(s) \longrightarrow Na(s) + \tfrac{1}{2}Cl_2(g)$ $\quad \Delta H_1 = -\Delta H_f^\circ[NaCl(s)] = +411\ kJ$
2. $Na(s) \longrightarrow Na^+(g) + e^-$ $\quad \Delta H_2 = 604\ kJ$
3. $e^- + \tfrac{1}{2}Cl_2(g) \longrightarrow Cl^-(g)$ $\quad \Delta H_3 = -227\ kJ$

4. $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ $\quad \Delta H_4 = 788\ kJ = \Delta H_{lattice}$

This process is described as a "cycle" because it corresponds to the scheme in **Figure 8.6**, which shows how all the quantities we have just calculated are related. The sum of all the blue "up" arrow energies has to be equal to the sum of all the red "down" arrow energies in this cycle. Born and Haber recognized that if we know the value of every quantity in the cycle except the lattice energy, we can calculate it from this cycle.

Related Exercises: 8.60–8.62, 8.90



▲ **Figure 8.6 Born–Haber cycle for formation of NaCl.** This Hess's law representation shows the energetic relationships in the formation of the ionic solid from its elements.

Transition Metal Ions

Because ionization energies increase rapidly for each successive electron removed, the lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only three electrons from atoms. Thus, we find cations with charges of 1+, 2+, or 3+ in ionic compounds. Most transition metals, however, have more than three electrons beyond a noble-gas core. Silver, for example, has a $[Kr]4d^{10}5s^1$ electron configuration. Metals of Group 11 (Cu, Ag, Au) often occur as 1+ ions (as in CuBr and AgCl). In forming Ag^+, the 5*s* electron is lost, leaving a completely filled 4*d* subshell. As in this example, transition metals generally do not form ions that have a noble-gas configuration. The octet rule, although useful, is clearly limited in scope.

Sample Exercise 8.2

Charges on Ions

Predict the ion generally formed by (**a**) Sr, (**b**) S, (**c**) Al.

SOLUTION

Analyze We must decide how many electrons are most likely to be gained or lost by atoms of Sr, S, and Al.

Plan In each case, we can use the element's position in the periodic table to predict whether the element forms a cation or an anion. We can then use its electron configuration to determine the most likely ion formed.

Solve

(**a**) Strontium is a metal in Group 2 and therefore forms a cation. Its electron configuration is $[Kr]5s^2$, and so we expect that the two valence electrons will be lost to give an Sr^{2+} ion.

(**b**) Sulfur is a nonmetal in Group 16 and will thus tend to be found as an anion. Its electron configuration ($[Ne]3s^23p^4$) is two electrons short of a noble-gas configuration. Thus, we expect that sulfur will form S^{2-} ions.

(**c**) Aluminum is a metal in Group 13. We therefore expect it to form Al^{3+} ions.

Check The ionic charges we predict here are confirmed in Tables 2.4 and 2.5.

Practice Exercise

Predict the charges on the ions formed when magnesium reacts with nitrogen.

Recall from Section 7.4 that when a positive ion forms from an atom, electrons are always lost first from the subshell having the largest value of n. Thus, *in forming ions, transition metals lose the valence-shell* s *electrons first, then as many* d *electrons as required to reach the charge of the ion*. For instance, in forming Fe^{2+} from Fe, which has the electron configuration $[Ar]3d^64s^2$, the two 4*s* electrons are lost, leading to an $[Ar]3d^6$ configuration. Removal of an additional electron gives Fe^{3+}, whose electron configuration is $[Ar]3d^5$.

Self-Assessment Exercises

8.5 Which combination of elements gives an ionic compound?

(a) H and Cl

(b) Ca and Br

(c) S and F

8.6 Which combination of ions gives the solid with the highest lattice energy?

(a) Al^{3+} and O^{2-}

(b) Ba^{2+} and O^{2-}

(c) K^+ and O^{2-}

Exercises

8.7 (**a**) Using Lewis symbols, make a sketch of the reaction between potassium and bromine atoms to give the ionic substance KBr. (**b**) How many electrons are transferred? (**c**) Which atom loses electrons in the reaction?

8.8 Predict the chemical formula of the ionic compound formed between the following pairs of elements: (**a**) Al and Cl, (**b**) Mg and O, (**c**) Zn and Cl, (**d**) Li and O.

8.9 Write the electron configuration for each of the following ions, and determine which ones possess noble-gas configurations: (**a**) Be^{2+}, (**b**) Mn^{2+}, (**c**) Cd^{2+}, (**d**) Fe^{3+}, (**e**) Tl^+, (**f**) At^-.

8.10 (**a**) Is lattice energy usually endothermic or exothermic? (**b**) Write the chemical equation that represents the process of lattice energy for the case of NaCl. (**c**) Would you expect salts like NaCl, which have singly charged ions, to have larger or smaller lattice energies compared to salts like CaO which are composed of doubly-charged ions?

8.11 The substances NaF and CaO are isoelectronic (have the same number of valence electrons). (**a**) What are the charges on each of the cations in each compound? (**b**) What are the charges of each of the anions in each compound? (**c**) Without looking up lattice energies, which compound is predicted to have the larger lattice energy? (**d**) Using the lattice energies in Table 8.1, predict the lattice energy of ScN.

8.12 Consider the ionic compounds KF, NaCl, NaBr, and LiCl. (**a**) Use ionic radii (Figure 7.8) to estimate the cation–anion distance for each compound. (**b**) Based on your answer to part (a), arrange these four compounds in order of decreasing lattice energy. (**c**) Check your predictions in part (b) with the experimental values of lattice energy from Table 8.1. Are the predictions from ionic radii correct?

8.13 Energy is required to remove two electrons from Ca to form Ca^{2+}, and energy is required to add two electrons to O to form O^{2-}. Yet CaO is stable relative to the free elements. Which statement is the best explanation? (**a**) The lattice energy of CaO is large enough to overcome these processes. (**b**) CaO is a covalent compound, and these processes are irrelevant. (**c**) CaO has a higher molar mass than either Ca or O. (**d**) The enthalpy of formation of CaO is small. (**e**) CaO is stable to atmospheric conditions.

Answers to Self-Assessment Exercises

8.5 (b) 8.6 (a)

8.3 | Covalent Bonding



This 30 m high sculpture called Molecular Man, created by American sculptor Jonathan Borofsky, stands in the Spree River at the intersection of three districts in the city of Berlin.

The vast majority of the substances with which we come into daily contact—such as water, the air we breathe, the food we eat, and indeed our own composition—are not ionic but molecular materials. In this section, we examine the bonding in molecules. By the end of this section, you should be able to

- Use electron configurations and the octet rule to draw Lewis structures for molecules.

For the very large class of substances that do not behave like ionic substances, we need a different model to describe the bonding between atoms. G. N. Lewis reasoned that atoms might acquire a noble-gas electron configuration by sharing electrons with other atoms. A chemical bond formed by sharing a pair of electrons is a *covalent bond*.

The hydrogen molecule, H_2, provides the simplest example of a covalent bond. When two hydrogen atoms are close to each other, the two positively charged nuclei repel each other, the two negatively charged electrons repel each other, and

the nuclei and electrons attract each other, as shown in **Figure 8.7(a)**. Because the molecule is stable, we know that the attractive forces must overcome the repulsive ones. Let's take a closer look at the attractive forces that hold this molecule together.

By using quantum mechanical methods analogous to those used for atoms in Section 6.5, we can calculate the distribution of electron density in molecules. Such a calculation for H_2 shows that the attractions between the nuclei and the electrons cause electron density to concentrate between the nuclei, as shown in Figure 8.7(b). As a result, the overall electrostatic interactions are attractive. Thus, the atoms in H_2 are held together principally because the two positive nuclei are attracted to the concentration of negative charge between them. In essence, the shared pair of electrons in any covalent bond acts as a kind of "glue" to bind atoms together.

Lewis Structures

The formation of covalent bonds can be represented with Lewis symbols. The formation of the H_2 molecule from two H atoms, for example, can be represented as

$$H\cdot + \cdot H \longrightarrow H{:}H$$

In forming the covalent bond, each hydrogen atom acquires a second electron, achieving the stable, two-electron, noble-gas electron configuration of helium.

Formation of a covalent bond between two Cl atoms to give a Cl_2 molecule can be represented in a similar way:

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}{:}\ddot{\underset{\cdot\cdot}{Cl}}:$$

By sharing the bonding electron pair, each chlorine atom has eight electrons (an octet) in its valence shell, thus achieving the noble-gas electron configuration of argon.

The structures shown here for H_2 and Cl_2 are **Lewis structures**, or *Lewis dot structures*. While these structures show circles to indicate electron sharing, the more common convention is to show each shared electron pair or **bonding pair**, as a line and any unshared electron pairs (also called **lone pairs** or **nonbonding pairs**) as dots. Written this way, the Lewis structures for H_2 and Cl_2 are

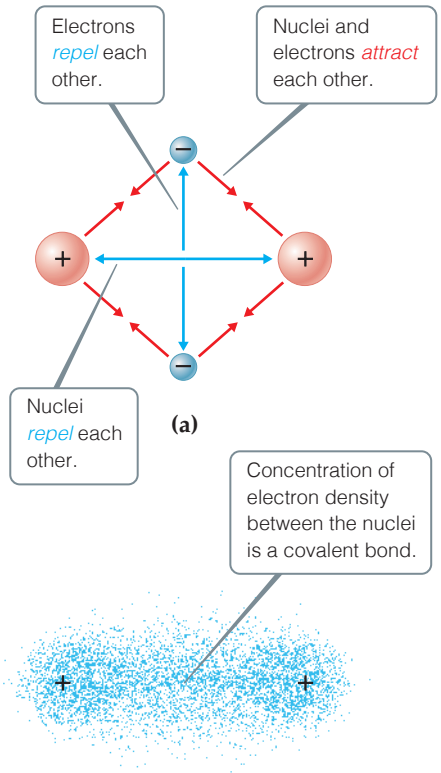
$$H{-}H \qquad :\ddot{\underset{\cdot\cdot}{Cl}}{-}\ddot{\underset{\cdot\cdot}{Cl}}:$$

For nonmetals, the number of valence electrons in a neutral atom is the same as the group number minus 10. Therefore, one might predict that Group 17 elements, such as F, would form one covalent bond to achieve an octet; Group 16 elements, such as O, would form two covalent bonds; Group 15 elements, such as N, would form three; and Group 14 elements, such as C, would form four. These predictions are borne out in many compounds, as in, for example, the compounds with hydrogen of the nonmetals of the second row of the periodic table:

$$H{-}\ddot{\underset{\cdot\cdot}{F}}: \qquad H{-}\ddot{\underset{\cdot\cdot}{O}}{:}\ \ (H) \qquad H{-}\ddot{\underset{\cdot\cdot}{N}}{-}H\ \ (H) \qquad H{-}\overset{H}{\overset{|}{C}}{-}H\ \ (H)$$

Go Figure

What would happen to the concentration of electron density between the nuclei in (b) if you pulled the nuclei further apart?



▲ **Figure 8.7 The covalent bond in H_2.** (**a**) The attractions and repulsions among electrons and nuclei in the hydrogen molecule. (**b**) Electron distribution in the H_2 molecule.

Sample Exercise 8.3

Lewis Structure of a Compound

Given the Lewis symbols for nitrogen and fluorine in Figure 8.2, predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine and draw its Lewis structure.

SOLUTION

Analyze The Lewis symbols for nitrogen and fluorine reveal that nitrogen has five valence electrons and fluorine has seven.

Plan We need to find a combination of the two elements that results in an octet of electrons around each atom. Nitrogen requires three additional electrons to complete its octet, and fluorine requires one. Sharing a pair of electrons between one N atom and one F atom will result in an octet of electrons for fluorine but not for nitrogen. We therefore need to figure out a way to get two more electrons for the N atom.

Solve Nitrogen must share a pair of electrons with three fluorine atoms to complete its octet. Thus, the binary compound these two elements form must be NF_3:



Check The Lewis structure in the center shows that each atom is surrounded by an octet of electrons. Once you are accustomed to thinking of each line in a Lewis structure as representing *two* electrons, you can just as easily use the structure on the right to check for octets.

Practice Exercise

Which of these molecules has the same number of shared electron pairs as unshared electron pairs?
(**a**) HCl (**b**) H_2S (**c**) PF_3 (**d**) CCl_2F_2 (**e**) Br_2

Multiple Bonds

A shared electron pair constitutes a single covalent bond, generally referred to simply as a **single bond**. In many molecules, atoms attain complete octets by sharing more than one pair of electrons. When two electron pairs are shared by two atoms, two lines are drawn in the Lewis structure, representing a **double bond**. In carbon dioxide, for example, bonding occurs between carbon, with four valence electrons, and oxygen, with six:



As the diagram shows, each oxygen atom acquires an octet by sharing two electron pairs with carbon. In the case of CO_2, carbon acquires an octet by sharing two electron pairs with each of the two oxygen atoms; each double bond involves four electrons.

A **triple bond** corresponds to the sharing of three pairs of electrons, such as in the N_2 molecule:



Because each nitrogen atom has five valence electrons, three electron pairs must be shared to achieve the octet configuration.

The properties of N_2 are in complete accord with its Lewis structure. Nitrogen is a diatomic gas with exceptionally low reactivity that results from the very stable nitrogen–nitrogen bond. The nitrogen atoms are separated by only 110 pm. The short separation distance between the two N atoms is a result of the triple bond between the atoms. From studies of the structures of many different substances in which nitrogen atoms share one or two electron pairs, we have learned that the average distance between bonded nitrogen atoms varies with the number of shared electron pairs:

N—N	N=N	N≡N
147 pm	124 pm	110 pm

As a general rule, the length of the bond between two atoms decreases as the number of shared electron pairs increases. We will explore this point in greater detail in Section 8.8.

Self-Assessment Exercise

8.14 The atoms of the molecule acetylene are bonded in the order: HCCH. Which represents the correct Lewis structure of acetylene?

(a) H—Ċ—Ċ—H

(b) H—C̈—C̈—H

(c) H—C≡C—H

Exercises

8.15 Using Lewis symbols and Lewis structures, make a sketch of the formation of NCl_3 from N and Cl atoms, showing valence-shell electrons. (**a**) How many valence electrons does N have initially? (**b**) How many bonds Cl has to make in order to achieve an octet? (**c**) How many valence electrons surround the N in the NCl_3 molecule? (**d**) How many valence electrons surround each Cl in the NCl_3 molecule? (**e**) How many lone pairs of electrons are in the NCl_3 molecule?

8.16 (**a**) Construct a Lewis structure for O_2 in which each atom achieves an octet of electrons. (**b**) How many bonding electrons are in the structure? (**c**) Would you expect the O—O bond in O_2 to be shorter or longer than the O—O bond in compounds that contain an O—O single bond? Explain.

8.17 Draw the Lewis structure of the following molecules: H_2S, HF, NCl_3, H_3CCH_3, and H_2CCH_2.

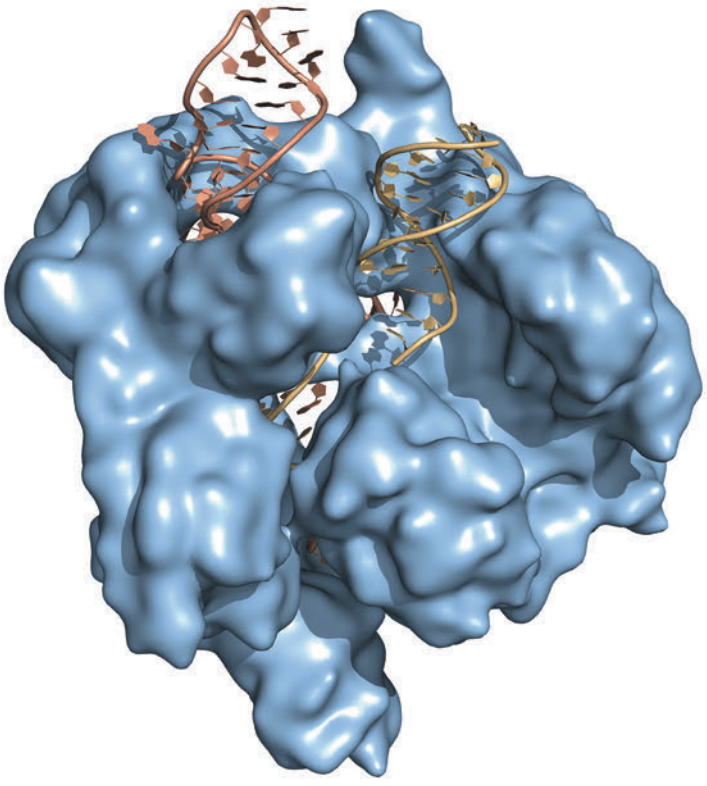
8.18 Draw the Lewis structure of the following molecules and polyatomic ions: HCN, –CN, H_2O, and –OH.

8.19 Draw the Lewis structure of the following molecule and polyatomic ion: NH_3 and NH_4^+

Answers to Self-Assessment Exercises

8.14 (c)

8.4 Bond Polarity and Electronegativity



Building a 'ball and stick' model of a molecule has long been a useful way to help visualize the size and shape of that molecule. While this can aid bridging the divide between a microscopic (molecular) scale and a macroscopic (human) experience, there are limitations. Such models usually do not display the dynamic nature of a molecule or the distribution of the electron cloud over the surface of the bonded atoms. With the advent of powerful desktop computers coupled with color displays, the area of *molecular graphics* has been born.

In this section, we use it to visualize the electron distribution in a few diatomic molecules. It can also be employed to portray the bumps and cavities on the surface of an enzyme and help pharmaceutical companies predict the likelihood of an interaction with a particular substrate.

By the end of this section, you should be able to

- Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds.

When two identical atoms bond, as in Cl_2 or H_2, the electron pairs must be shared equally. When two atoms from opposite sides of the periodic table bond, such as NaCl, there is relatively little sharing of electrons, which means that NaCl is best described as an ionic compound composed of Na^+ and Cl^- ions. The 3*s* electron of the Na atom is, in effect, transferred completely to chlorine. The bonds that are found in most substances fall somewhere between these extremes.

Bond polarity is a measure of how equally or unequally the electrons in any covalent bond are shared. A **nonpolar covalent bond** is one in which the electrons are shared equally, as in Cl_2 and N_2. In a **polar covalent bond**, one of the atoms exerts a greater attraction for the bonding electrons than the other. If the difference in relative ability to attract electrons is large enough, an ionic bond is formed.

Electronegativity

We use a quantity called electronegativity to estimate whether a given bond is nonpolar covalent, polar covalent, or ionic.

Electronegativity is defined as the ability of an atom *in a molecule* to attract electrons to itself.

The greater an atom's electronegativity, the greater its ability to attract electrons to itself. The electronegativity of an atom in a molecule is related to the atom's ionization energy and electron affinity, which are properties of isolated atoms. An atom with a very negative electron affinity and a high ionization energy both attracts electrons from other atoms and resists having its electrons attracted away; therefore, it is highly electronegative.

Electronegativity values can be based on a variety of properties, not just ionization energy and electron affinity. The American chemist Linus Pauling (1901–1994) developed the first and most widely used electronegativity scale, which is based on thermochemical data. As **Figure 8.8** shows, there is generally an increase in electronegativity from left to right across a period—that is, from the most metallic to the most nonmetallic elements. With some exceptions (especially in the transition metals), electronegativity decreases with increasing atomic number in a group. This is what we expect because we know that ionization energies decrease with increasing atomic number in a group and electron affinities do not change very much.

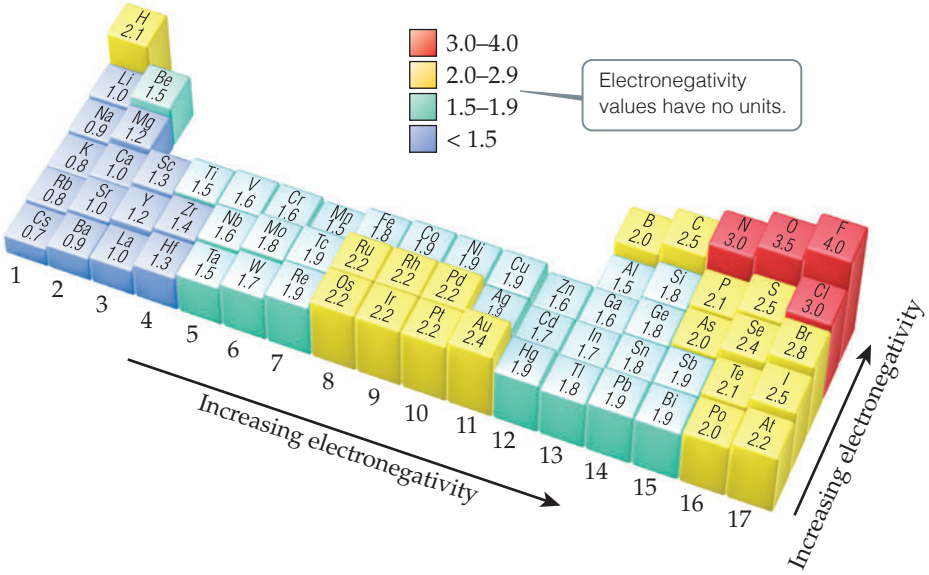
You do not need to memorize electronegativity values. Instead, you should know the periodic trends so that you can predict which of two elements is more electronegative.

Electronegativity and Bond Polarity

We can use the difference in electronegativity between two atoms to gauge the polarity of the bond the atoms form. Consider these three fluorine-containing compounds:

	F_2	HF	LiF
Electronegativity difference	$4.0 - 4.0 = 0$	$4.0 - 2.1 = 1.9$	$4.0 - 1.0 = 3.0$
Type of bond	Nonpolar covalent	Polar covalent	Ionic

Go Figure For the Group 16 elements, what is the trend in electronegativity with increasing atomic number?



▲ **Figure 8.8** **Electronegativity values based on Pauling's thermochemical data.**

In F_2, the electrons are shared equally between the fluorine atoms and, thus, the covalent bond is *nonpolar*. A nonpolar covalent bond results when the electronegativities of the bonded atoms are equal.

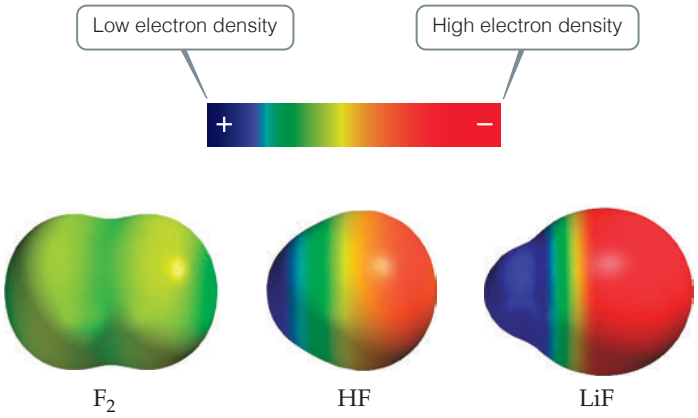
In HF the fluorine atom has a greater electronegativity than the hydrogen atom, with the result that the electrons are shared unequally—the bond is *polar*. In general, a polar covalent bond results when the atoms differ in electronegativity. In HF the more electronegative fluorine atom attracts electron density away from the less electronegative hydrogen atom, leaving a partial positive charge on the hydrogen atom and a partial negative charge on the fluorine atom. We can represent this charge distribution as

$$\begin{matrix} \delta+ & \delta- \\ \mathrm{H}\text{—}\mathrm{F} & \end{matrix}$$

The $\delta+$ and $\delta-$ (read "delta plus" and "delta minus") symbolize the partial positive and negative charges, respectively. In a polar bond, these numbers are less than the full charges of the ions.

In LiF the electronegativity difference is very large, meaning that the electron density is shifted far toward F. The resulting bond is therefore most accurately described as *ionic*. Thus, if we considered the bond in LiF to be fully ionic, we could say $\delta+$ for Li is 1+ and $\delta-$ for F is 1−. If two atoms differ in electronegativity by more than 2.0, many chemists would consider their bond to be an ionic bond.

The shift of electron density toward the more electronegative atom in a bond can be seen from the results of calculations of electron-density distributions. For the three species in our example, the calculated electron-density distributions are shown in **Figure 8.9**. You can see that in F_2 the distribution is symmetrical, in HF the electron density is clearly shifted toward fluorine, and in LiF the shift is even greater. These examples illustrate, therefore, that *the greater the difference in electronegativity between two atoms, the more polar their bond*.



▶ **Figure 8.9 Electron-density distribution.** This computer-generated rendering shows the calculated electron-density distribution on the surface of the F_2, HF, and LiF molecules.

Sample Exercise 8.4

Bond Polarity

In each case, which bond is more polar? (**a**) B—Cl or C—Cl, (**b**) P—F or P—Cl. Indicate in each case which atom has the partial negative charge.

SOLUTION

Analyze We are asked to determine relative bond polarities, given nothing but the atoms involved in the bonds.

Plan Because we are not asked for quantitative answers, we can use the periodic table and our knowledge of electronegativity trends to answer the question.

Solve

(**a**) The chlorine atom is common to both bonds. Therefore, we just need to compare the electronegativities of B and C. Because boron is to the left of carbon in the periodic table, we predict that boron has the lower electronegativity. Chlorine, being on the right side of the table, has high electronegativity. The more polar bond will be the one between the atoms with the biggest differences in electronegativity. Consequently, the B—Cl bond is more polar; the chlorine atom carries the partial negative charge because it has a higher electronegativity.

(**b**) In this example, phosphorus is common to both bonds, and so we just need to compare the electronegativities of F and Cl. Because fluorine is above chlorine in the periodic table, it should be more electronegative and will form the more polar bond with P. The higher electronegativity of fluorine means that it will carry the partial negative charge.

Check

(**a**) Using Figure 8.8: The difference in the electronegativities of chlorine and boron is 3.0 − 2.0 = 1.0; the difference between the electronegativities of chlorine and carbon is 3.0 − 2.5 = 0.5. Hence, the B—Cl bond is more polar, as we had predicted.

(**b**) Using Figure 8.8: The difference in the electronegativities of chlorine and phosphorus is 3.0 − 2.1 = 0.9; the difference between the electronegativities of fluorine and phosphorus is 4.0 − 2.1 = 1.9. Hence, the P—F bond is more polar, as we had predicted.

▶ Practice Exercise

Which of the following bonds is the most polar?
(**a**) H—F (**b**) H—I (**c**) Se—F (**d**) N—P (**e**) Ga—Cl

Dipole Moments

The difference in electronegativity between H and F leads to a polar covalent bond in the HF molecule. As a consequence, there is a concentration of negative charge on the more electronegative F atom, leaving the less electronegative H atom at the positive end of the molecule. A molecule such as HF, in which the centers of positive and negative charge do not coincide, is a **polar molecule**. Thus, we describe both bonds and entire molecules as being polar and nonpolar.

We can indicate the polarity of the HF molecule in two ways:

$$\overset{\delta+}{\mathrm{H}}\!-\!\overset{\delta-}{\mathrm{F}} \quad \textit{or} \quad \overset{\longrightarrow}{\mathrm{H}\!-\!\mathrm{F}}$$

In the notation on the right, the arrow denotes the shift in electron density toward the fluorine atom. The crossed end of the arrow can be thought of as a plus sign designating the positive end of the molecule.

Polarity helps determine many properties we observe at the macroscopic level in the laboratory and in everyday life. Polar molecules align themselves with respect to one another, with the negative end of one molecule and the positive end of another attracting each other. Polar molecules are likewise attracted to ions. The negative end of a polar molecule is attracted to a positive ion, and the positive end is attracted to a negative ion. These interactions account for many properties of liquids, solids, and solutions, as you will see in Chapters 11, 12, and 13. Charge separation within molecules plays an important role in energy conversion processes such as photosynthesis and in solar cells.

How can we quantify the polarity of a molecule? Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a **dipole** is established. The quantitative measure of the magnitude of a dipole is called its **dipole moment**, denoted with the Greek letter mu, μ. If two equal and opposite charges $Q+$ and $Q-$ are separated by a distance r, as in **Figure 8.10**, the magnitude of the dipole moment is the product of Q and r:

$$\mu = Qr \qquad [8.10]$$

This expression tells us that the dipole moment increases as the magnitude of Q increases and as r increases. The larger the dipole moment, the more polar the bond. For a nonpolar molecule, such as F_2, the dipole moment is zero because there is no charge separation.

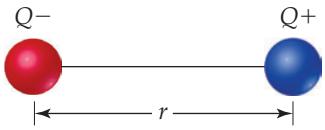
Dipole moments are experimentally measurable and are usually reported in *debyes* (D), a unit that equals 3.34×10^{-30} coulomb meters (C m). For molecules, we usually measure charge in units of the electronic charge e, 1.60×10^{-19} C, and distance in meters. This means we need to convert units whenever we want to report a dipole moment in debyes. Suppose that two charges 1+ and 1− (in units of e) are separated by 100 pm. The dipole moment produced is

$$\mu = Qr = (1.60 \times 10^{-19}\,\cancel{C})(100\,\cancel{\text{pm}})\left(\frac{10^{-12}\,\cancel{\text{m}}}{1\,\cancel{\text{pm}}}\right)\left(\frac{1\text{ D}}{3.34 \times 10^{-30}\,\cancel{C\text{-m}}}\right) = 4.79\text{ D}$$

Measurement of the dipole moments can provide us with valuable information about the charge distributions in molecules, as illustrated in Sample Exercise 8.5.

Go Figure

If the charged particles are moved closer together, does μ increase, decrease, or stay the same?



Dipole moment $\mu = Qr$

▲ **Figure 8.10 Dipole and dipole moment.** When charges of equal magnitude and opposite sign $Q+$ and $Q-$ are separated by a distance r, a dipole is produced.

Sample Exercise 8.5

Dipole Moments of Diatomic Molecules

The bond length in the HCl molecule is 127 pm. (**a**) Calculate the dipole moment, in debyes, that results if the charges on the H and Cl atoms were 1+ and 1− respectively. (**b**) The experimentally measured dipole moment of HCl(*g*) is 1.08 D. What magnitude of charge, in units of e, on the H and Cl atoms leads to this dipole moment?

SOLUTION

Analyze and Plan We are asked in part (a) to calculate the dipole moment of HCl that would result if there were a full charge transferred from H to Cl. We can use Equation 8.10 to obtain this result. In part (b), we are given the actual dipole moment for the molecule and will use that value to calculate the actual partial charges on the H and Cl atoms.

Solve

(**a**) The charge on each atom is the electronic charge, $e = 1.60 \times 10^{-19}$ C. The separation is 127 pm. The dipole moment is therefore:

$$\mu = Qr = (1.60 \times 10^{-19}\,\cancel{C})(127\,\cancel{\text{pm}})\left(\frac{10^{-12}\,\cancel{\text{m}}}{1\,\cancel{\text{pm}}}\right)\left(\frac{1\text{ D}}{3.34 \times 10^{-30}\,\cancel{C\text{-m}}}\right) = 6.08\text{ D}$$

(**b**) We know the value of μ, 1.08 D, and the value of r, 127 pm. We want to calculate the value of Q:

$$Q = \frac{\mu}{r} = \frac{(1.08\,\cancel{\text{D}})\left(\frac{3.34 \times 10^{-30}\,\text{C-}\cancel{\text{m}}}{1\,\cancel{\text{D}}}\right)}{(127\,\cancel{\text{pm}})\left(\frac{10^{-12}\,\cancel{\text{m}}}{1\,\cancel{\text{pm}}}\right)} = 2.84 \times 10^{-20}\text{ C}$$

Continued

We can readily convert this charge to units of e:

$$\text{Charge in } e = (2.84 \times 10^{-20}\,\text{C})\left(\frac{1e}{1.60 \times 10^{-19}\,\text{C}}\right) = 0.178e$$

Thus, the experimental dipole moment indicates that the charge separation in the HCl molecule is:

$$\overset{0.178+}{\text{H}}\!\!-\!\!\overset{0.178-}{\text{Cl}}$$

Because the experimental dipole moment is less than that calculated in part (a), the charges on the atoms are much less than a full electronic charge. We could have anticipated this because the H—Cl bond is polar covalent rather than ionic.

Practice Exercise

The dipole moment of chlorine monofluoride, ClF(g), is 0.88 D. The bond length of the molecule is 163 pm. (**a**) Which atom is expected to have the partial negative charge? (**b**) What is the charge on that atom in units of e?

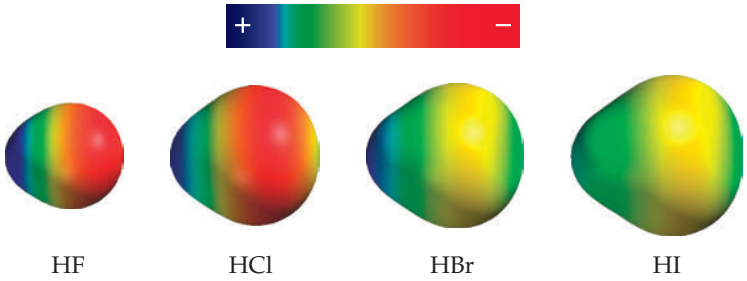
Table 8.2 presents the bond lengths and dipole moments of the hydrogen halides. Notice that as we proceed from HF to HI, the electronegativity difference decreases and the bond length increases. The first effect decreases the amount of charge separated and causes the dipole moment to decrease from HF to HI, even though the bond length is increasing. Calculations identical to those used in Sample Exercise 8.5 show that the charges on the atoms decrease from 0.41+ and 0.41− in HF to 0.057+ and 0.057− in HI. We can visualize the varying degree of electronic charge shift in these substances from computer-generated renderings based on calculations of electron distribution, as shown in Figure 8.11. For these molecules, the change in the electronegativity difference has a greater effect on the dipole moment than does the change in bond length.

Before leaving this section, let's return to the LiF "molecule" in Figure 8.9. Under standard conditions, LiF exists as an ionic solid with an arrangement of atoms analogous to the sodium chloride structure shown in Figure 8.4. However, it is possible to generate LiF *molecules* by vaporizing the ionic solid at high temperature. The molecules have a dipole moment

TABLE 8.2 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (pm)	Electronegativity Difference	Dipole Moment (D)
HF	92	1.9	1.82
HCl	127	0.9	1.08
HBr	141	0.7	0.82
HI	161	0.4	0.44

Go Figure As you go from HF to HI, does the H—X bond become more or less polar?



▲ **Figure 8.11 Charge separation in the hydrogen halides.** In HF, the strongly electronegative F pulls much of the electron density away from H. In HI, the I, being much less electronegative than F, does not attract the shared electrons as strongly, and, consequently, there is far less polarization of the bond.

of 6.28 D and a bond distance of 153 pm. From these values we can calculate the charge on lithium and fluorine to be 0.857+ and 0.857−, respectively. This bond is extremely polar, and the presence of such large charges strongly favors the formation of an extended ionic lattice in which each lithium ion is surrounded by fluoride ions and vice versa. But even here, the experimentally determined charges on the ions are still not 1+ and 1−. This tells us that even in ionic compounds, there is still some covalent contribution to the bonding.

Comparing Ionic and Covalent Bonding

To understand the interactions responsible for chemical bonding, it is advantageous to treat ionic and covalent bonding separately. That is the approach taken in this chapter, as well as in most other undergraduate-level chemistry texts. In reality, however, there is a continuum between the extremes of ionic and covalent bonding. This lack of a well-defined separation between the two types of bonding may seem unsettling or confusing at first.

The simple models of ionic and covalent bonding presented in this chapter go a long way toward understanding and predicting the structures and properties of chemical compounds. When covalent bonding is dominant, we expect compounds to exist as molecules,* having all the properties we associate with molecular substances, such as relatively low melting and boiling points and nonelectrolyte behavior when dissolved in water. When ionic bonding is dominant, we expect the compounds to be brittle, high-melting solids with extended lattice structures, exhibiting strong electrolyte behavior when dissolved in water.

Naturally, there are exceptions to these general characterizations, some of which we examine later in the book. Nonetheless, the ability to quickly categorize the predominant bonding interactions in a substance as covalent or ionic imparts considerable insight into the properties of that substance. The question then becomes the best way to recognize which type of bonding dominates.

The simplest approach is to assume that the interaction between a metal and a nonmetal is ionic and that between two nonmetals is covalent. While this classification scheme is reasonably predictive, there are far too many exceptions to use it blindly. For example, tin is a metal and chlorine is a nonmetal, but $SnCl_4$ is a molecular substance that exists as a colorless liquid at room temperature. It freezes at −33 °C and boils at 114 °C. The characteristics of $SnCl_4$ are not those typical of an ionic substance. Is there a more predictable way of determining what type of bonding is prevalent in a compound? A more sophisticated approach is to use the difference in electronegativity as the main criterion for determining whether ionic or covalent bonding will be dominant. This approach correctly predicts the bonding in $SnCl_4$ to be polar covalent based on an electronegativity difference of 1.2 and at the same time correctly predicts the bonding in NaCl to be predominantly ionic based on an electronegativity difference of 2.1.

Evaluating bonding based on electronegativity difference is a useful system, but it has one shortcoming. The electronegativity values given in Figure 8.8 do not take into account changes in bonding that accompany changes in the oxidation state of the metal. For example, Figure 8.8 gives the electronegativity difference between manganese and oxygen as $3.5 - 1.5 = 2.0$, which falls in the range where the bonding is normally considered ionic (the electronegativity difference for NaCl is $3.0 - 0.9 = 2.1$). Therefore, it is not surprising to learn that manganese(II) oxide, MnO, is a green solid that melts at 1842 °C and has the same crystal structure as NaCl.

However, the bonding between manganese and oxygen is not always ionic. Manganese(VII) oxide, Mn_2O_7, is a green liquid that freezes at 5.9 °C, an indication that covalent rather than ionic bonding dominates. The change in the oxidation state of manganese is responsible for the change in bonding. In general, as the oxidation state of a metal increases, so does the degree of covalent bonding. When the oxidation state of the metal is highly positive (roughly speaking, +4 or larger), we can expect significant covalency in the bonds it forms with nonmetals. Thus, metals in high oxidation states form molecular substances, such as Mn_2O_7, or polyatomic ions, such as MnO_4^- and CrO_4^{2-}, rather than ionic compounds.

* There are some exceptions to this statement, such as network solids, including diamond, silicon, and germanium, where an extended structure is formed even though the bonding is clearly covalent. These substances are discussed in Section 12.4.

Self-Assessment Exercise

8.20 Which of the following substances is expected to contain polar covalent bonds?

(a) N_2
(b) NH_3
(c) K_3N

Exercises

8.21 Which of the following statements about electronegativity is false? (**a**) Electronegativity is the ability of an atom in a molecule to attract electron density toward itself. (**b**) Electronegativity is the same thing as electron affinity. (**c**) The numerical values for electronegativity have no units. (**d**) Fluorine is the most electronegative element. (**e**) Cesium is the least electronegative element.

8.22 Using only the periodic table as your guide, select the most electronegative atom in each of the following sets: (**a**) Se, Te, Br, I; (**b**) Be, Mg, C, Si; (**c**) Al, Si, P, S; (**d**) O, P, Ge, In.

8.23 Which of the following bonds are polar? (**a**) C—O, (**b**) Sl—F, (**c**) N—Cl, (**d**) C—Cl. Which is the more electronegative atom in each polar bond?

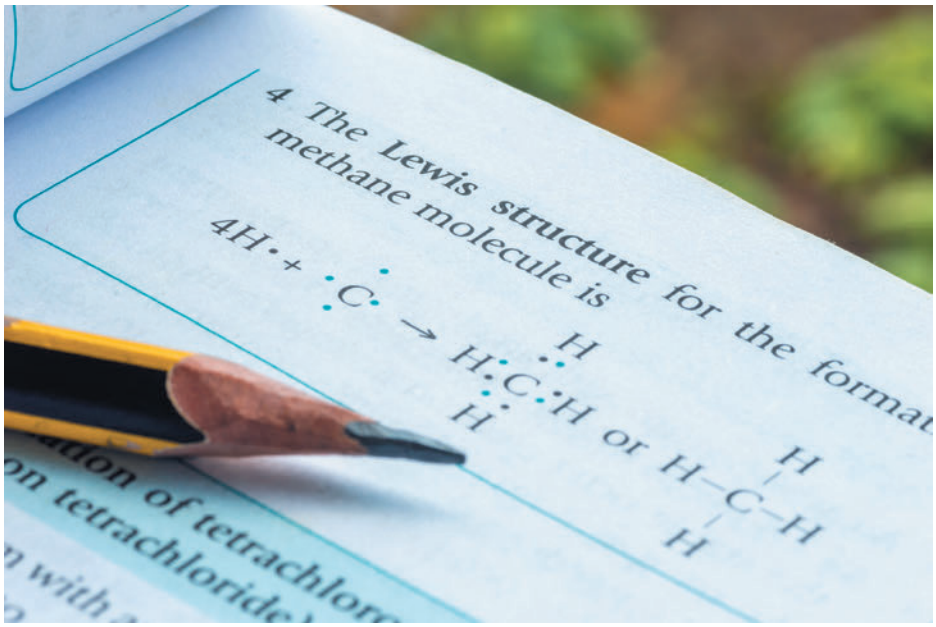
8.24 (**a**) From the data in Table 8.2, calculate the effective charges on the H and Br atoms of the HBr molecule in units of the electronic charge, *e*. (**b**) If you were to put HBr under very high pressure, so its bond length decreased significantly, would its dipole moment increase, decrease, or stay the same, if you assume that the effective charges on the atoms do not change?

8.25 In the following pairs of binary compounds, determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: (**a**) SiF_4 and LaF_3, (**b**) $FeCl_2$ and $ReCl_6$, (**c**) $PbCl_4$ and RbCl.

Answers to Self-Assessment Exercises

8.20 (b)

8.5 | Drawing Lewis Structures



The nexus between the microscopic (how the atoms are arranged), the macroscopic (the measurable properties of a substance), and the symbolic (how we portray the structure of a substance) is often an incomplete one. We have developed models to aid our understanding, which they have done, but we must bear in mind that they all have their limitations. One of the most successful models describes covalent bonding. It allows us to predict stable bonding arrangements of atoms and gives us an insight into the sort of reactions a compound may undergo.

By the end of this section, you should be able to

- Calculate formal charges from Lewis structures and use those formal charges to identify the dominant Lewis structure for a molecule or ion.

Lewis structures can help us understand the bonding in many compounds and are frequently used when discussing the properties of molecules. For this reason, drawing Lewis structures is an important skill that you should practice.

How to Draw Lewis Structures

1. **Sum the valence electrons from all atoms, taking into account overall charge.** Use the periodic table to help you determine the number of valence electrons in each atom. For an anion, add one electron to the total for each negative charge. For a cation, subtract one electron from the total for each positive charge. Do not worry about keeping track of which electrons come from which atoms. Only the total number is important.
2. **Write the symbols for the atoms, show which atoms are attached to which, and connect them with a single bond (*a line, representing* two *electrons*).** Chemical formulas are often written in the order in which the atoms are connected in the molecule or ion. The formula HCN, for example, tells you that the carbon atom is bonded to the H and to the N. In many polyatomic molecules and ions, the central atom is usually written first, as in CO_3^{2-} and SF_4. Remember that the central atom is generally less electronegative than the atoms surrounding it. In other cases, you may need more information before you can draw the Lewis structure.
3. **Complete the octets around all the atoms bonded to the central atom.** Keep in mind that a hydrogen atom has only a single pair of electrons around it.
4. **Place any remaining electrons on the central atom,** even if doing so results in more than an octet of electrons around the atom.
5. **If there are not enough electrons to give the central atom an octet, try multiple bonds.** Use one or more of the unshared pairs of electrons on the atoms bonded to the central atom to form double or triple bonds.

The following examples of this procedure will help you put it into practice.

Sample Exercise 8.6

Drawing a Lewis Structure

Draw the Lewis structure for phosphorus trichloride, PCl_3.

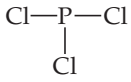
SOLUTION

Analyze and Plan We are asked to draw a Lewis structure from a molecular formula. Our plan is to follow the five-step procedure just described.

Solve First, we sum the valence electrons. Phosphorus (Group 15) has five valence electrons, and each chlorine (Group 17) has seven. The total number of valence electrons is therefore

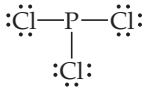
$$5 + (3 \times 7) = 26$$

Second, we arrange the atoms to show which atom is connected to which, and we draw a single bond between them. There are various ways the atoms might be arranged. It helps to know, though, that in binary compounds the first element in the chemical formula is generally surrounded by the remaining atoms. So we proceed to draw a skeleton structure in which a single bond connects the P atom to each Cl atom:

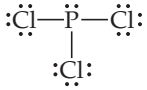


(It is not crucial that the Cl atoms be to the left of, right of, and below the P atom—any structure that shows each of the three Cl atoms bonded to P will work.)

Third, we add Lewis electron dots to complete the octets on the atoms bonded to the central atom. Completing the octets around each Cl atom accounts for 24 electrons (remember, each line in our structure represents *two* electrons):



Fourth, recalling that our total number of electrons is 26, we place the remaining two electrons on the central atom, P, which completes its octet:



This structure gives each atom an octet, so we stop at this point. (In checking for octets, remember to count a single bond as two electrons.)

Practice Exercise

(**a**) How many valence electrons should appear in the Lewis structure for CH_2Cl_2?
(**b**) Draw the Lewis structure.

Sample Exercise 8.7

Lewis Structure with a Multiple Bond

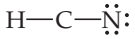
Draw the Lewis structure for HCN.

SOLUTION

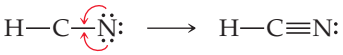
Hydrogen has one valence electron, carbon (Group 14) has four, and nitrogen (Group 15) has five. The total number of valence electrons is, therefore, $1 + 4 + 5 = 10$. In principle, there are different ways in which we might choose to arrange the atoms. Because hydrogen can accommodate only one electron pair, it always has only one single bond associated with it. Therefore, H—C—N is an impossible arrangement. The remaining two possibilities are H—C—N and H—N—C. The first is the arrangement found experimentally. You might have guessed this because the formula is written with the atoms in this order, and carbon is less electronegative than nitrogen. Thus, we begin with the skeleton structure

$$H—C—N$$

The two bonds account for four electrons. The H atom can have only two electrons associated with it, and so we will not add any more electrons to it. If we place the remaining six electrons around N to give it an octet, we do not achieve an octet on C:



We therefore try a double bond between C and N, using one of the unshared pairs we placed on N. Again we end up with fewer than eight electrons on C, and so we next try a triple bond. This structure gives an octet around both C and N:



The octet rule is satisfied for the C and N atoms, and the H atom has two electrons around it. This is a correct Lewis structure.

Practice Exercise

Draw the Lewis structure(s) for the molecule with the chemical formula C_2H_3N, where the N is connected to only one other atom. How many double bonds are there in the correct Lewis structure?
(**a**) zero (**b**) one (**c**) two (**d**) three (**e**) four

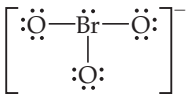
Sample Exercise 8.8

Lewis Structure for a Polyatomic Ion

Draw the Lewis structure for the BrO_3^- ion.

SOLUTION

Bromine (Group 17) has seven valence electrons, and oxygen (Group 16) has six. We must add one more electron to our sum to account for the 1− charge of the ion. The total number of valence electrons is, therefore, $7 + (3 \times 6) + 1 = 26$. For oxyanions—$SO_4^{2-}$, NO_3^-, CO_3^{2-}, and so forth—the oxygen atoms surround the central nonmetal atom. After arranging the O atoms around the Br atom, drawing single bonds, and distributing the unshared electron pairs, we have



Notice that the Lewis structure for an ion is written in brackets and the charge is shown outside the brackets at the upper right.

Practice Exercise

How many nonbonding electron pairs are there in the Lewis structure of the peroxide ion, O_2^{2-}?
(**a**) 7 (**b**) 6 (**c**) 5 (**d**) 4 (**e**) 3

Formal Charge and Alternative Lewis Structures

When we draw a Lewis structure, we are describing how the electrons are distributed in a molecule or polyatomic ion. In some instances, we can draw two or more valid Lewis structures for a molecule that all obey the octet rule. All of these structures can be thought of as contributing to the *actual* arrangement of the electrons in the molecule, but not all of them will contribute to the same extent. How do we decide which one of several Lewis structures is the most important? One approach is to do some "bookkeeping" of the valence electrons to determine the *formal charge* of each atom in each Lewis structure. The **formal charge** of any atom in a molecule is the charge the atom would have if each bonding electron pair in the molecule were shared equally between its two atoms.

How to Calculate the Formal Charges of Atoms in Lewis Structures

1. *All* unshared (nonbonding) electrons are assigned to the atom on which they are found.
2. For any bond—single, double, or triple—*half* of the bonding electrons are assigned to each atom in the bond.
3. The formal charge of each atom is calculated by subtracting the number of electrons assigned to the atom from the number of valence electrons in the neutral atom:

$$\textbf{Formal charge} = \text{valence electrons} - \tfrac{1}{2}(\text{bonding electrons}) - \text{nonbonding electrons} \qquad [8.11]$$

Let's practice by calculating the formal charges for the atoms in the cyanide ion, CN^-, which has the Lewis structure

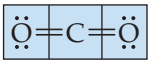
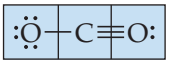
$$[:C\equiv N:]^-$$

The neutral C atom has four valence electrons. There are six electrons in the cyanide triple bond and two nonbonding electrons on C. We calculate the formal charge on C as $4 - \frac{1}{2}(6) - 2 = -1$. For N, the valence electron count is five; there are six electrons in the cyanide triple bond, and two nonbonding electrons on the N. The formal charge on N is $5 - \frac{1}{2}(6) - 2 = 0$. We can draw the whole ion with its formal charges as

$$\overset{-1}{[:}C\equiv \overset{0}{N:}]^-$$

Notice that the sum of the formal charges equals the overall charge on the ion, 1–. The formal charges on a neutral molecule must add to zero, whereas those on an ion add to give the charge on the ion.

If we can draw several Lewis structures for a molecule, the concept of formal charge can help us decide which is the most important, which we shall call the *dominant* Lewis structure. One Lewis structure for CO_2, for instance, has two double bonds. However, we can also satisfy the octet rule by drawing a Lewis structure having one single bond and one triple bond. Calculating formal charges in these structures, we have

						
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

Note that in both cases the formal charges add up to zero, as they must because CO_2 is a neutral molecule. So, which is the dominant structure? As a general rule, when more than one Lewis structure is possible, we will use the following guidelines to choose the dominant one:

How to Identify the Dominant Lewis Structure

1. The dominant Lewis structure is generally the one in which the atoms bear formal charges closest to zero.
2. A Lewis structure in which any negative charges reside on the more electronegative atoms is generally more dominant than one that has negative charges on the less electronegative atoms.

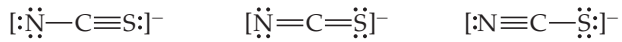
Thus, the first Lewis structure of CO_2 is the dominant one because the atoms carry no formal charges and so satisfy the first guideline. The other Lewis structure shown (and the similar one that has a triple bond to the left O and a single bond to the right O) contribute to the actual structure to a much smaller extent.

Although the concept of formal charge helps us to arrange alternative Lewis structures in order of importance, it is important to remember that *formal charges do not represent real charges on atoms*. These charges are just a bookkeeping convention. The actual charge distributions in molecules and ions are determined not by formal charges but by a number of other factors, including electronegativity differences between atoms.

Sample Exercise 8.9

Lewis Structures and Formal Charges

Three possible Lewis structures for the thiocyanate ion, NCS^-, are

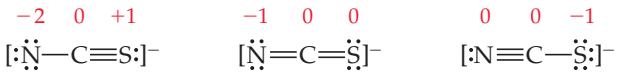


(**a**) Determine the formal charges in each structure.

(**b**) Based on the formal charges, which Lewis structure is the dominant one?

SOLUTION

(**a**) Neutral N, C, and S atoms have five, four, and six valence electrons, respectively. We can determine the formal charges in the three structures by using the rules we just discussed:



As they must, the formal charges in all three structures sum to 1−, the overall charge of the ion.

(**b**) The dominant Lewis structure generally produces formal charges of the smallest magnitude (guideline 1). That eliminates the left structure as the dominant one. Further, as discussed in Section 8.4, N is more electronegative than C or S. Therefore, we expect any negative formal charge to reside on the N atom (guideline 2). For these two reasons, the middle Lewis structure is the dominant one for NCS^-.

Practice Exercise

The sulfate ion, SO_4^{2-}, can be drawn in many ways. If you minimize formal charge on the sulfur, how many S═O double bonds should you draw in the Lewis structure?
(**a**) 0 (**b**) 1 (**c**) 2 (**d**) 3 (**e**) 4

A CLOSER LOOK Oxidation Numbers, Formal Charges, and Actual Partial Charges

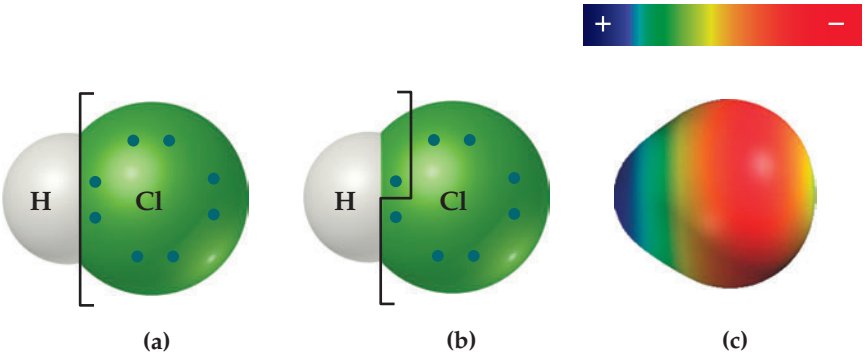
In Chapter 4, we introduced the rules for assigning *oxidation numbers* to atoms. The concept of electronegativity is the basis of these numbers. An atom's oxidation number is the charge the atom would have if its bonds were completely ionic. That is, in determining oxidation number, all shared electrons are counted with the more electronegative atom. For example, consider the Lewis structure of HCl in **Figure 8.12**(**a**). To assign oxidation numbers, both electrons in the covalent bond between the atoms are assigned to the more electronegative Cl atom. This procedure gives Cl eight valence electrons, one more than in the neutral atom. Thus, its oxidation number is −1. Hydrogen has no valence electrons when they are counted this way, giving it an oxidation number of +1.

In assigning formal charges to the atoms in HCl [Figure 8.12(b)], we ignore electronegativity; the electrons in bonds are assigned equally to the two bonded atoms. In this case Cl has seven assigned electrons, the same as that of the neutral Cl atom, and H has one assigned electron. Thus, the formal charges of both Cl and H in this compound are 0.

Neither oxidation number nor formal charge gives an accurate depiction of the actual charges on atoms because oxidation numbers overstate the role of electronegativity and formal charges ignore it. It seems reasonable that electrons in covalent bonds should be apportioned according to the relative electronegativities of the bonded atoms. Figure 8.8 (page 383) shows that Cl has an electronegativity of 3.0, while the electronegativity value of H is 2.1. The more electronegative Cl atom might therefore be expected to have roughly $3.0/(3.0 + 2.1) = 0.59$ of the electrical charge in the bonding pair, whereas the H atom would have $2.1/(3.0 + 2.1) = 0.41$ of the charge. Because the bond consists of two electrons, the Cl atom's share is $0.59 \times 2e = 1.18e$, or $0.18e$ more than the neutral Cl atom. This gives rise to a partial negative charge of 0.18− on Cl and therefore a partial positive charge of 0.18+ on H. (Notice again that we place the plus and minus signs *before* the magnitude in writing oxidation numbers and formal charges but *after* the magnitude in writing actual charges.)

The dipole moment of HCl gives an experimental measure of the partial charge on each atom. In Sample Exercise 8.5 we saw that the dipole moment of HCl corresponds to a partial charge of 0.178+ on H and 0.178− on Cl, in remarkably good agreement with our simple approximation based on electronegativities. Although our approximation method provides ballpark numbers for the magnitude of charge on atoms, the relationship between electronegativities and charge separation is generally more complicated. As we have already seen, computer programs employing quantum-mechanical principles have been developed to obtain more accurate estimates of the partial charges on atoms, even in complex molecules. A computer-graphical representation of the calculated charge distribution in HCl is shown in Figure 8.12(c).

Related Exercises: 8.28, 8.29, 8.37, 8.50, 8.71, 8.72, 8.78, 8.97, 8.98



▲ **Figure 8.12** (a) Oxidation number, (b) formal charge, and (c) electron-density distribution for the HCl molecule.

Self-Assessment Exercise

8.26 Dinitrogen oxide has the formula N_2O. Which of the three valid Lewis structures is the dominant structure?

(a) $\ddot{\underset{\cdot\cdot}{N}}=N=\ddot{\underset{\cdot\cdot}{O}}$

(b) $\ddot{\underset{\cdot\cdot}{N}}\equiv N-\ddot{\underset{\cdot\cdot}{O}}:$

(c) $:\ddot{\underset{\cdot\cdot}{N}}-N\equiv\ddot{O}$

Exercises

8.27 Draw Lewis structures for the following: (**a**) CH_2Cl_2, (**b**) ClCN, (**c**) AsF_5, (**d**) CH_2O (C the central atom), (**e**) OF_2, (**f**) NO_3^-.

8.28 Which one of these statements about formal charge is true? (**a**) Formal charge is the same as oxidation number. (**b**) To draw the best Lewis structure, you should minimize formal charge. (**c**) Formal charge takes into account the different electronegativities of the atoms in a molecule. (**d**) Formal charge is most useful for ionic compounds. (**e**) Formal charge is used in calculating the dipole moment of a diatomic molecule.

8.29 Write Lewis structures that obey the octet rule for each of the following, and assign oxidation numbers and formal charges to each atom: (**a**) OCS, (**b**) $SOCl_2$ (S is the central atom), (**c**) BrO_3^-, (**d**) $HClO_2$ (H is bonded to O).

Answers to Self-Assessment Exercises

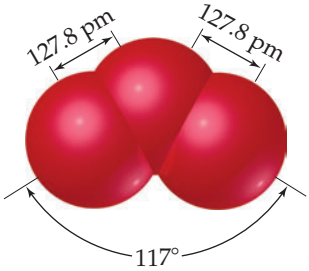
8.26 (b)

8.6 Resonance Structures



Go Figure

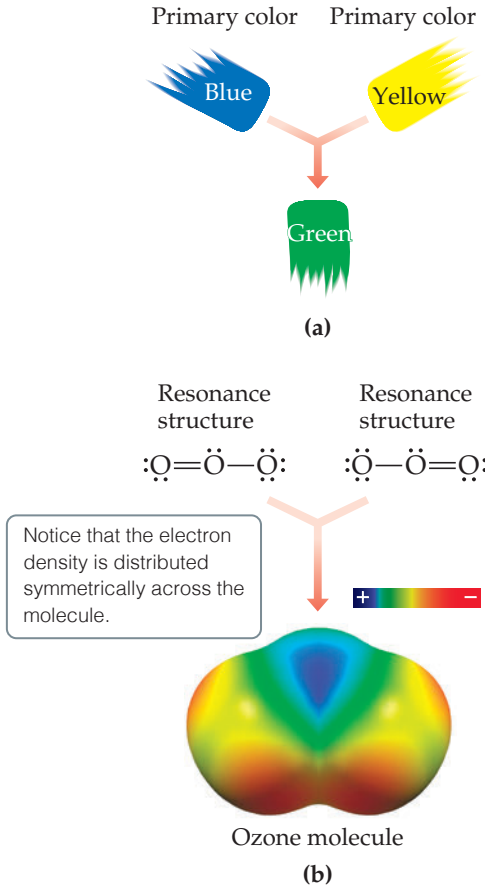
What feature of this structure suggests that the two outer O atoms are in some way equivalent to each other?



▲ **Figure 8.13** **Molecular structure of ozone.**

Go Figure

Is the electron density consistent with equal contributions from the two resonance structures for O_3? Explain.

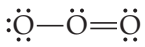


▲ **Figure 8.14** **Resonance.** Describing a molecule as a blend of different resonance structures is similar to describing a paint color as a blend of primary colors. (**a**) Green paint is a blend of blue and yellow. We cannot describe green as a single primary color. (**b**) The ozone molecule is a blend of two resonance structures. We cannot describe the ozone molecule in terms of a single Lewis structure.

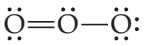
One skill an artist develops is to mix a limited range of pigments to create a myriad of colors. In this section, we mix valid Lewis structures in order to create a blend that better describes the actual structure of a molecule or ion. By the end of this section, you should be able to

- Recognize molecules where resonance structures are needed to describe the bonding and draw the dominant resonance structures.

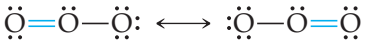
We sometimes encounter molecules and ions in which the experimentally determined arrangement of atoms is not adequately described by a single dominant Lewis structure. Consider ozone, O_3, which is a bent molecule with two equal O—O bond lengths (**Figure 8.13**). Because each oxygen atom contributes 6 valence electrons, the ozone molecule has 18 valence electrons. This means the Lewis structure must have one O—O single bond and one O=O double bond to attain an octet about each atom:



However, this single structure cannot by itself be dominant because it requires that one O—O bond be different from the other, contrary to the observed structure—we would expect the O=O double bond to be shorter than the O—O single bond. In drawing the Lewis structure, however, we could just as easily have put the O=O bond on the left:



There is no reason for one of these Lewis structures to be dominant because they are equally valid representations of the molecule. The placement of the atoms in these two alternative but completely equivalent Lewis structures is the same, but the placement of the electrons is different; we call Lewis structures of this sort **resonance structures**. To describe the structure of ozone properly, we write both resonance structures and use a double-headed arrow to indicate that the real molecule is described by an average of the two:

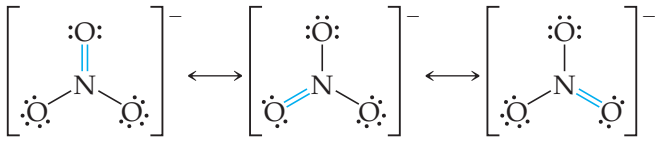


To understand why certain molecules require more than one resonance structure, we can draw an analogy to mixing paint (**Figure 8.14**). Blue and yellow are both primary colors of paint pigment. An equal blend of blue and yellow pigments produces green pigment. We cannot describe green paint in terms of a single primary color, yet it still has its own identity. Green paint does not oscillate between its two primary colors: It is not blue part of the time and yellow the rest of the time. Similarly, molecules such as ozone cannot be described as oscillating between the two individual Lewis structures shown previously—there are two equivalent dominant Lewis structures that contribute equally to the actual structure of the molecule.

The actual arrangement of the electrons in molecules such as O_3 must be considered as a blend of two (or more) Lewis structures. By analogy to the green paint, the molecule has its own identity separate from the individual resonance structures. For example, the ozone molecule always has two equivalent O—O bonds whose lengths are intermediate between the lengths of an oxygen–oxygen single bond and an oxygen–oxygen double bond. Another way of looking at it is to say that the rules for drawing Lewis structures do not allow us to have a single dominant structure for the ozone molecule. For example, there are no rules for drawing half-bonds.

We can get around this limitation by drawing two equivalent Lewis structures that, when averaged, amount to something very much like what is observed experimentally.

As an additional example of resonance structures, consider the nitrate ion, NO_3^-, for which three equivalent Lewis structures can be drawn:

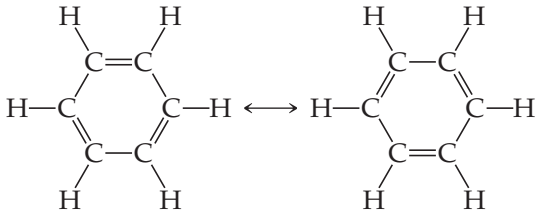


Notice that the arrangement of atoms is the same in each structure—only the placement of electrons differs. In writing resonance structures, the same atoms must be bonded to each other in all structures, so that the only differences are in the arrangements of electrons. All three NO_3^- Lewis structures are equally dominant and taken together adequately describe the ion, in which all three N—O bond lengths are the same.

For some molecules or ions, all possible Lewis structures may not be equivalent; in other words, one or more resonance structures are more dominant than others. We will encounter examples of this as we proceed.

Resonance in Benzene

Resonance is an important concept in describing the bonding in organic molecules, particularly *aromatic* organic molecules, a category that includes the hydrocarbon *benzene,* C_6H_6. The six C atoms are bonded in a hexagonal ring, and one H atom is bonded to each C atom. We can write two equivalent dominant Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance:



Note that the double bonds are in different places in the two structures. Each of these resonance structures shows three carbon–carbon single bonds and three carbon–carbon double bonds. However, experimental data show that all six C—C bonds are of equal length, 140 pm, intermediate between the typical bond lengths for a C—C single bond (154 pm) and a C=C double bond (134 pm). Each of the C—C bonds in benzene can be thought of as a blend of a single bond and a double bond.

The bonding arrangement in benzene confers special stability to the molecule. As a result, millions of organic compounds contain the six-membered ring characteristic of benzene. Many of these compounds are important in biochemistry, in pharmaceuticals, and in the production of modern materials.

Sample Exercise 8.10

Resonance Structures

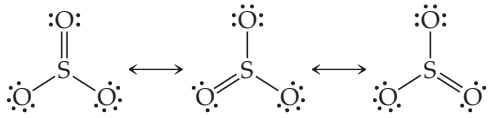
Which is predicted to have the shorter sulfur–oxygen bonds, SO_3 or SO_3^{2-}?

SOLUTION

The sulfur atom has six valence electrons, as does oxygen. Thus, SO_3 contains 24 valence electrons. In writing the Lewis structure, we see that three equivalent resonance structures can be drawn:

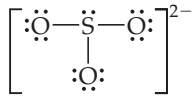
Our analysis of the Lewis structures thus far leads us to conclude that SO_3 should have the shorter S—O bonds and SO_3^{2-} the longer ones. This conclusion is correct: The experimentally measured S—O bond lengths are 142 pm in SO_3 and 151 pm in SO_3^{2-}.

Continued



As with NO_3^- the actual structure of SO_3 is an equal blend of all three. Thus, each S—O bond length should be about one-third of the way between the length of a single bond and the length of a double bond. That is, S—O should be shorter than single bonds but not as short as double bonds.

The SO_3^{2-} ion has 26 electrons, which leads to a dominant Lewis structure in which all the S—O bonds are single:



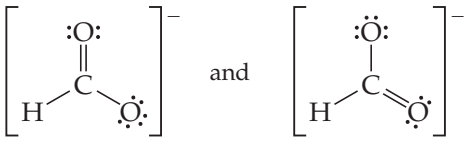
Practice Exercise

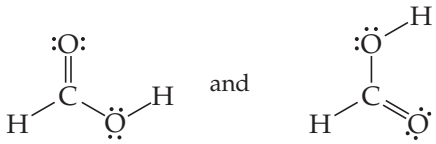
Which of these statements about resonance is true?

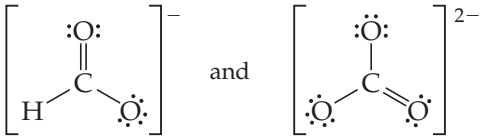
(**a**) When you draw resonance structures, it is permissible to alter the way atoms are connected.
(**b**) The nitrate ion has one long N—O bond and two short N—O bonds.
(**c**) "Resonance" refers to the idea that molecules are resonating rapidly between different bonding patterns.
(**d**) The cyanide ion has only one dominant resonance structure.
(**e**) All of these are true.

Self-Assessment Exercise

8.30 Which of the following pairs are resonance structures?

(**a**) 

(**b**) 

(**c**) 

Exercises

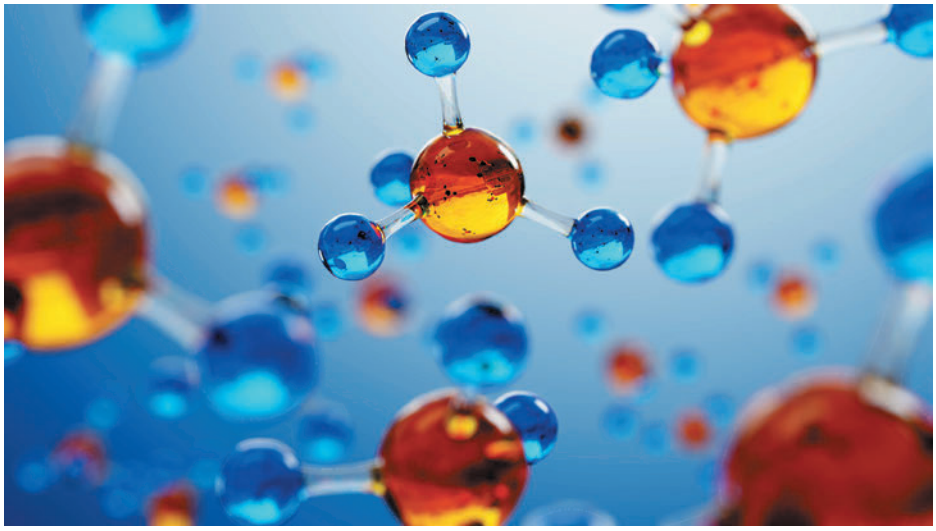
8.31 (**a**) Draw the best Lewis structure(s) for the nitrite ion, NO_2^-. (**b**) With what allotrope of oxygen is it isoelectronic? (**c**) What would you predict for the lengths of the bonds in NO_2^- relative to N—O single bonds and double bonds?

8.32 Based on Lewis structures, predict the ordering, from shortest to longest, of N—O bond lengths in NO^+, NO_2^-, and NO_3^-.

Answers to Self-Assessment Exercises

8.30 (a)

8.7 Exceptions to the Octet Rule



We mentioned at the start of section 8.5 that Lewis structures provide a simple and effective model for describing covalent bonding in molecules and ions. As with all models, there are limitations to this one and this results in exceptions to the 'rule'. It is important to understand the occurrence of these exceptions but also to bear in mind that they represent fairly few compounds among the millions that are described adequately by a Lewis structure.

By the end of this section, you should be able to

- Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed.

The octet rule is so simple and useful in introducing the basic concepts of bonding that you might assume it is always obeyed. In Section 8.2, however, we noted its limitation in dealing with ionic compounds of the transition metals. The rule also fails in many situations involving covalent bonding. These exceptions to the octet rule are of three main types:

1. Molecules and polyatomic ions containing an odd number of electrons
2. Molecules and polyatomic ions in which an atom has fewer than an octet of valence electrons
3. Molecules and polyatomic ions in which an atom has more than an octet of valence electrons

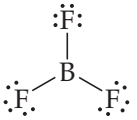
Odd Number of Electrons

In the vast majority of molecules and polyatomic ions, the total number of valence electrons is even, and complete pairing of electrons occurs. However, in a few molecules and polyatomic ions, such as ClO_2, NO, NO_2, and O_2^-, the number of valence electrons is odd. Complete pairing of these electrons is impossible, and an octet around each atom cannot be achieved. For example, NO contains 5 + 6 = 11 valence electrons. The two most important Lewis structures for this molecule are

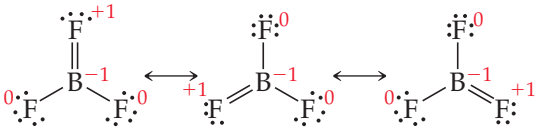


Less Than an Octet of Valence Electrons

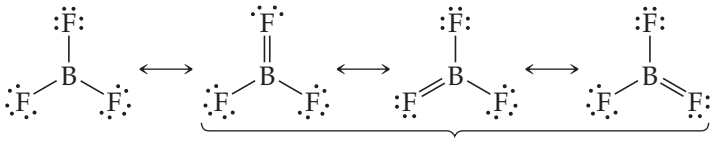
A second type of exception occurs when there are fewer than eight valence electrons around an atom in a molecule or polyatomic ion. This situation is also relatively rare (with the exception of hydrogen and helium as we have already discussed), and is most often encountered in compounds of boron and beryllium. As an example, let's consider boron trifluoride, BF_3. If we follow the first steps of our procedure for drawing Lewis structures, we obtain the structure



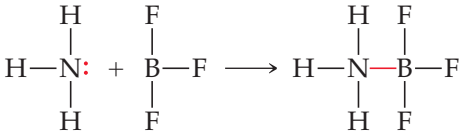
which has only six electrons around the boron atom. The formal charge is zero on both B and F, and we could complete the octet around boron by forming a double bond (recall that if there are not enough electrons to give the central atom an octet, a multiple bond may be the answer). In so doing, we see that there are three equivalent resonance structures (the formal charges are shown in red):



Each of these structures forces a fluorine atom to share additional electrons with the boron atom, which is inconsistent with the high electronegativity of fluorine. In fact, the formal charges tell us that this is an unfavorable situation. In each structure, the F atom involved in the B═F double bond has a formal charge of +1, while the less electronegative B atom has a formal charge of −1. Thus, the resonance structures containing a B═F double bond are less important than the one in which there are fewer than an octet of valence electrons around boron:



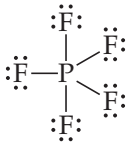
We usually represent BF_3 solely by the dominant resonance structure, in which there are only six valence electrons around boron. The chemical behavior of BF_3 is consistent with this representation. In particular, BF_3 reacts energetically with molecules having an unshared pair of electrons that can be used to form a bond with boron, as, for example, in the reaction

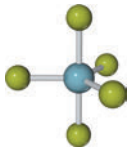


In the stable compound NH_3BF_3, boron has an octet of valence electrons.

More Than an Octet of Valence Electrons

The third and largest class of exceptions consists of molecules or polyatomic ions in which there are more than eight electrons in the valence shell of an atom. When we draw the Lewis structure for PF_5, for example, we are forced to place ten electrons around the central phosphorus atom:





Molecules and ions with more than an octet of electrons around the central atom are often called *hypervalent*. Other examples of hypervalent species are SF_4, AsF_6^-, and ICl_4^-. The corresponding molecules with a second-period atom as the central atom, such as NCl_5 and OF_4, do *not* exist.

Hypervalent molecules are formed only for central atoms from Period 3 and below in the periodic table. The principal reason for their formation is the relatively larger size of the central atom. For example, a P atom is large enough that five F (or even five Cl) atoms can be bonded to it without being too crowded. By contrast, an N atom is too small to accommodate five atoms bonded to it. Because size is a factor, hypervalent molecules occur most often when the central atom is bonded to the smallest and most electronegative atoms—F, Cl, and O.

The notion that a valence shell can contain more than eight electrons is also consistent with the presence of unfilled *nd* orbitals in atoms from Period 3 and below. By comparison, in elements of the second period, only the 2*s* and 2*p* valence orbitals are available for bonding. However, theoretical work on the bonding in molecules such as PF_5 and SF_6 suggests that the presence of unfilled 3*d* orbitals in P and S has a relatively minor impact on the formation of hypervalent molecules. Most chemists now believe that the larger size of the atoms from Periods 3 through 6 is more important to explain hypervalency than is the presence of unfilled *d* orbitals.

Sample Exercise 8.11

Lewis Structure for an Ion with More Than an Octet of Electrons

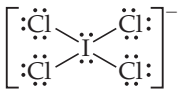
Draw the Lewis structure for ICl_4^-.

SOLUTION

Iodine (Group 17) has seven valence electrons. Each chlorine atom (Group 17) also has seven. An extra electron is added to account for the 1− charge of the ion. Therefore, the total number of valence electrons is $7 + (4 \times 7) + 1 = 36$.

The I atom is the central atom in the ion. Putting eight electrons around each Cl atom (including a pair of electrons between I and each Cl to represent the single bond between these atoms) requires $8 \times 4 = 32$ electrons.

We are thus left with $36 - 32 = 4$ electrons to be placed on the larger iodine:

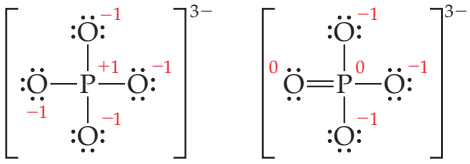


Iodine has 12 valence electrons around it, four more than needed for an octet.

Practice Exercise

In which of these molecules or ions is there only one lone pair of electrons on the central sulfur atom?
(**a**) SF_4 (**b**) SF_6 (**c**) SOF_4 (**d**) SF_2 (**e**) SO_4^{2-}

Finally, there are Lewis structures where you might have to choose between satisfying the octet rule and obtaining the most favorable formal charges by using more than an octet of electrons. For example, consider these Lewis structures for the phosphate ion, PO_4^{3-}:

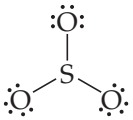


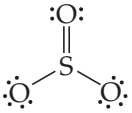
The formal charges on the atoms are shown in red. In the left structure, the P atom obeys the octet rule. In the right structure, however, the P atom has five electron pairs, leading to smaller formal charges on the atoms. (You should be able to see that there are three additional resonance structures for the Lewis structure on the right.)

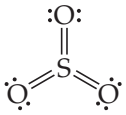
Chemists are still debating which of these two structures is dominant for PO_4^{3-}. Recent theoretical calculations based on quantum mechanics suggest to some researchers that the left structure is the dominant one. Other researchers claim that the bond lengths in the ion are more consistent with the right structure being dominant. This disagreement is a convenient reminder that, in general, multiple Lewis structures can contribute to the actual electron distribution in an atom or molecule.

Self-Assessment Exercise

8.33 Use formal charge to decide which of the following structures best represents sulfur trioxide, SO_3?

(a) 

(b) 

(c) 

Exercises

8.34 Draw the dominant Lewis structures for these chlorine–oxygen molecules/ions: ClO, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-. Which of these do not obey the octet rule?

8.35 Draw the Lewis structures for each of the following ions or molecules. Identify those in which the octet rule is not obeyed; state which atom in each compound does not follow the octet rule; and state, for those atoms, how many electrons surround them: (**a**) HCl, (**b**) ICl_5, (**c**) NO, (**d**) CF_2Cl_2, (**e**) I_3^-.

8.36 In the vapor phase, $BeCl_2$ exists as a discrete molecule. (**a**) Draw the Lewis structure of this molecule, using only single bonds. Does this Lewis structure satisfy the octet rule? (**b**) What other resonance structures are possible that satisfy the octet rule? (**c**) On the basis of the formal charges, which Lewis structure is expected to be dominant for $BeCl_2$?

8.37 There are many Lewis structures you could draw for sulfuric acid, H_2SO_4 (each H is bonded to an O). (**a**) What Lewis structure(s) would you draw to satisfy the octet rule? (**b**) What Lewis structure(s) would you draw to minimize formal charge?

Answers to Self-Assessment Exercises

8.33 (c)

8.8 Strengths and Lengths of Covalent Bonds



Covalent bonds are sometimes described as being like springs that may be stretched or compressed but naturally resume a characteristic resting length. We take this analogy a little further when we examine the vibrations present in a covalent bond in Section 32.2. For the present, we look at the correlation between bond strength and bond length. By the end of this section, you should be able to

- Understand the relationship between bond type (single, double, and triple), bond strength (or enthalpy), and bond length.

The stability of a molecule is related to the strengths of its covalent bonds. We saw in Chapter 5 that we can measure the average bond enthalpy of many single bonds (Table 5.4). Table 5.4 is repeated here as **Table 8.3**. As you might expect, Table 8.3 shows that multiple bonds are generally stronger than single bonds.

Just as we can define an average bond enthalpy, we can also define an average bond length for a number of common bonds (**Table 8.4**). Of particular interest is the relationship, in any atom pair, among bond enthalpy, bond length, and number of bonds between the atoms. For example, we can use data in Tables 8.3 and 8.4 to compare the bond lengths and bond enthalpies of carbon–carbon single, double, and triple bonds:

C—C	C=C	C≡C
154 pm	134 pm	120 pm
348 kJ/mol	614 kJ/mol	839 kJ/mol

TABLE 8.3 Average Bond Enthalpies (kJ/mol)

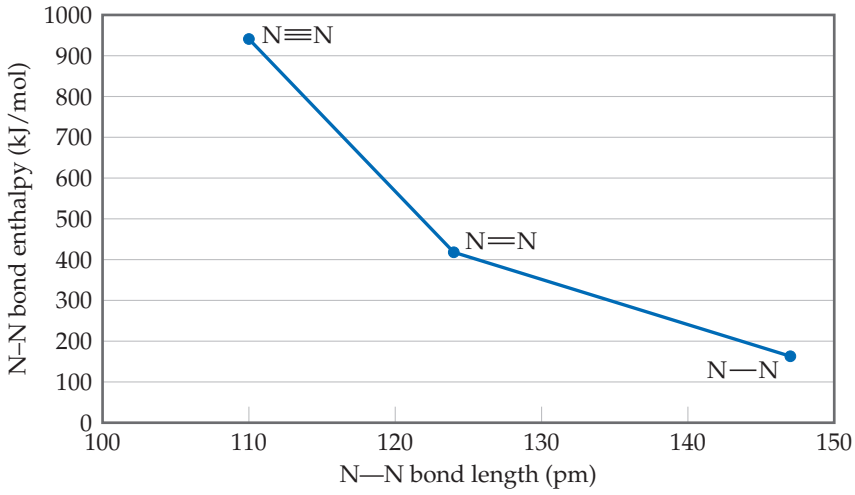
Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						
Multiple Bonds							
C=C	614	N=N	418	O=O	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

TABLE 8.4 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (pm)	Bond	Bond Length (pm)
C—C	154	N—N	147
C=C	134	N=N	124
C≡C	120	N≡N	110
C—N	143	N—O	136
C=N	138	N=O	122
C≡N	116		
		O—O	148
C—O	143	O=O	121
C=O	123		
C≡O	113		

As the number of bonds between the carbon atoms increases, the bond length decreases and the bond enthalpy increases. That is, the carbon atoms are held more closely and more tightly together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger*. This trend is illustrated in **Figure 8.15** for N—N single, double, and triple bonds.

Go Figure Predict the N—N bond enthalpy for an N—N bond that has resonance forms that include equal contributions from single and double N—N bonds.



▲ **Figure 8.15** **Bond strength versus bond length for N—N bonds.**

Self-Assessment Exercise

8.38 Ozone, O_3, may be represented by two resonance structures. The measured bond length is 127.8 pm



Average bond enthalpies and bond lengths are given in Table 8.3 and 8.4. What do you predict the average bond enthalpy of a bond in ozone to be?

(a) 148 kJ/mol

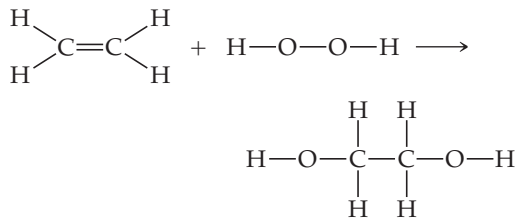
(b) 364 kJ/mol

(c) 495 kJ/mol

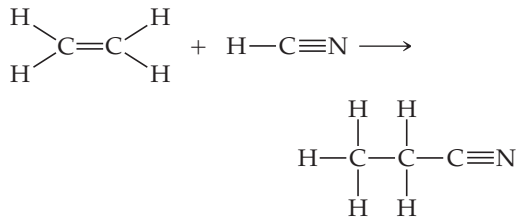
Exercises

8.39 Using Table 8.3, estimate ΔH for each of the following gas-phase reactions (note that lone pairs on atoms are not shown):

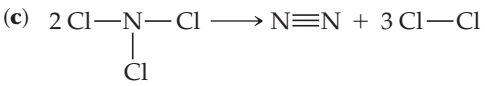
(a)



(b)



(c)



8.40 State whether each of these statements is true or false. (**a**) The longer the bond, the stronger the bond. (**b**) C—C bonds are stronger than C—F bonds. (**c**) A typical double bond length is in the 500–1000 pm range. (**d**) Energy is required to form a chemical bond. (**e**) The longer the bond, the more energy is stored chemical bonds.

8.41 We can define average bond enthalpies and bond lengths for ionic bonds, just like we have for covalent bonds. Which ionic bond is predicted to be stronger, Na—Cl or Ca—O?

8.42 Draw the Lewis structure for NO^+. Is the nitrogen–oxygen bond in NO^+ longer, shorter, or the same length as the nitrogen–oxygen bond in NO? Explain.

Answers to Self-Assessment Exercises

8.39 (b)

Sample Integrative Exercise

Putting Concepts Together

Phosgene, a substance used in poisonous gas warfare during World War I, is so named because it was first prepared by the action of sunlight on a mixture of carbon monoxide and chlorine gases. Its name comes from the Greek words *phos* (light) and *genes* (born of). Phosgene has the following elemental composition: 12.14% C, 16.17% O, and 71.69% Cl by mass. Its molar mass is 98.9 g/mol. (**a**) Determine the molecular formula of this compound. (**b**) Draw three Lewis structures for the molecule that satisfy the octet rule for each atom. (The Cl and O atoms bond to C.) (**c**) Using formal charges, determine which Lewis structure is the dominant one. (**d**) Using average bond enthalpies, estimate ΔH for the formation of gaseous phosgene from $CO(g)$ and $Cl_2(g)$.

SOLUTION

(**a**) The empirical formula of phosgene can be determined from its elemental composition. Assuming 100 g of the compound and calculating the number of moles of C, O, and Cl in this sample, we have:

$$(12.14\ \text{g}\cancel{\text{C}})\left(\frac{1\ \text{mol C}}{12.01\ \text{g}\cancel{\text{C}}}\right) = 1.011\ \text{mol C}$$

$$(16.17\ \text{g}\cancel{\text{O}})\left(\frac{1\ \text{mol O}}{16.00\ \text{g}\cancel{\text{O}}}\right) = 1.011\ \text{mol O}$$

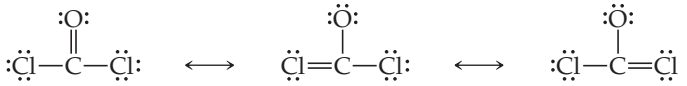
$$(71.69\ \text{g}\cancel{\text{Cl}})\left(\frac{1\ \text{mol Cl}}{35.45\ \text{g}\cancel{\text{Cl}}}\right) = 2.022\ \text{mol Cl}$$

The ratio of the number of moles of each element, obtained by dividing each number of moles by the smallest quantity, indicates that there is one C and one O for each two Cl in the empirical formula, $COCl_2$.

The molar mass of the empirical formula is 12.01 + 16.00 + 2(35.45) = 98.91 g/mol, the same as the molar mass of the molecule. Thus, $COCl_2$ is the molecular formula.

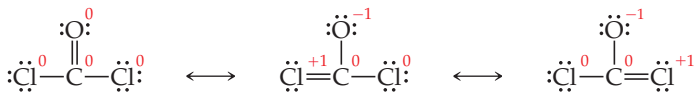
Continued

(**b**) Carbon has four valence electrons, oxygen has six, and chlorine has seven, giving $4 + 6 + 2(7) = 24$ electrons for the Lewis structures. Drawing a Lewis structure with all single bonds does not give the central carbon atom an octet. Using multiple bonds, we find that three structures satisfy the octet rule:

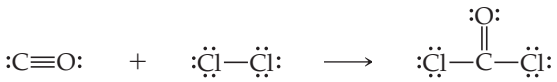


(**c**) Calculating the formal charges on each atom gives:

The first structure is expected to be the dominant one because it has the lowest formal charges on each atom. Indeed, the molecule is usually represented by this single Lewis structure.



(**d**) Writing the chemical equation in terms of the Lewis structures of the molecules, we have:



Thus, the reaction involves breaking a C≡O bond and a Cl—Cl bond and forming a C=O bond and two C—Cl bonds. Using bond enthalpies from Table 8.3, we have:

$$\Delta H = [D(\text{C}{\equiv}\text{O}) + D(\text{Cl} - \text{Cl})] - [D(\text{C}{=}\text{O}) + 2D(\text{C}{-}\text{Cl})]$$
$$= [1072\ \text{kJ} + 242\ \text{kJ}] - [799\ \text{kJ} + 2(328\ \text{kJ})] = -141\ \text{kJ}$$

Notice that the reaction is exothermic. Nevertheless, energy is needed from sunlight or another source for the reaction to begin, as is the case for the combustion of $H_2(g)$ and $O_2(g)$ to form $H_2O(g)$.

Chapter Summary and Key Terms

CHEMICAL BONDS, LEWIS SYMBOLS, AND THE OCTET RULE (INTRODUCTION AND SECTION 8.1) In this chapter, we have focused on the interactions that lead to the formation of **chemical bonds**. We classify these bonds into three broad groups: **ionic bonds**, which result from the electrostatic forces that exist between ions of opposite charge; **covalent bonds**, which result from the sharing of electrons by two atoms; and **metallic bonds**, which result from a delocalized sharing of electrons in metals. The formation of bonds involves interactions of the outermost electrons of atoms, their valence electrons. The valence electrons of an atom can be represented by electron-dot symbols, called **Lewis symbols**. The tendencies of atoms to gain, lose, or share their valence electrons often follow the **octet rule**, which says that the atoms in molecules or ions (usually) have eight valence electrons.

IONIC BONDING (SECTION 8.2) Ionic bonding results from the transfer of electrons from one atom to another, leading to the formation of a three-dimensional lattice of charged particles. The stabilities of ionic substances result from the strong electrostatic attractions between an ion and the surrounding ions of opposite charge. The magnitude of these interactions is measured by the **lattice energy**, which is the energy needed to separate an ionic lattice into gaseous ions. Lattice energy increases with increasing charge on the ions and with decreasing distance between the ions. The **Born–Haber cycle** is a useful thermochemical cycle in which we use Hess's law to calculate the lattice energy as the sum of several steps in the formation of an ionic compound.

COVALENT BONDING (SECTION 8.3) A covalent bond results from the sharing of valence electrons between atoms. We can represent the electron distribution in molecules by means of **Lewis structures**, which indicate how many valence electrons are involved in forming bonds and how many remain as **nonbonding electron pairs** (or **lone pairs**). The octet rule helps determine how many bonds will be formed between two atoms. The sharing of one pair of electrons produces a **single bond**; the sharing of two or three pairs of electrons between two atoms produces **double** or **triple bonds**, respectively. Double and triple bonds are examples of multiple bonding between atoms. The bond length decreases as the number of bonds between the atoms increases.

BOND POLARITY AND ELECTRONEGATIVITY (SECTION 8.4) In covalent bonds, the electrons may not necessarily be shared equally between two atoms. **Bond polarity** helps describe unequal sharing of electrons in a bond. In a **nonpolar covalent bond**, the electrons in the

bond are shared equally by the two atoms; in a **polar covalent bond**, one of the atoms exerts a greater attraction for the electrons than the other.

Electronegativity is a numerical measure of the ability of an atom to compete with other atoms for the electrons shared between them. Fluorine is the most electronegative element, meaning it has the greatest ability to attract electrons from other atoms. Electronegativity values range from 0.7 for Cs to 4.0 for F. Electronegativity generally increases from left to right in a row of the periodic table and decreases going down a column. The difference in the electronegativities of bonded atoms can be used to determine the polarity of a bond. The greater the electronegativity difference, the more polar the bond.

A **polar molecule** is one whose centers of positive and negative charge do not coincide. Thus, a polar molecule has a positive side and a negative side. This separation of charge produces a **dipole**, the magnitude of which is given by the **dipole moment**, which is measured in debyes (D). Dipole moments increase with increasing amount of charge separated and increasing distance of separation. Any diatomic molecule X—Y in which X and Y have different electronegativities is a polar molecule.

Most bonding interactions lie between the extremes of covalent and ionic bonding. While it is generally true that the bonding between a metal and a nonmetal is predominantly ionic, exceptions to this guideline are not uncommon when the difference in electronegativity of the atoms is relatively small or when the oxidation state of the metal becomes large.

DRAWING LEWIS STRUCTURES AND RESONANCE STRUCTURES (SECTIONS 8.5 AND 8.6) If we know which atoms are connected to one another, we can draw Lewis structures for molecules and ions by a simple procedure. Once we do so, we can determine the **formal charge** of each atom in a Lewis structure, which is the charge that the atom would have if all atoms had the same electronegativity. In general, the dominant Lewis structure will have low formal charges, with any negative formal charges residing on more electronegative atoms.

Sometimes a single dominant Lewis structure is inadequate to represent a particular molecule (or ion). In such situations, we describe the molecule by using two or more **resonance structures** for the molecule. The molecule is envisioned as a blend of these multiple resonance structures. Resonance structures are important in describing the bonding in molecules such as ozone, O_3, and the organic molecule benzene, C_6H_6.

EXCEPTIONS TO THE OCTET RULE (SECTION 8.7) The octet rule is not obeyed in all cases. Exceptions occur when (**a**) a molecule has an odd number of electrons, (**b**) it is not possible to complete an octet around an atom without forcing an unfavorable distribution of electrons, or (**c**) a large atom is surrounded by a sufficiently large number of small electronegative atoms that it has more than an octet of electrons around it. Lewis structures with more than an octet of electrons are observed for atoms in the third row and beyond in the periodic table.

STRENGTHS AND LENGTHS OF COVALENT BONDS (SECTION 8.8) The average strengths and lengths of many common covalent bonds can be measured. Average bond enthalpies for multiple bonds are generally larger than those of single bonds. The average bond length between two atoms decreases as the number of bonds between the atoms increases, consistent with the bond being stronger as the number of bonds increases.

Learning Outcomes After studying this chapter, you should be able to:

- Write Lewis symbols for atoms and ions. (Section 8.1) *Related Exercises: 8.4, 8.9, 8.53, 8.56*
- Define lattice energy and be able to arrange compounds in order of increasing lattice energy based on the charges and sizes of the ions involved. (Section 8.2) *Related Exercises: 8.10, 8.11, 8.57, 8.58*
- Use atomic electron configurations and the octet rule to draw Lewis structures for molecules. (Section 8.3) *Related Exercises: 8.16, 8.27, 8.64, 8.70*
- Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds. (Section 8.4) *Related Exercises: 8.21, 8.22, 8.65*
- Calculate charge separation in diatomic molecules based on the experimentally measured dipole moment and bond length. (Section 8.4) *Related Exercises: 8.24, 8.68*
- Calculate formal charges from Lewis structures and use those formal charges to identify the dominant Lewis structure for a molecule or ion. (Section 8.5) *Related Exercises: 8.28, 8.29, 8.71, 8.72*
- Recognize molecules where resonance structures are needed to describe the bonding and draw the dominant resonance structures. (Section 8.6) *Related Exercises: 8.31, 8.32, 8.73*
- Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed. (Section 8.7) *Related Exercises: 8.35, 8.77*
- Predict the relationship between bond type (single, double, and triple), bond strength (or enthalpy), and bond length. (Section 8.8) *Related Exercises: 8.40, 8.41, 8.81, 8.82*

Key Equations

- $E_{el} = \dfrac{\kappa Q_1 Q_2}{d}$ [8.4] The potential energy of two interacting charges
- $\mu = Qr$ [8.10] The dipole moment of two charges of equal magnitude but opposite sign, separated by a distance r
- Formal charge $=$ valence electrons $-$ $\frac{1}{2}$(bonding electrons) $-$ nonbonding electrons [8.11] The definition of formal charge

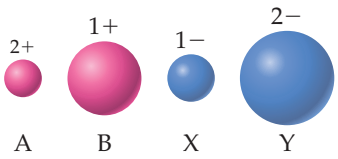
Exercises

Visualizing Concepts

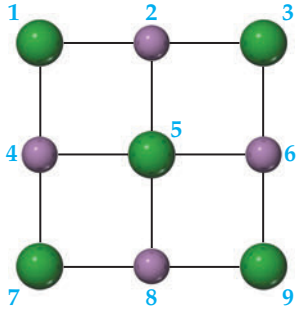
8.43 For each of these Lewis symbols, indicate the group in the periodic table in which the element X belongs: [Section 8.1]

(**a**) $\cdot\dot{\underset{\cdot}{\mathrm{X}}}\cdot$ (**b**) $\cdot\mathrm{X}\cdot$ (**c**) $:\dot{\underset{\cdot}{\mathrm{X}}}\cdot$

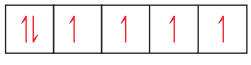
8.44 Illustrated are four ions — A, B, X, and Y— showing their relative ionic radii. The ions shown in red carry positive charges: a 2+ charge for A and a 1+ charge for B. Ions shown in blue carry negative charges: a 1− charge for X and a 2− charge for Y. (**a**) Which combinations of these ions produce ionic compounds where there is a 1:1 ratio of cations and anions? (**b**) Among the combinations in part (a), which leads to the ionic compound having the largest lattice energy? [Section 8.2]



8.45 A portion of a two-dimensional "slab" of NaCl(*s*) is shown here (see Figure 8.2) in which the ions are numbered. (**a**) Which colored balls must represent sodium ions? (**b**) Which colored balls must represent chloride ions? (**c**) Consider ion 5. How many attractive electrostatic interactions are shown for it? (**d**) Consider ion 5. How many repulsive interactions are shown for it? (**e**) Is the sum of the attractive interactions in part (c) larger or smaller than the sum of the repulsive interactions in part (d)? (**f**) If this pattern of ions was extended indefinitely in two dimensions, would the lattice energy be positive or negative? [Section 8.2]

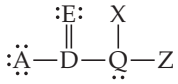


8.46 The orbital diagram that follows shows the valence electrons for a 2+ ion of an element. (**a**) What is the element? (**b**) What is the electron configuration of an atom of this element? [Section 8.2]



4*d*

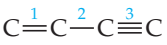
8.47 In the Lewis structure shown here, A, D, E, Q, X, and Z represent elements in the first two rows of the periodic table. Identify all six elements so that the formal charges of all atoms are zero. [Section 8.3]



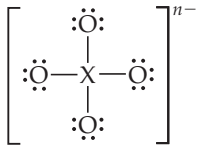
8.48 Incomplete Lewis structures for the nitrous acid molecule, HNO_2, and the nitrite ion, NO_2^-, are shown here. (**a**) Complete each Lewis structure by adding electron pairs as needed. (**b**) Is the formal charge on N the same or different in these two species? (**c**) Would either HNO_2 or NO_2^- be expected to exhibit resonance? (**d**) Would you expect the N═O bond in HNO_2 to be longer, shorter, or the same length as the N—O bonds in NO_2^-? [Sections 8.5 and 8.6]



8.49 The partial Lewis structure that follows is for a hydrocarbon molecule. In the full Lewis structure, each carbon atom satisfies the octet rule, and there are no unshared electron pairs in the molecule. The carbon—carbon bonds are labeled 1, 2, and 3. (**a**) How many hydrogen atoms are in the molecule? (**b**) Rank the carbon–carbon bonds in order of increasing bond length. (**c**) Which carbon—carbon bond is the strongest one? [Sections 8.3 and 8.8]



8.50 Consider the Lewis structure for the polyatomic oxyanion shown here, where X is an element from the third period (Na − Ar). By changing the overall charge, *n*, from 1− to 2− to 3− we get three different polyatomic ions. For each of these ions (**a**) identify the central atom, X; (**b**) determine the formal charge of the central atom, X; (**c**) draw a Lewis structure that makes the formal charge on the central atom equal to zero. [Sections 8.5, 8.6, and 8.7]



Lewis Symbols (Section 8.1)

8.51 (**a**) True or false: The hydrogen atom is most stable when it has a full octet of electrons. (**b**) How many electrons must a sulfur atom gain to achieve an octet in its valence shell? **(c)** If an atom has the electron configuration $1s^2 2s^2 2p^3$, how many electrons must it gain to achieve an octet?

8.52 (**a**) Write the electron configuration for the element titanium, Ti. How many valence electrons does this atom possess? (**b**) Hafnium, Hf, is also found in Group 4. Write the electron configuration for Hf. (**c**) Ti and Hf behave as though they possess the same number of valence electrons. Which of the subshells in the electron configuration of Hf behave as valence orbitals? Which behave as core orbitals?

8.53 What is the Lewis symbol for each of the following atoms or ions? (**a**) Be, (**b**) Rb, (**c**) I^-, (**d**) Se^{2-}.

Ionic Bonding (Section 8.2)

8.54 (**a**) Use Lewis symbols to represent the reaction that occurs between Li and O atoms. (**b**) What is the chemical formula of the most likely product? (**c**) How many electrons are transferred? (**d**) Which atom loses electrons in the reaction?

8.55 Which ionic compound is expected to form from combining the following pairs of elements? (**a**) calcium and nitrogen, (**b**) cesium and bromine, (**c**) strontium and sulfur, (**d**) aluminum and selenium.

8.56 Write the electron configurations for the following ions, and determine which have noble-gas configurations: (**a**) Fe^{2+}, (**b**) V^{3+}, (**c**) Ni^{2+}, (**d**) Pt^{2+}, (**e**) Ge^{2-}, (**f**) Ba^{2+}.

8.57 NaCl and KF have the same crystal structure. The only difference between the two is the distance that separates cations and anions. (**a**) The lattice energies of NaCl and KF are given in Table 8.1. Based on the lattice energies, would you expect the Na—Cl or the K—F distance to be longer? (**b**) Use the ionic radii given in Figure 7.8 to estimate the Na—Cl and K—F distances.

8.58 (**a**) Does the lattice energy of an ionic solid increase or decrease (i) as the charges of the ions increase, (ii) as the sizes of the ions increase? (**b**) Arrange the following substances not listed in Table 8.1 according to their expected lattice energies, listing them from lowest lattice energy to the highest: MgS, KI, GaN, LiBr.

8.59 Which of the following trends in lattice energy is due to differences in ionic radii? (**a**) LiF > NaF > CsF, (**b**) CaO > KCl, (**c**) PbS > Li_2O.

8.60 List the individual steps used in constructing a Born–Haber cycle for the formation of BaI_2 from the elements. Which of the steps would you expect to be exothermic?

8.61 Use data from Appendix C, Figure 7.10, and Figure 7.12 to calculate the lattice energy of RbCl.

8.62 (**a**) Based on the lattice energies of $MgCl_2$ and $SrCl_2$ given in Table 8.1, what is the range of values that you would expect for the lattice energy of $CaCl_2$? (**b**) Using data from Appendix C, Figure 7.10, Figure 7.12, and the value of the second ionization energy for Ca, 1145 kJ/mol, calculate the lattice energy of $CaCl_2$.

Covalent Bonding, Electronegativity, and Bond Polarity (Sections 8.3 and 8.4)

8.63 Using Lewis symbols and Lewis structures, diagram the formation of BF_3 from B and F atoms, showing valence-shell electrons. (**a**) How many valence electrons does B have initially? (**b**) How many bonds F has to make in order to achieve an octet? (**c**) How many valence electrons surround the B in the BF_3 molecule? (**d**) How many valence electrons surround each F in the BF_3 molecule? (**e**) Does BF_3 obey the octet rule?

8.64 (**a**) Construct a Lewis structure for hydrogen peroxide, H_2O_2, in which each atom achieves an octet of electrons. (**b**) How many bonding electrons are between the two oxygen atoms? (**c**) Do you expect the O—O bond in H_2O_2 to be longer or shorter than the O—O bond in O_2? Explain.

8.65 (**a**) What is the trend in electronegativity going from left to right in a row of the periodic table? (**b**) How do electronegativity values generally vary going down a column in the periodic table? (**c**) True or false: The most easily ionizable elements are the most electronegative.

8.66 By referring only to the periodic table, select (**a**) the most electronegative element in Group 13; (**b**) the least electronegative element in the group As, Se, and Br; (**c**) the most electronegative element in the group K, Mg, Al, and In; (**d**) the element in the group Na, Be, Si, Ar, that is most likely to form an ionic compound with Br.

8.67 Arrange the bonds in each of the following sets in order of increasing polarity: (**a**) C—F, O—F, Be—F; (**b**) O—Cl, S—Br, C—P; (**c**) C—S, B—F, N—O.

8.68 The iodine monobromide molecule, IBr, has a bond length of 249 pm and a dipole moment of 1.21 D. (**a**) Which atom of the molecule is expected to have a negative charge? (**b**) Calculate the effective charges on the I and Br atoms in IBr in units of the electronic charge, *e*.

8.69 In the following pairs of binary compounds, determine which one is a molecular substance and which one is an ionic substance. Use the appropriate naming convention (for ionic or molecular substances) to assign a name to each compound: (**a**) $TiCl_4$ and CaF_2, (**b**) ClF_3 and VF_3, (**c**) $SbCl_5$ and AlF_3.

Lewis Structures; Resonance Structures (Sections 8.5 and 8.6)

8.70 Write Lewis structures for the following: (**a**) H_2CO (both H atoms are bonded to C), (**b**) H_2O_2, (**c**) C_2F_6 (contains a C—C bond), (**d**) AsO_3^{3-}, (**e**) H_2SO_3 (H is bonded to O), (**f**) NH_2Cl.

8.71 (**a**) Draw the dominant Lewis structure for the phosphorus trifluoride molecule, PF_3. (**b**) Determine the oxidation numbers of the P and F atoms. (**c**) Determine the formal charges of the P and F atoms.

8.72 For each of the following molecules or ions of sulfur and oxygen, write a single Lewis structure that obeys the octet rule, and calculate the oxidation numbers and formal charges on all the atoms: (**a**) SO_2, (**b**) SO_3, (**c**) SO_3^{2-}. (**d**) Arrange these molecules/ions in order of increasing S—O bond length.

8.73 Consider the formate ion, HCO_2^-, which is the anion formed when formic acid loses an H^+ ion. The H and the two O atoms are bonded to the central C atom. (**a**) Draw the best Lewis structure(s) for this ion. (**b**) Are resonance structures needed to describe the structure? (**c**) Would you predict that the C—O bond lengths in the formate ion would be longer or shorter relative to those in CO_2?

8.74 Compare the O—O bond length in O_2 versus H_2O_2. Which bond is shorter? Why?

Exceptions to the Octet Rule (Section 8.7)

8.75 (**a**) Which of these compounds is an exception to the octet rule: carbon dioxide, water, ammonia, phosphorus trifluoride, or arsenic pentafluoride? (**b**) Which of these compounds or ions is an exception to the octet rule:

borohydride (BH_4^-), borazine ($B_3N_3H_6$, which is analogous to benzene with alternating B and N in the ring), or boron trichloride?

8.76 For Group 13–17 elements in the third row of the periodic table and beyond, the octet rule is often not obeyed. A friend of yours says this is because these heavier elements are more likely to make double or triple bonds. Another friend of yours says that this is because the heavier elements are larger and can make bonds to more than four atoms at a time. Which friend is more correct?

8.77 Draw the Lewis structures for each of the following molecules or ions. Identify instances where the octet rule is not obeyed; state which atom in each compound does not follow the octet rule; and state how many electrons surround these atoms: (**a**) PF_6^-, (**b**) $BeCl_2$, (**c**) NH_3, (**d**) XeF_2O (the Xe is the central atom), (**e**) SO_4^{2-}.

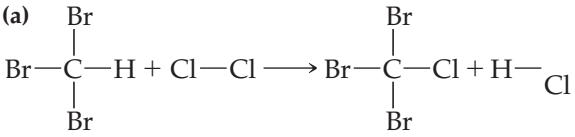
8.78 (**a**) Describe the molecule xenon trioxide, XeO_3, using four possible Lewis structures, one each with zero, one, two, or three Xe—O double bonds. (**b**) Do any of these resonance structures satisfy the octet rule for every atom in the molecule? (**c**) Do any of the four Lewis structures have multiple resonance structures? If so, how many resonance structures do you find? (**d**) Which of the Lewis structures in part (a) yields the most favorable formal charges for the molecule?

8.79 Some chemists believe that satisfaction of the octet rule should be the top criterion for choosing the dominant Lewis structure of a molecule or ion. Other chemists believe that achieving the best formal charges should be the top criterion. Consider the dihydrogen phosphate ion, $H_2PO_4^-$, in which the H atoms are bonded to O atoms. (**a**) What is the predicted dominant Lewis structure if satisfying the octet rule is the top criterion? (**b**) What is the predicted dominant Lewis structure if achieving the best formal charges is the top criterion?

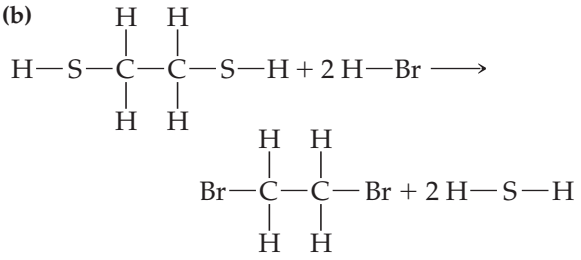
Strengths and Lengths of Covalent Bonds (Section 8.8)

8.80 Using Table 8.3, estimate ΔH for the following gas-phase reactions:

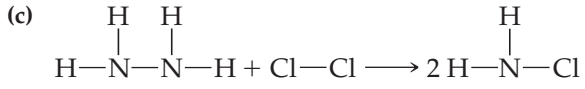
(**a**)



(**b**)



(**c**)



8.81 State whether each of these statements is true or false. (**a**) An oxygen–oxygen double bond is shorter than an oxygen–oxygen single bond. (**b**) There are three lone pair electrons in the NH_3 molecule. (**c**) The C—C bond in ethene is longer than the C—C bond in polyethene. (**d**) The C—Cl bond is shorter than the C—Br bond. (**e**) The greater the difference in the electronegativity of atoms in a bond, the stronger the bond.

8.82 We can define average bond enthalpies and bond lengths for ionic bonds, just like we have for covalent bonds. Which ionic bond is predicted to have the smaller bond enthalpy, Li—F or Cs—F?

8.83 A *carbene* is a compound that has a carbon bonded to two atoms and a lone pair remaining on the carbon. Many carbenes are very reactive. (**a**) Draw the Lewis structure for the simplest carbene, H_2C. (**b**) Predict the length of the carbon–carbon bond you would expect if two H_2C molecules reacted with each other by a combination reaction.

Additional Exercises

8.84 A new compound is made that has a C—O bond length of 120 pm. Is this bond likely to be a single, double, or triple C—O bond?

8.85 A new compound is made that has a C—N bond length of 118 pm. Is this bond likely to be a single, double, or triple C—N bond?

8.86 Consider the lattice energies of the following Group 2 compounds: BeH_2, 3205 kJ/mol; MgH_2, 2791 kJ/mol; CaH_2, 2410 kJ/mol; SrH_2, 2250 kJ/mol; BaH_2, 2121 kJ/mol. (**a**) What is the oxidation number of H in these compounds? (**b**) Assuming that all of these compounds have the same three-dimensional arrangement of ions in the solid, which of these compounds has the shortest cation–anion distance? (**c**) Consider BeH_2. Does it require 3205 kJ of energy to break one mole of the solid into its ions, or does breaking up one mole of solid into its ions release 3205 kJ of energy? (**d**) The lattice energy of ZnH_2 is 2870 kJ/mol. Considering the trend in lattice enthalpies in the Group 2 compounds, predict which Group 2 element is most similar in ionic radius to the Zn^{2+} ion.

8.87 Based on data in Table 8.1, estimate (within 30 kJ/mol) the lattice energy for (**a**) LiBr, (**b**) CsBr, (**c**) $CaCl_2$.

8.88 A metal oxide has a lattice energy in the range of 3300 kJ/mol. Is the charge on the metal ion M likely to be 1^+, 2^+, or 3^+? Explain.

8.89 The ionic compound CaO crystallizes with the same structure as sodium chloride (Figure 8.3). (**a**) In this structure, how many O^{2-} are in contact with each Ca^{2+} ion (*Hint:* Remember the pattern of ions shown in Figure 8.3 repeats over and over again in all three directions.) (**b**) Would energy be consumed or released if a crystal of CaO was converted to a collection of widely separated Ca—O ion pairs? (**c**) From the ionic radii given in Figure 7.8, calculate the potential energy of a single Ca—O ion pair that is just touching (the magnitude of electronic charge is given on the inside back cover). (**d**) Calculate the energy of a mole of such pairs.

How does this compare to the lattice energy of CaO? (**e**) What factor do you think accounts for most of the discrepancy between the energies in part (d)—the bonding in CaO is more covalent than ionic, or the electrostatic interactions in a crystal lattice are more complicated than those in a single ion pair?

8.90 Construct a Born–Haber cycle for the formation of the hypothetical compound $NaCl_2$, where the sodium ion has a 2+ charge (the second ionization energy for sodium is given in Table 7.2). (**a**) How large would the lattice energy need to be for the formation of $NaCl_2$ to be exothermic? (**b**) If we were to estimate the lattice energy of $NaCl_2$ to be roughly equal to that of $MgCl_2$ (2326 kJ/mol from Table 8.1), what value would you obtain for the standard enthalpy of formation, ΔH_f°, of $NaCl_2$?

8.91 A classmate of yours is convinced that he knows everything about electronegativity. (**a**) In the case of atoms X and Y having different electronegativities, he says, the diatomic molecule X—Y must be polar. Is your classmate correct? (**b**) Your classmate says that the farther the two atoms are apart in a bond, the larger the dipole moment will be. Is your classmate correct?

8.92 Consider the collection of nonmetallic elements: B, As, O, and I. (**a**) Which two would form the most polar single bond? (**b**) Which two would form the longest single bond? (**c**) Which one would be likely to form a compound of formula XY_3?(**d**) Which element would likely to participate in two covalent bonds?

8.93 The substance chlorine monoxide, ClO(*g*), is important in atmospheric processes that lead to depletion of the ozone layer. The ClO molecule has an experimental dipole moment of 4.1×10^{-30} C-m, and the Cl—O bond length is 160 pm. (**a**) Determine the magnitude of the charges on the Cl and O atoms in units of the electronic charge, *e*. (**b**) Based on the electronegativities of the elements, which atom would you expect to have a partial negative charge in the ClO molecule? (**c**) Using formal charges as a guide, propose the dominant Lewis structure for the molecule. (**d**) The anion ClO^- exists. What is the formal charge on the Cl for the best Lewis structure for ClO^-?

8.94 (**a**) Using the electronegativities of Br and Cl, estimate the partial charges on the atoms in the Br—Cl molecule. (**b**) Using these partial charges and the atomic radii given in Figure 7.8, estimate the dipole moment of the molecule. (**c**) The measured dipole moment of BrCl is 0.57 D. If you assume the bond length in BrCl is the sum of the atomic radii, what are the partial charges on the atoms in BrCl using the experimental dipole moment?

8.95 A major challenge in implementing the "hydrogen economy" is finding a safe, lightweight, and compact way of storing hydrogen for use as a fuel. The hydrides of light metals are attractive for hydrogen storage because they can store a high weight percentage of hydrogen in a small volume. For example, $NaAlH_4$ can release 5.6% of its mass as H_2 upon decomposing to NaH(*s*), Al(*s*), and $H_2(g)$. $NaAlH_4$ possesses both covalent bonds, which hold polyatomic anions together, and ionic bonds. (**a**) Write a balanced equation for the decomposition of $NaAlH_4$. (**b**) Which element in $NaAlH_4$ is the most electronegative? Which one is the least electronegative? (**c**) Based on electronegativity differences, predict the identity of the polyatomic anion. Draw a Lewis structure for this ion. (**d**) What is the formal charge on hydrogen in the polyatomic ion?

8.96 Although I_3^- is a known ion, F_3^- is not. (**a**) Draw the Lewis structure for I_3^- (it is linear, not a triangle). (**b**) One of your classmates says that F_3^- does not exist because F is too electronegative to make bonds with another atom. Give an example that proves your classmate is wrong. (**c**) Another classmate says F_3^- does not exist because it would violate the octet rule. Is this classmate possibly correct? (**d**) Yet another classmate says F_3^- does not exist because F is too small to make bonds to more than one atom. Is this classmate possibly correct?

8.97 Calculate the formal charge on the indicated atom in each of the following molecules or ions: (**a**) the central oxygen atom in O_3, (**b**) phosphorus in PF_6^-, (**c**) nitrogen in NO_2, (**d**) iodine in ICl_3, (**e**) chlorine in $HClO_4$ (hydrogen is bonded to O).

8.98 The hypochlorite ion, ClO^-, is the active ingredient in bleach. The perchlorate ion, ClO_4^-, is a main component of rocket propellants. Draw Lewis structures for both ions. (**a**) What is the formal charge of Cl in the hypochlorite ion? (**b**) What is the formal charge of Cl in the perchlorate ion, assuming the Cl—O bonds are all single bonds? (**c**) What is the oxidation number of Cl in the hypochlorite ion? (**d**) What is the oxidation number of Cl in the perchlorate ion, assuming the Cl—O bonds are all single bonds? (**e**) In a redox reaction, which ion would you expect to be more easily reduced?

8.99 The following three Lewis structures can be drawn for N_2O:



(**a**) Using formal charges, which of these three resonance forms is likely to be the most important? (**b**) The N—N bond length in N_2O is 112 pm, slightly longer than a typical N≡N bond; and the N—O bond length is 119 pm, slightly shorter than a typical N=O bond (see Table 8.4). Based on these data, which resonance structure best represents N_2O?

Integrative Exercises

8.100 Consider the hypothetical molecule A—A=A with a bent shape. Are the following statements true or false? (**a**) This molecule cannot exist. (**b**) If this molecule exists, it must possess an odd electron.

8.101 An important reaction for the conversion of natural gas to other useful hydrocarbons is the conversion of methane to ethane.

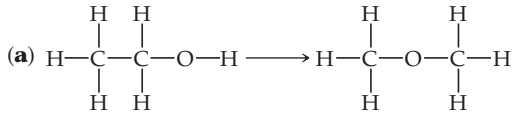
$$2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

In practice, this reaction is carried out in the presence of oxygen, which converts the hydrogen produced into water.

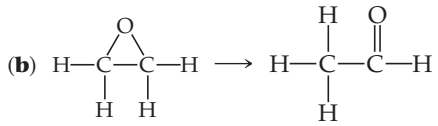
$$2\,CH_4(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_6(g) + H_2O(g)$$

Use Table 8.3 to estimate ΔH for these two reactions. Why is the conversion of methane to ethane more favorable when oxygen is used?

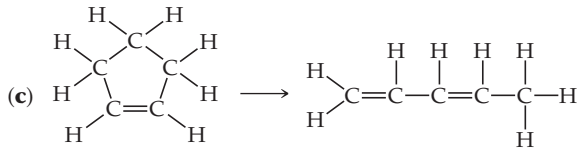
8.102 Two compounds are isomers if they have the same chemical formula but different arrangements of atoms. Use Table 8.3 to estimate ΔH for each of the following gas-phase isomerization reactions and indicate which isomer has the lower enthalpy.



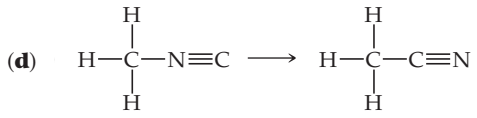
(**a**) Ethanol → Dimethyl ether



(**b**) Ethylene oxide → Acetaldehyde



(**c**) Cyclopentene → Pentadiene



(**d**) Methyl isocyanide → Acetonitrile

8.103 The Ti^{2+} ion is isoelectronic with the Ca atom. (**a**) Write the electron configurations of Ti^{2+} and Ca. (**b**) Calculate the number of unpaired electrons for Ca and for Ti^{2+}. (**c**) What charge would Ti have to be isoelectronic with Ca^{2+}?

8.104 (**a**) Draw the Lewis structure for hydrogen peroxide, H_2O_2. (**b**) What is the weakest bond in hydrogen peroxide? (**c**) Hydrogen peroxide is sold commercially as an aqueous solution in brown bottles to protect it from light. Calculate the longest wavelength of light that has sufficient energy to break the weakest bond in hydrogen peroxide.

8.105 The electron affinity of oxygen is −141 kJ/mol, corresponding to the reaction

$$O(g) + e^- \longrightarrow O^-(g)$$

The lattice energy of $K_2O(s)$ is 2238 kJ/mol. Use these data along with data in Appendix C and Figure 7.10 to calculate the "second electron affinity" of oxygen, corresponding to the reaction

$$O^-(g) + e^- \longrightarrow O^{2-}(g)$$

8.106 You and a partner are asked to complete a lab entitled "Carbonates of Group 2 metal" that is scheduled to extend over two lab periods. The first lab, which is to be completed by your partner, is devoted to carrying out compositional analysis and determine the identity of the Group 2 metal (M). In the second lab, you are to determine the melting point of this compound. Upon going to lab you find two unlabeled vials containing white powder. You also find the following notes in your partner's notebook—*Compound 1*: 40.04% M and 12.00% C, 47.96% O (by mass), *Compound 2*: 69.59% M, 6.09% C, and 24.32% O (by mass). (**a**) What is the empirical formula for Compound 1 and the identity of M? (**b**) What is the empirical formula for Compound 2 and the identity of M? Upon determining the melting points of these two compounds, you find that both compounds do not melt up to the maximum temperature of your apparatus, instead, the compounds decompose and liberate colorless gas. (**c**) What is the identity of the colorless gas? (**d**) Write the chemical equation for the decomposition reactions of Compound 1 and Compound 2. (**e**) Are Compound 1 and Compound 2 ionic or molecular?

8.107 One scale for electronegativity is based on the concept that the electronegativity of any atom is proportional to the ionization energy of the atom minus its electron affinity: electronegativity = $k(I - EA)$, where k is a proportionality constant. (**a**) How does this definition explain why the electronegativity of F is greater than that of Cl, even though Cl has the greater electron affinity? (**b**) Why are both ionization energy and electron affinity relevant to the notion of electronegativity? (**c**) By using data in Chapter 7, determine the value of k that would lead to an electronegativity of 4.0 for F under this definition. (**d**) Use your result from part (c) to determine the electronegativities of Cl and O using this scale. (**e**) Another scale for electronegativity defines electronegativity as the average of an atom's first ionization energy and its electron affinity. Using this scale, calculate the electronegativities for the halogens, and scale them so that fluorine has an electronegativity of 4.0. On this scale, what is Br's electronegativity?

8.108 The compound chloral hydrate, known in detective stories as knockout drops, is composed of 14.52% C, 1.83% H, 64.30% Cl, and 13.35% O by mass, and has a molar mass of 165.4 g/mol. (**a**) What is the empirical formula of this substance? (**b**) What is the molecular formula of this substance? (**c**) Draw the Lewis structure of the molecule, assuming that the Cl atoms bond to a single C atom and that there are a C—C bond and two C—O bonds in the compound.

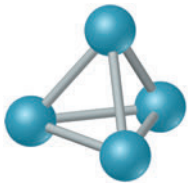
8.109 Potassium peroxide is composed of 70.96% K and 29.04% O. Each peroxide ion has a net charge of 2^-. (**a**) Given the molecular weight of the compound is 110.19, determine the chemical formula of potassium peroxide. (**b**) What is the number of valance electron pairs in the peroxide ion? (**c**) Draw the Lewis structure of the peroxide ion. (**d**) Compare the O—O bond distance in oxygen molecule and potassium peroxide.

8.110 Acetylene (C_2H_2) and nitrogen (N_2) both contain a triple bond, but they differ greatly in their chemical properties. (**a**) Write the Lewis structures for the two substances. (**b**) By referring to Appendix C, look up the enthalpies of formation of acetylene and nitrogen. Which compound is more stable? (**c**) Write balanced chemical equations for the complete oxidation of N_2 to form $N_2O_5(g)$ and of acetylene to form $CO_2(g)$ and $H_2O(g)$. (**d**) Calculate the enthalpy of oxidation per mole for N_2 and for C_2H_2 (the enthalpy of formation of $N_2O_5(g)$ is 11.30 kJ/mol). (**e**) Both N_2 and C_2H_2 possess triple bonds with quite high bond enthalpies (Table 8.3). Calculate the enthalpy of hydrogenation per mole for both compounds: acetylene plus H_2 to make methane, CH_4; nitrogen plus H_2 to make ammonia, NH_3.

8.111 Under special conditions, sulfur reacts with anhydrous liquid ammonia to form a binary compound of sulfur and nitrogen. The compound is found to consist of 69.6% S and 30.4% N. Measurements of its molecular mass yield a value of 184.3 g/mol. The compound occasionally detonates on being struck or when heated rapidly. The sulfur and nitrogen atoms of the molecule are joined in a ring. All the bonds in the ring are of the same length. (**a**) Calculate the empirical and molecular formulas for the substance. (**b**) Write Lewis structures for the molecule, based on the information you are given. (*Hint:* You should find a relatively small number of dominant Lewis structures.) **(c)** Predict the bond distances between the atoms

in the ring. (*Note*: The S—S distance in the S_8 ring is 205 pm.) (**d**) The enthalpy of formation of the compound is estimated to be 480 kJ/mol^{-1}. ΔH_f° of S(*g*) is 222.8 kJ/mol. Estimate the average bond enthalpy in the compound.

8.112 A common form of elemental phosphorus is the white phosphorus, where four P atoms are arranged in a tetrahedron. All four phosphorus atoms are equivalent.



White phosphorus reacts spontaneously with the oxygen in air to form P_4O_6. (**a**) How many valance electron pairs are in the P_4O_6 molecule? (**b**) When P_4O_6 is dissolved in water, it produces a H_3PO_3 molecule. H_3PO_3 has two forms, P forms three covalent bonds in the first form and P forms five covalent bonds in the second form. Draw two possible Lewis structures of H_3PO_3. (**c**) Which structure obeys the octet rule?

8.113 Trifluoroacetic acid has the chemical formula CF_3CO_2H. It is a colorless liquid that has a density of 1.489 g/mL. (**a**) Trifluoroacetic acid contains one CF_3 unit and is connected to the other C atom which bonds with both O's. Draw the Lewis structure for trifluoroacetic acid. (**b**) Trifluoroacetic acid can react with NaOH in aqueous solution to produce the trifluoroacetate ion, CF_3COO^-. Write the balanced chemical equation for this reaction. (**c**) Draw the Lewis structure of the trifluoroacetate ion, showing resonance if present. (**d**) How many milliliters of a 0.500 M solution of NaOH would it take to neutralize 10.5 mL of trifluoroacetic acid?

8.114 Ammonia reacts with boron trifluoride to form a stable compound, as we saw in Section 8.7. (**a**) Draw the Lewis structure of the ammonia–boron trifluoride reaction product. (**b**) The B—N bond is obviously more polar than the C—C bond. Draw the charge distribution you expect on the B—N bond within the molecule (using the delta plus and delta minus symbols mentioned in Section 8.4). (**c**) Boron trichloride also reacts with ammonia in a similar way to the trifluoride. Predict whether the B—N bond in the trichloride reaction product would be more or less polar than the B—N bond in the trifluoride product, and justify your reasoning.

8.115 Ammonium chloride, NH_4Cl, is a very soluble salt in water. (**a**) Draw the Lewis structures of the ammonium and chloride ions. (**b**) Is there an N—Cl bond in solid ammonium chloride? (**c**) If you dissolve 14 g of ammonium chloride in 500.0 mL of water, what is the molar concentration of the solution? (**d**) How many grams of silver nitrate do you need to add to the solution in part (c) to precipitate all of the chloride as silver chloride?

Design an Experiment

You have learned that the resonance of benzene, C_6H_6, gives the compound special stability.

(**a**) By using data in Appendix C, compare the heat of combustion of 1.0 mol $C_6H_6(g)$ to the heat of combustion of 3.0 mol acetylene, $C_2H_2(g)$. Which has the greater fuel value, 1.0 mol $C_6H_6(g)$ or 3.0 mol $C_2H_2(g)$? Are your calculations consistent with benzene being especially stable? (**b**) Repeat part (a), with the appropriate molecules, for toluene ($C_6H_5CH_3$), a derivative of benzene that has a —CH_3 group in place of one H. (**c**) Another reaction you can use to compare molecules is *hydrogenation*, the reaction of a carbon–carbon double bond with H_2 to make a C—C single bond and two C—H single bonds. The experimental heat of hydrogenation of benzene to make cyclohexane (C_6H_{12}, a six-membered ring with 6 C—C single bonds and 12 C—H bonds) is 208 kJ/mol. The experimental heat of hydrogenation of cyclohexene (C_6H_{10}, a six-membered ring with one C=C double bond, 5 C—C single bonds, and 10 C—H bonds) to make cyclohexane is 120 kJ/mol. Show how these data can provide you with an estimate of the *resonance stabilization energy* of benzene. (**d**) Are the bond lengths or angles in benzene, compared to other hydrocarbons, sufficient to decide if benzene exhibits resonance and is especially stable? Discuss.

WHAT'S AHEAD

9.1 ▶ Molecular Shapes

9.2 ▶ The VSEPR Model

9.3 ▶ Molecular Shape and Molecular Polarity

9.4 ▶ Covalent Bonding and Orbital Overlap

9.5 ▶ Hybrid Orbitals

9.6 ▶ Multiple Bonds

9.7 ▶ Molecular Orbitals

9.8 ▶ Bonding in Period 2 Diatomic Molecules

9

MOLECULAR GEOMETRY AND BONDING THEORIES

9.1 | Molecular Shapes



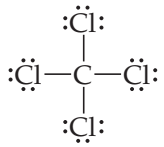
Orchid flowers demonstrate the intimate connection between shape and function. The bee orchid (*ophrys apifera*), for example, has a central labellum that mimics the abdomen of a bee, and is even slightly hairy. The scent of the orchid is similar to that of a female bee. Pollen gets transferred when a male bee attempts to mate with the orchid, to be carried by the unwitting insect to another bee orchid.

In this chapter, our first goal is to understand the relationship between two-dimensional Lewis structures and three-dimensional molecular shapes. We will see the intimate relationship between the number of electrons in a molecule and the overall shape it adopts. Armed with this knowledge, we can examine more closely the nature of covalent bonds. The lines used to depict bonds in Lewis structures provide important clues about the orbitals that molecules use in bonding. By examining these orbitals, we can gain a greater understanding of the behavior of molecules.

By the end of this section, you should be able to

- Recognize the five basic shapes from which geometries of AB_n molecules are derived

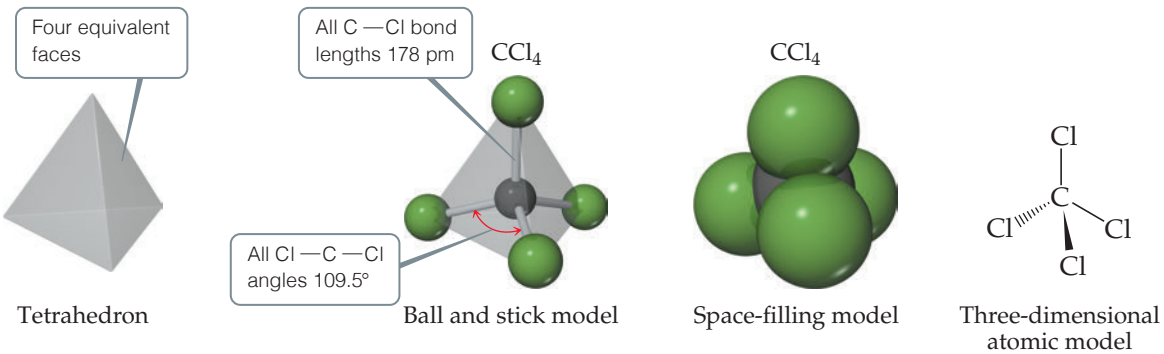
In Chapter 8, we used Lewis structures to account for the formulas of covalent compounds. Lewis structures, however, do not indicate the shapes of molecules; they simply show the number and types of bonds. For example, the Lewis structure of CCl_4 tells us only that four Cl atoms are bonded to a central C atom:



The Lewis structure is drawn with the atoms all in the same plane. As shown in **Figure 9.1**, however, the actual three-dimensional arrangement has the Cl atoms at the corners of a *tetrahedron*, a geometric object with four corners and four faces, each an equilateral triangle.

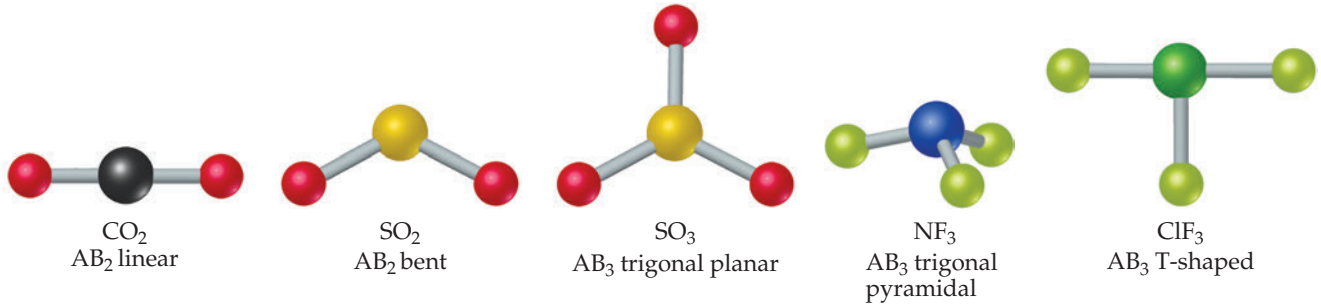
The shape of a molecule is determined by its **bond angles**, the angles made by the lines joining the nuclei of the atoms in the molecule. The bond angles of a molecule, together with the bond lengths, define the shape and size of the molecule. In Figure 9.1, you should be able to see that there are six Cl—C—Cl bond angles in CCl_4, all of which have the same value. That bond angle, 109.5°, is characteristic of a tetrahedron. In addition, all four C—Cl bonds are of the same length (178 pm). Thus, the shape and size of CCl_4 are completely described by stating that the molecule is tetrahedral with C—Cl bonds of length 178 pm. To draw the three-dimensional structure of a molecule on paper, chemists use a convention shown in Figure 9.1: Regular lines imply the bond is the plane of the paper, a heavy wedge is used to show that the bond is coming out of the paper toward you, and the dashed line is used to show that the bond is pointing away from you, through the back of the paper.

Go Figure In the space-filling model, what determines the relative sizes of the spheres?



▲ **Figure 9.1** **Tetrahedral shape of CCl_4.**

Go Figure Which of these structures is not planar?



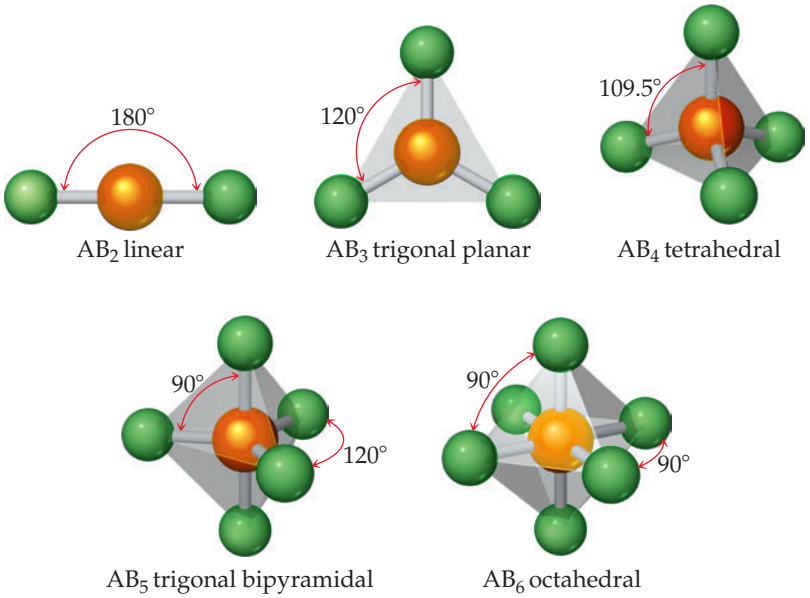
▲ **Figure 9.2** **Shapes of AB_2 and AB_3 molecules.**

We begin our discussion of molecular shapes with molecules (and ions) that, like CCl_4, have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula AB_n in which the central atom A is bonded to n B atoms. Both CO_2 and H_2O are AB_2 molecules, for example, whereas SO_3 and NH_3 are AB_3 molecules, and so on.

The number of shapes possible for AB_n molecules depends on the value of n. Those commonly found for AB_2 and AB_3 molecules are shown in **Figure 9.2**. An AB_2 molecule must be either *linear* (bond angle = 180°) or *bent* (bond angle ≠ 180°). For AB_3 molecules, the two most common shapes place the B atoms at the corners of an equilateral triangle. If the A atom lies in the same plane as the B atoms, the shape is called *trigonal planar*. If the A atom lies above the plane of the B atoms, the shape is called *trigonal pyramidal* (a pyramid with an equilateral triangle as its base). Some AB_3 molecules, such as ClF_3, are *T-shaped*, a relatively unusual shape shown in Figure 9.2. The atoms lie in one plane with two B—A—B angles of about 90°, and a third angle close to 180°.

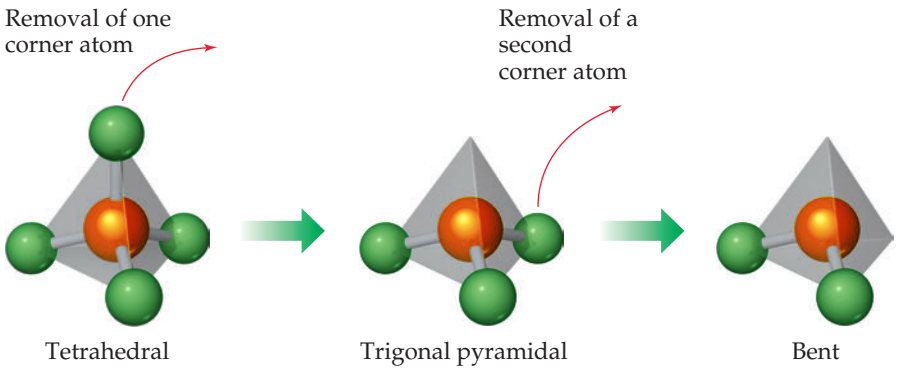
Quite remarkably, the shapes of most AB_n molecules can be derived from just five basic geometric arrangements, shown in **Figure 9.3**. All of these are highly symmetric arrangements of the n B atoms around the central A atom. We have already seen the first three shapes: linear, trigonal planar, and tetrahedral. The trigonal bipyramid shape for

Go Figure Which of these molecular shapes do you expect for the SF_6 molecule?



▲ **Figure 9.3** **Shapes allowing maximum distances between B atoms in AB_n molecules.**

Go Figure In going from the tetrahedral shape to the bent shape, does it matter which two of the atoms we choose to remove?



▲ **Figure 9.4** **Derivatives of the tetrahedral molecular shape.**

AB_5 can be thought of as a trigonal planar AB_3 arrangement with two additional atoms, one above and one below the equilateral triangle. The octahedral shape for AB_6 has all six B atoms at the same distance from atom A with 90° B—A—B angles between all neighboring B atoms. Its symmetric shape (and its name) is derived from the *octahedron*, with eight faces, all of which are equilateral triangles.



Octahedron

You may have noticed that some of the shapes we have already discussed are *not* among the five shapes in Figure 9.3. For example, in Figure 9.2, neither the bent shape of the SO_2 molecule nor the trigonal pyramidal shape of the NF_3 molecule is among the shapes in Figure 9.3. However, as we soon will see, we can derive additional shapes, such as bent and trigonal pyramidal, by starting with one of our five basic arrangements. Starting with a tetrahedron, for example, we can remove atoms successively from the vertices, as shown in **Figure 9.4**. When an atom is removed from one vertex of a tetrahedron, the remaining AB_3 fragment has a trigonal-pyramidal geometry. When a second atom is removed, the remaining AB_2 fragment has a bent geometry.

Why do most AB_n molecules have shapes related to those shown in Figure 9.3? Can we predict these shapes? When A is a representative element (one from the *s* block or *p* block of the periodic table), we can answer these questions by using the **valence-shell electron-pair repulsion (VSEPR) model**. Although the name is rather imposing, the model is quite simple. It has useful predictive capabilities, as we will see in Section 9.2.

Self-Assessment Exercise

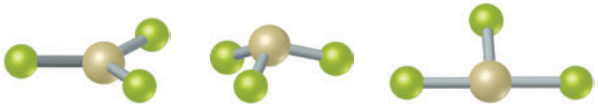
9.1 In addition to tetrahedral, another common shape for AB_4 molecules is *square planar*. All five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square. Which shape in Figure 9.3 could lead to a square-planar shape upon removal of one or more atoms?

(a) Tetrahedral
(b) Trigonal bipyramidal
(c) Octahedral

Exercises

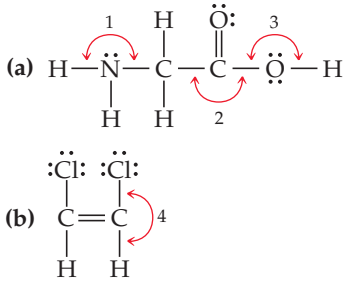
9.2 How many nonbonding electron pairs are there in each of the following molecules: (**a**) $N(CH_3)_3$, (**b**) CO, (**c**) BF_3, (**d**) SO_2?

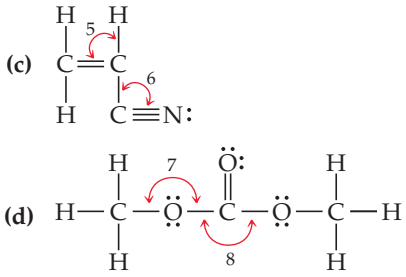
9.3 The figure that follows shows ball-and-stick drawings of three possible shapes of an AF_3 molecule. (**a**) For each shape, give the electron-domain geometry on which the molecular geometry is based. (**b**) For each shape, how many nonbonding electron domains are there on atom A? (**c**) Which of the following elements will lead to an AF_3 molecule with the shape in (ii): Li, B, N, Al, P, Cl? (**d**) Name an element A that is expected to lead to the AF_3 structure shown in (iii).



(i) (ii) (iii)

9.4 Give the approximate values for the indicated bond angles in the following molecules:

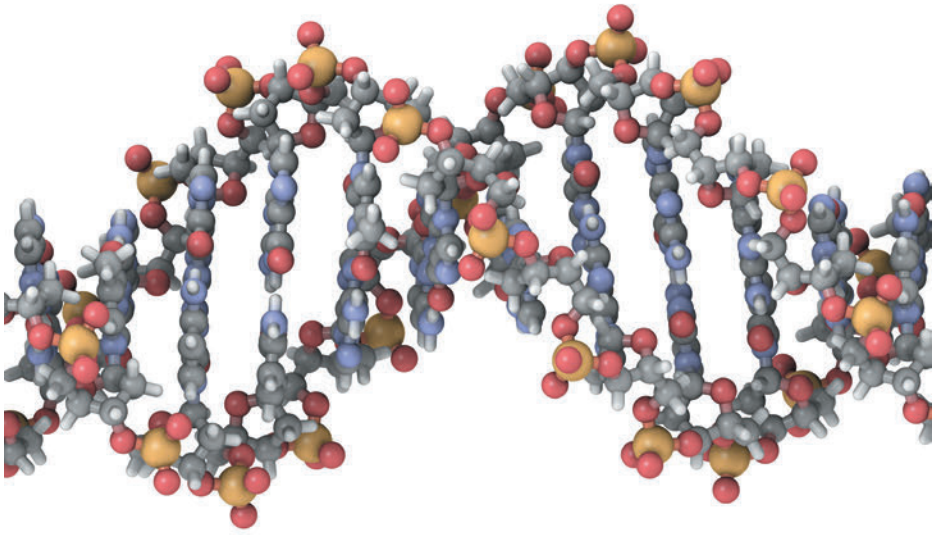




Answers to Self-Assessment Exercise

9.1 (c)

9.2 The VSEPR Model



One of the most iconic shapes of a large molecules is the double helix structure of DNA. We instantly recognize it as a three-dimensional object. Less obvious is the association between a formula written on a page and the shape of the substance, yet every compound has a unique size and shape.

Lewis structures help us understand the compositions of molecules and their covalent bonds. However, Lewis structures do not show one of the most important aspects of molecules—their overall shapes. The shape and size of molecules—sometimes referred to as molecular architecture—are defined by the angles and distances between the nuclei of the component atoms.

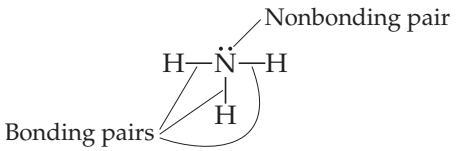
By the end of this section, you should be able to

- Draw and name the predicted three-dimensional shapes of molecules using the VSEPR model.

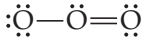
Imagine tying two identical balloons together at their ends. As shown in **Figure 9.5**, the two balloons naturally orient themselves to point away from each other; that is, they try to "get out of each other's way" as much as possible. If we add a third balloon, the

balloons orient themselves toward the vertices of an equilateral triangle, and if we add a fourth balloon, they adopt a tetrahedral shape. We see that an optimum geometry exists for each number of balloons.

In some ways, the electrons in molecules behave like these balloons. We have seen that a single covalent bond is formed between two atoms when a pair of electrons occupies the space between the atoms. A *bonding pair* of electrons thus defines a region in which the electrons are most likely to be found. We will refer to such a region as an **electron domain**. Likewise, a *nonbonding pair* (or *lone pair*) of electrons, which was also discussed in Section 8.3, defines an electron domain that is located principally on one atom. For example, the Lewis structure of NH_3 has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):



Each multiple bond in a molecule also constitutes a single electron domain. Thus, the following resonance structure for O_3 has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):



In general, *each nonbonding pair, single bond, or multiple bond produces a single electron domain around the central atom in a molecule.*

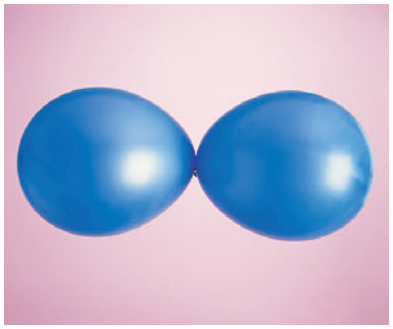
The VSEPR model is based on the idea that electron domains are negatively charged and therefore repel one another. Like the balloons in Figure 9.5, electron domains try to stay out of one another's way.

The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.

In fact, the analogy between electron domains and balloons is so close that the same preferred geometries are found in both cases. Like the balloons in Figure 9.5, two electron domains orient *linearly*, three domains orient in a *trigonal-planar* fashion, and four orient *tetrahedrally*. These arrangements, together with those for five- and six-electron domains, are summarized in **Table 9.1**. If you compare the geometries in Table 9.1 with those in Figure 9.3, you will see that they are the same.

The shapes of different AB_n molecules or ions depend on the number of electron domains surrounding the central atom.

The arrangement of electron domains about the central atom of an AB_n molecule or ion is called its **electron-domain geometry**. In contrast, the **molecular geometry** is the arrangement of *only the atoms* in a molecule or ion—any nonbonding pairs in the molecule are *not* part of the description of the molecular geometry.



Two balloons
linear orientation



Three balloons
trigonal-planar orientation



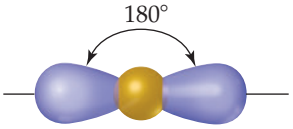
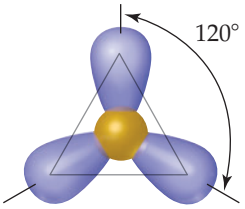
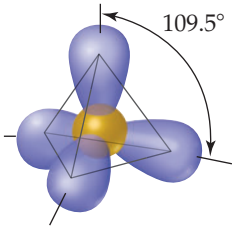
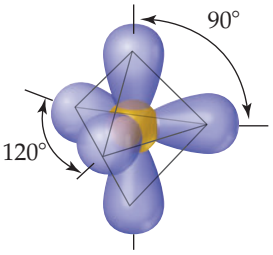
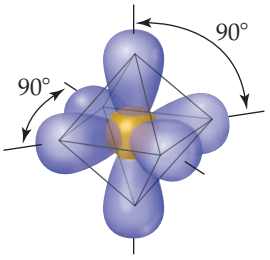
Four balloons
tetrahedral orientation

▲ **Figure 9.5** **A balloon analogy for electron domains.**

Applying the VSEPR Model to Determine Molecular Shapes

In determining the shape of any molecule, we first use the VSEPR model to predict the electron-domain geometry. From knowing how many of the domains are due to nonbonding pairs, we can then predict the molecular geometry. When all the electron domains in a molecule arise from bonds, the molecular geometry is identical to the electron-domain geometry. When, however, one or more domains involve nonbonding pairs of electrons, we must remember that *the molecular geometry involves only electron domains due to bonds* even though the nonbonding pairs contribute to the electron-domain geometry.

TABLE 9.1 Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains*	Arrangement of Electron Domains	Electron Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

*The number of electron domains is sometimes called the *coordination number* of the atom.

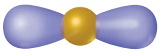
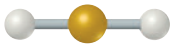
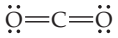
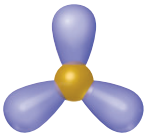
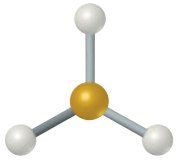
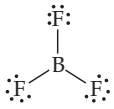
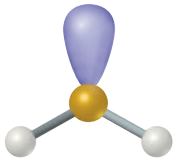
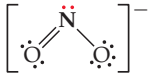
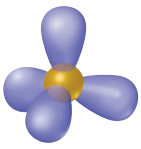
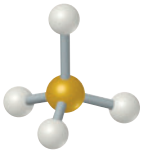
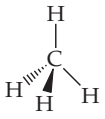
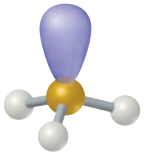
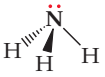
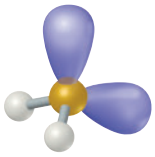
How to Predict the Shapes of Molecules and Ions Using the VSEPR Model

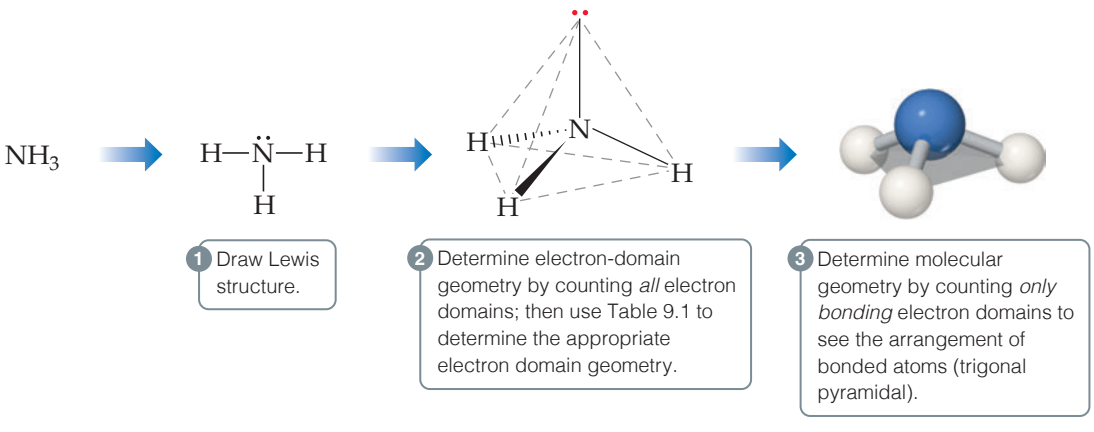
1. Draw the Lewis structure of the molecule or ion, and count the number of electron domains around the central atom. Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.
2. Determine the *electron-domain geometry* by arranging the electron domains about the central atom so that the repulsions among them are minimized, as shown in Table 9.1.
3. Use the arrangement of the bonded atoms to determine the *molecular geometry*.

Table 9.2 summarizes the possible molecular geometries when an AB_n molecule has four or fewer electron domains about A. These geometries are important because they include all the shapes usually seen in molecules or ions that obey the octet rule.

Figure 9.6 shows how to use the three steps in the VSEPR model to predict the geometry of the NH_3 molecule. The three bonds and one nonbonding pair in the Lewis

TABLE 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

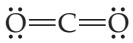


◀ **Figure 9.6 Determining the molecular geometry of NH_3.**

structure tell us we have four electron domains. Thus, from Table 9.1, the electron-domain geometry of NH_3 is tetrahedral. We know from the Lewis structure that one electron domain is due to a nonbonding pair, which occupies one of the four vertices of the tetrahedron. In determining the molecular geometry, we consider only the three N—H bond domains, which leads to a trigonal pyramidal geometry. The situation is just like the middle drawing in Figure 9.4 in which removing one atom from a tetrahedral molecule results in a trigonal pyramidal molecule. Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular geometry.

Because the trigonal-pyramidal molecular geometry is based on a tetrahedral electron-domain geometry, the ideal bond angles are 109.5°. As we will soon see, bond angles deviate from ideal values when the surrounding atoms and electron domains are not identical.

As one more example, let's determine the shape of the CO_2 molecule. Its Lewis structure reveals two electron domains (each one a double bond) around the central carbon:



Two electron domains orient in a linear electron-domain geometry (Table 9.1). Because neither domain is a nonbonding pair of electrons, the molecular geometry is also linear, and the O—C—O bond angle is 180°.

Sample Exercise 9.1

Using the VSEPR Model

Use the VSEPR model to predict the molecular geometry of (**a**) O_3, (**b**) $SnCl_3^-$.

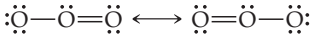
SOLUTION

Analyze We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table. (Notice that for O_3, the A and B atoms are all oxygen atoms.)

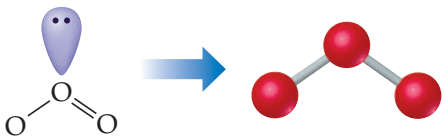
Plan To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

Solve

(**a**) We can draw two resonance structures for O_3:

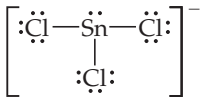


Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures, the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1). Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecular geometry is bent with an ideal bond angle of 120° (Table 9.2).

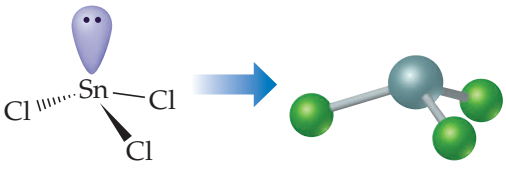


Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(**b**) The Lewis structure for $SnCl_3^-$ is:



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning a tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied by a nonbonding pair of electrons. A tetrahedral electron-domain geometry with three bonding and one nonbonding domains leads to a trigonal-pyramidal molecular geometry (Table 9.2).

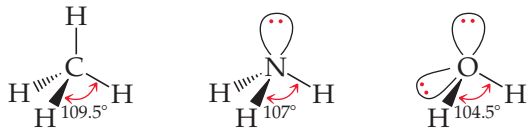


Practice Exercise

Predict the electron-domain and molecular geometries for (**a**) $SeCl_2$, (**b**) CO_3^{2-}.

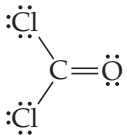
Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to explain slight distortions from the ideal geometries summarized in Table 9.2. For example, consider methane (CH_4), ammonia (NH_3), and water (H_2O). All three have a tetrahedral electron-domain geometry, but their bond angles differ slightly:

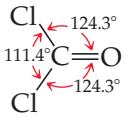


Notice that the bond angles decrease as the number of nonbonding electron pairs increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its electron domain is spread out more in space than is the electron domain for a bonding pair (**Figure 9.7**). Nonbonding electron pairs therefore take up more space than bonding pairs; in essence, they act as larger and fatter balloons in our analogy of Figure 9.5. As a result, *electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles*.

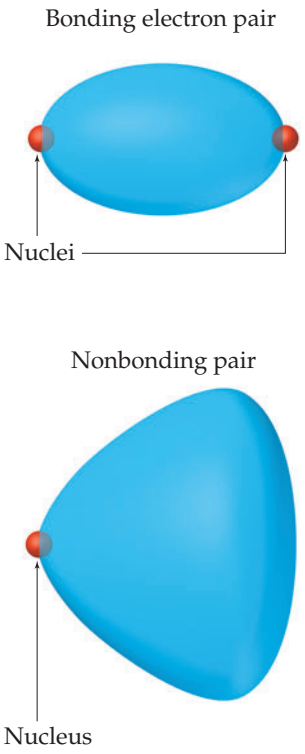
Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent enlarged electron domains. Consider the Lewis structure of *phosgene*, Cl_2CO:



Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl—C—Cl bond angle to 111.4°:



In general, *electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds*.



▲ **Figure 9.7** **Relative volumes occupied by bonding and nonbonding electron domains.**

Molecules with Expanded Valence Shells

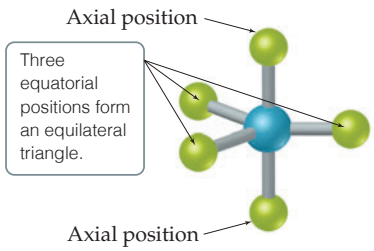
Atoms from Period 3 and beyond may be surrounded by more than four electron pairs. Molecules with five or six electron domains around the central atom have molecular geometries based on either a *trigonal-bipyramidal* (five domains) or *octahedral* (six domains) electron-domain geometry (**Table 9.3**).

The most stable electron-domain geometry for five electron domains is the trigonal bipyramid (two trigonal pyramids sharing a base). Unlike the other arrangements we have seen, the electron domains in a trigonal bipyramid can point toward two geometrically distinct types of positions. Two domains point toward *axial positions*, and three point toward *equatorial positions* (**Figure 9.8**). Each axial domain makes a 90° angle with any equatorial domain. Each equatorial domain makes a 120° angle with either of the other two equatorial domains and a 90° angle with either axial domain.

Suppose a molecule has five electron domains, and there are one or more nonbonding pairs. Will the domains from the nonbonding pairs occupy axial or equatorial positions? To answer this question, we must determine which location minimizes repulsion between domains. Repulsion between two domains is much greater when they are situated 90° from each other than when they are at 120°. An equatorial domain is 90° from only two other domains (the axial domains), but an axial domain is 90° from *three* other domains (the equatorial domains). Hence, an equatorial domain experiences

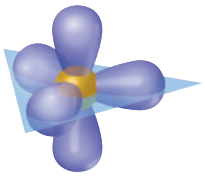
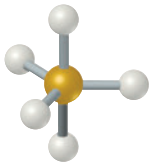
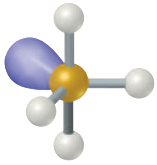
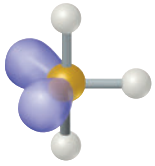
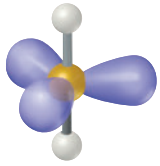
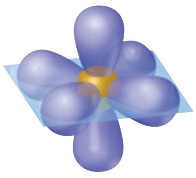
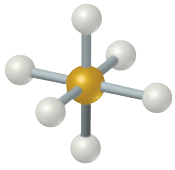
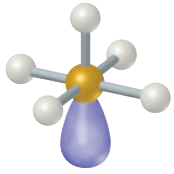
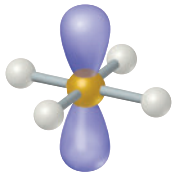
Go Figure

What is the bond angle formed by an axial atom, the central atom, and any equatorial atom?



▲ **Figure 9.8** **In a trigonal-bipyramidal geometry, there are two types of positions for the outer atoms.**

TABLE 9.3 Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

less repulsion than an axial domain. Because the domains from nonbonding pairs exert larger repulsions than those from bonding pairs, nonbonding domains *always* occupy the equatorial positions in a trigonal bipyramid.

The most stable electron-domain geometry for six electron domains is the *octahedron*. An octahedron is a polyhedron with six vertices and eight faces, each an equilateral triangle. An atom with six electron domains around it can be visualized as being at the center of the octahedron with the electron domains pointing toward the six vertices, as shown in Table 9.3. All the bond angles are 90°, and all six vertices are equivalent. Therefore, if an atom has five bonding electron domains and one nonbonding domain, we can put the nonbonding domain at any of the six vertices of the octahedron. The result is always a *square-pyramidal* molecular geometry. When there are two nonbonding electron domains, however, their repulsions are minimized by pointing them toward opposite sides of the octahedron, producing a *square-planar* molecular geometry, as shown in Table 9.3.

Sample Exercise 9.2

Molecular Geometries of Molecules with Expanded Valence Shells

Use the VSEPR model to predict the molecular geometry of (**a**) SF_4, (**b**) IF_5.

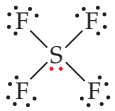
SOLUTION

Analyze The molecules are of the AB_n type with a central *p*-block atom.

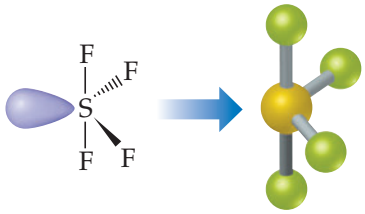
Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve

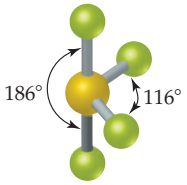
(**a**) The Lewis structure for SF_4 is:



The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as seesaw-shaped:

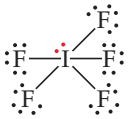


Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are "pushed" by the nonbonding domain, which exerts a greater repulsion (Figure 9.7).

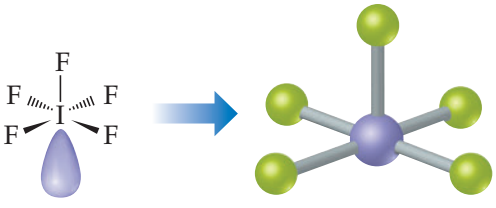


Solve

(**b**) The Lewis structure of IF_5 is:



The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is *square pyramidal* (Table 9.3):



Comment Because the nonbonding domain is larger than the bonding domains, we predict that the four F atoms in the base of the pyramid will be tipped up slightly toward the top F atom. Experimentally, we find that the angle between the base atoms and the top F atom is 82°, smaller than the ideal 90° angle of an octahedron.

Continued

Practice Exercise

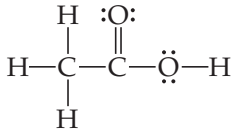
A certain AB_4 molecule has a square-planar molecular geometry. Which of the following statements about the molecule is or are true?

(i) The molecule has four electron domains about the central atom A.
(ii) The B—A—B angles between neighboring B atoms are 90°.
(iii) The molecule has two nonbonding pairs of electrons on atom A.

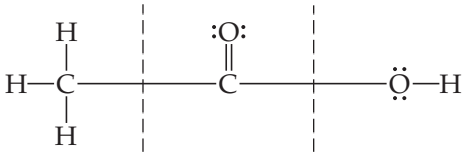
(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

Shapes of Larger Molecules

Although the molecules and ions we have considered contain only a single central atom, the VSEPR model can be extended to more complex molecules. Consider the acetic acid molecule:



We can use the VSEPR model to predict the geometry about each carbon atom and the oxygen atom:



Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

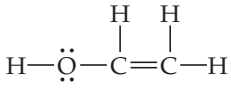
The C on the left has four electron domains (all bonding), so the electron-domain and molecular geometries around that atom are both tetrahedral. The central C has three electron domains (counting the double bond as one domain), making both the electron-domain and the molecular geometries trigonal planar. The O on the right has four electron domains (two bonding, two nonbonding), so its electron-domain geometry is tetrahedral and its molecular geometry is bent. The bond angles about the central C atom and the O atom are expected to deviate slightly from the ideal values of 120° and 109.5° because of the spatial demands of multiple bonds and nonbonding electron pairs.

Our analysis of the acetic acid molecule is shown in **Figure 9.9**.

Sample Exercise 9.3

Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:



Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

SOLUTION

Analyze We are given a Lewis structure and asked to determine two bond angles.

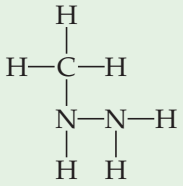
Plan To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the angle. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

Solve In H—O—C, the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5°. The H—O—C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5°.

To predict the O—C—C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120°. Because of the larger size of the C=C domain, the bond angle should be slightly greater than 120°.

Practice Exercise

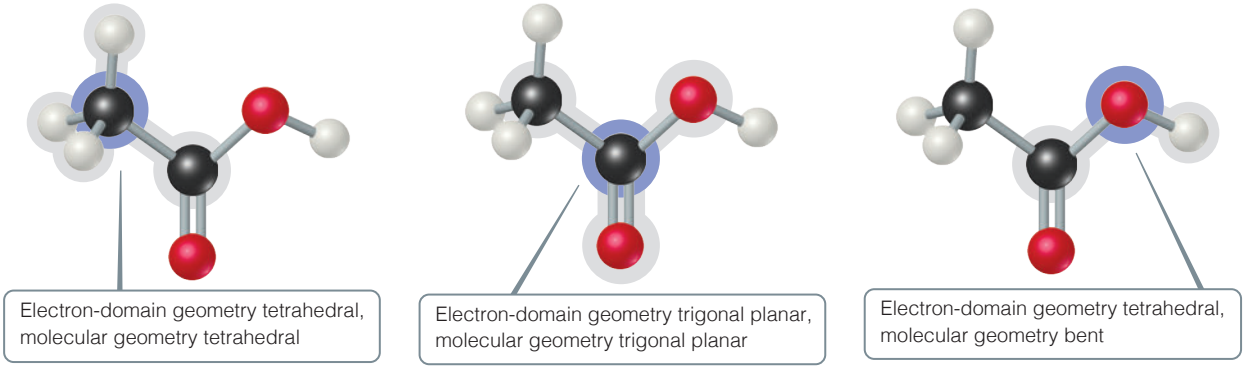
The atoms of the compound methylhydrazine, CH_6N_2, which is used as a rocket propellant, are connected as follows (note that lone pairs are not shown):



What do you predict for the ideal values of the C—N—N and H—N—H angles, respectively?

(**a**) 109.5° and 109.5° (**b**) 109.5° and 120° (**c**) 120° and 109.5° (**d**) 120° and 120° (**e**) None of these

Go Figure In the actual structure of acetic acid, which bond angle is expected to be the smallest?



▲ **Figure 9.9 The electron-domain and molecular geometries around the three central atoms of acetic acid, CH_3COOH.**

Self-Assessment Exercise

9.5 What is the O—S—O bond angle in sulfur trioxide, SO_3?

(a) 90°
(b) 109.5°
(c) 120°
(d) 180°

Exercises

9.6 (**a**) An AB_2 molecule is linear. How many nonbonding electron pairs are around the A atom from this information? (**b**) How many nonbonding electrons surround the Xe in XeF_2? (**c**) Is XeF_2 linear?

9.7 (**a**) An AB_6 molecule has no lone pairs of electrons on the A atom. What is its molecular geometry? (**b**) An AB_4 molecule has two lone pairs of electrons on the A atom (in addition to the four B atoms). What is the electron-domain geometry around the A atom? (**c**) For the AB_4 molecule in part (b), predict the molecular geometry.

9.8 In which of these molecules or ions does the presence of nonbonding electron pairs produce an effect on molecular shape? (**a**) CO_2, (**b**) CH_2Br_2, (**c**) OF_2, (**d**) BCl_3, (**e**) SF_6.

9.9 Give the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom: (**a**) four bonding domains and no nonbonding domains, (**b**) three bonding domains and two nonbonding domains, (**c**) five bonding domains and one nonbonding domain, (**d**) four bonding domains and two nonbonding domains.

9.10 Give the electron-domain and molecular geometries for the following molecules and ions: (**a**) BeF_2, (**b**) $AsCl_5$, (**c**) NO_2^-, (**d**) CS_2, (**e**) SF_4, (**f**) BrF_5.

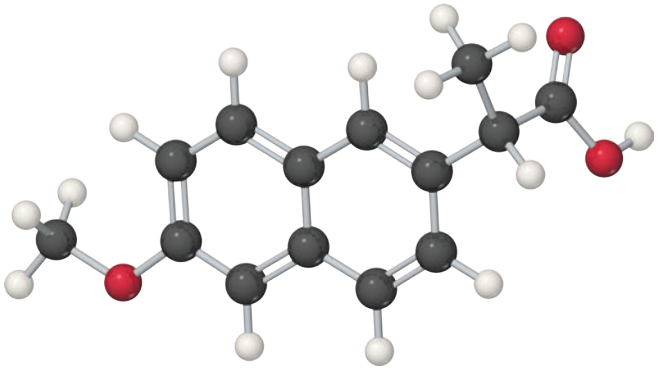
9.11 Ammonia, NH_3, reacts with incredibly strong bases to produce the amide ion, NH_2^-. Ammonia can also react with acids to produce the ammonium ion, NH_4^+. (**a**) Which species (amide ion, ammonia, or ammonium ion) has the largest H—N—H bond angle? (**b**) Which species has the smallest H—N—H bond angle?

9.12 (**a**) Explain why BrF_4^- is square planar, whereas BF_4^- is tetrahedral. (**b**) How would you expect the H—X—H bond angle to vary in the series H_2O, H_2S, H_2Se? Explain. (*Hint:* The size of an electron pair domain depends in part on the electronegativity of the central atom.)

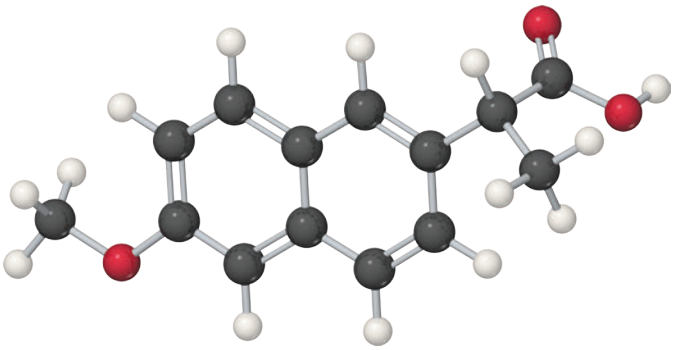
Answers to Self-Assessment Exercise

9.5 (c)

9.3 Molecular Shape and Molecular Polarity



(*S*)-naproxen



(*R*)-naproxen

The shape and size of a molecule of a substance, together with the strength and polarity of its bonds, largely determine the properties of that substance. Some of the most dramatic examples of the important roles of molecular architecture are seen in biochemical reactions. Drugs are examples of molecules in which small changes in the three-dimensional arrangement of atoms have huge consequences. In the image, we see two different molecules: their trade names are (*S*)-naproxen and (*R*)-naproxen. They have the same chemical formula and even the same number of the same kind of chemical bonds; but if you look closely, the positions of an H and a CH_3 group are reversed in one compared to the other. The (*S*) compound is prescribed to treat patients who experience the pain of arthritis; the (*R*) compound has no beneficial effects in humans and, in fact, causes liver poisoning. These compounds belong to a special class of structural isomers called *enantiomers* that we will learn more about later in the book. Much effort in the pharmaceutical industry goes into making, separating, and purifying one isomer of a compound from other isomers.

By the end of this section, you should be able to

- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments.

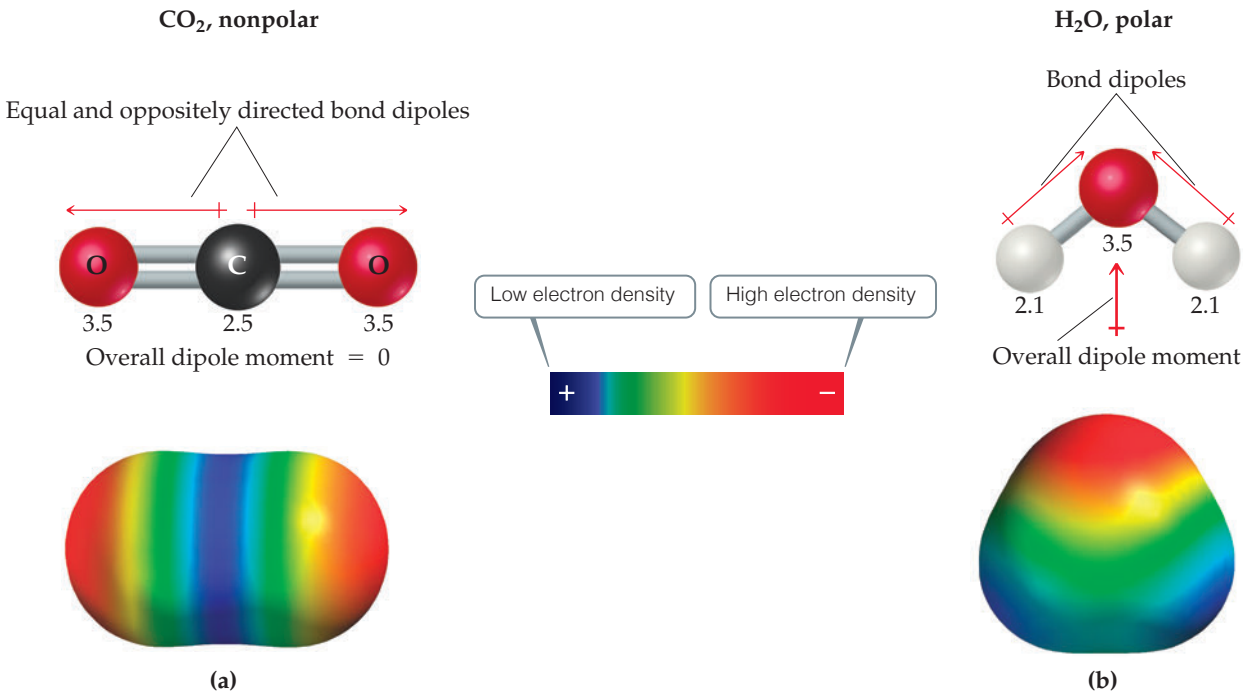
Now that we have a sense of the shapes that molecules adopt and why they do so, we will return to some topics that we first discussed in Section 8.4, namely, *bond polarity* and *dipole moments*. Recall that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond. As the difference in electronegativity between the two atoms increases, so does the bond polarity. We saw that the dipole moment of a diatomic molecule is a measure of the amount of charge separation in the molecule.

For a molecule consisting of more than two atoms, *the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule*. For each bond in the molecule, we consider the **bond dipole**, which is the dipole moment due only to the two atoms in that bond. Consider the linear CO_2 molecule, for example. As shown in **Figure 9.10(a)**, each C═O bond is polar, and because the C═O bonds are identical, the bond dipoles are equal in magnitude. A plot of the molecule's electron density clearly shows that the individual bonds are polar, but what can we say about the *overall* dipole moment of the molecule?

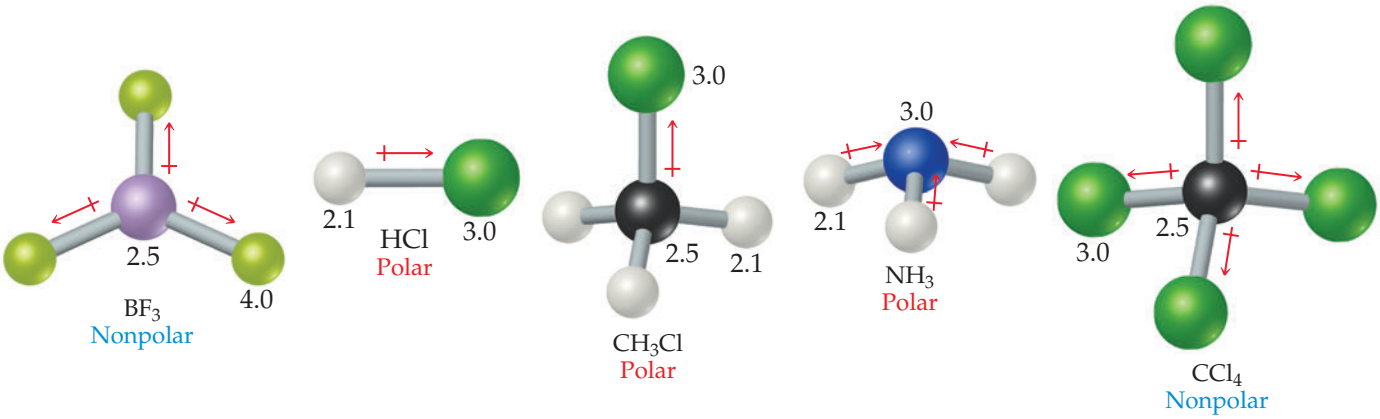
Bond dipoles and dipole moments are *vector quantities*; that is, they have both a magnitude and a direction. The dipole moment of a polyatomic molecule is the vector sum of its bond dipoles. Both the magnitudes *and* the directions of the bond dipoles must be considered when summing vectors. The two bond dipoles in CO_2, although equal in magnitude, are opposite in direction. Adding them is the same as adding two numbers that are equal in magnitude but opposite in sign, such as $100 + (-100)$. The bond dipoles, like the numbers, "cancel" each other. Therefore, the dipole moment of CO_2 is zero, even though the individual bonds are polar. The geometry of the molecule dictates that the overall dipole moment be zero, making CO_2 a *nonpolar* molecule.

Now let's consider H_2O, a bent molecule with two polar bonds (**Figure 9.10(b)**). Again, the two bonds are identical, and the bond dipoles are equal in magnitude. Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel. Hence, the H_2O molecule has an overall nonzero dipole moment (measured dipole moment, $\mu = 1.85$ D) and is therefore a *polar* molecule. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge, as shown in Figure 9.10(b).

Go Figure What is the sum of the two red vectors at the top of the left figure?



▲ **Figure 9.10 CO_2, a nonpolar molecule, and H_2O, a polar molecule.** The numbers are electronegativity values for these two atoms.



▲ **Figure 9.11 Polar and nonpolar molecules containing polar bonds.** The numbers are electronegativity values.

Figure 9.11 shows some examples of polar and nonpolar molecules, all with polar bonds. The molecules in which the central atom is symmetrically surrounded by identical atoms (BF_3 and CCl_4) are nonpolar. For AB_n molecules in which all the B atoms are the same, certain symmetrical shapes—linear (AB_2), trigonal planar (AB_3), tetrahedral and square planar (AB_4), trigonal bipyramidal (AB_5), and octahedral (AB_6)—must lead to nonpolar molecules even though the individual bonds might be polar.

Sample Exercise 9.4

Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (**a**) BrCl, (**b**) SO_2, (**c**) SF_6.

SOLUTION

Analyze We are given three molecular formulas and asked to predict whether the molecules are polar.

Plan A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

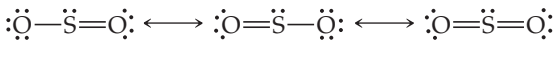
Solve

(**a**) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:

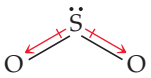


The measured dipole moment μ of BrCl is 0.57 D.

(**b**) Because oxygen is more electronegative than sulfur, SO_2 has polar bonds. Three resonance forms can be written:

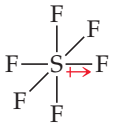


For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:



Experimentally, the dipole moment μ of SO_2 is 1.63 D.

(**c**) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one S—F dipole is shown. The six S—F bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

Practice Exercise

Consider an AB_3 molecule in which A and B differ in electronegativity. You are told that the molecule has an overall dipole moment of zero. Which of the following could be the molecular geometry of the molecule?
(**a**) Trigonal pyramidal (**b**) Trigonal planar
(**c**) T-shaped (**d**) Tetrahedral
(**e**) More than one of these options

Self-Assessment Exercise

9.13 Is phosphorus pentachloride, PCl_5, polar or nonpolar?

(a) Polar

(b) Nonpolar

Exercises

9.14 Consider a molecule with formula AX_2. Supposing the A—X bond is polar, how would you expect the dipole moment of the AX_2 molecule to change as the X—A—X bond angle decreases from 180° to 100°?

9.15 (**a**) Does CS_2 have a dipole moment? If so, in which direction does the net dipole point? (**b**) Does SO_2 have a dipole moment? If so, in which direction does the net dipole point?

9.16 (**a**) Is the molecule BF_3 polar or nonpolar? (**b**) If you react BF_3 to make the ion BF_3^{2-}, is this ion planar? (**c**) Does the molecule BF_2Cl have a dipole moment?

9.17 Predict whether each of the following molecules is polar or nonpolar: (**a**) IF, (**b**) CS_2, (**c**) SO_3, (**d**) PCl_3, (**e**) SF_6, (**f**) IF_5.

9.18 Dichloroethylene ($C_2H_2Cl_2$) has three forms (isomers), each of which is a different substance. (**a**) Draw Lewis structures of the three isomers, all of which have a carbon–carbon double bond. (**b**) Which of these isomers has a zero dipole moment? (**c**) How many isomeric forms can chloroethylene, C_2H_3Cl, have? Would they be expected to have dipole moments?

Answers to Self-Assessment Exercise

9.13 (b)

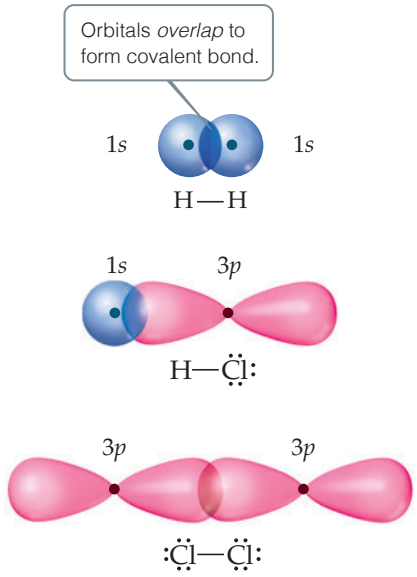
9.4 Covalent Bonding and Orbital Overlap



Electron orbitals overlap to form a chemical bond much as the two parts of a zipper come together to form a secure fastening. A compatible size and shape of the two components is necessary in both cases! By the end of this section, you should be able to

- Appreciate the role of orbital overlap in a chemical bond

The VSEPR model provides a simple means for predicting molecular geometries but does not explain why bonds exist between atoms. In developing theories of covalent bonding, chemists have approached the problem from another direction, using



▲ **Figure 9.12** **Covalent bonds in H_2, HCl, and Cl_2 result from overlap of atomic orbitals.**

quantum mechanics. How can we use atomic orbitals to explain bonding and to account for molecular geometries? The marriage of Lewis's notion of electron-pair bonds and the idea of atomic orbitals leads to a model of chemical bonding, called **valence-bond theory**, in which bonding electron pairs are concentrated in the regions between atoms, and nonbonding electron pairs lie in directed regions of space. By extending this approach to include the ways in which atomic orbitals can mix with one another, we obtain an explanatory picture that corresponds to the VSEPR model.

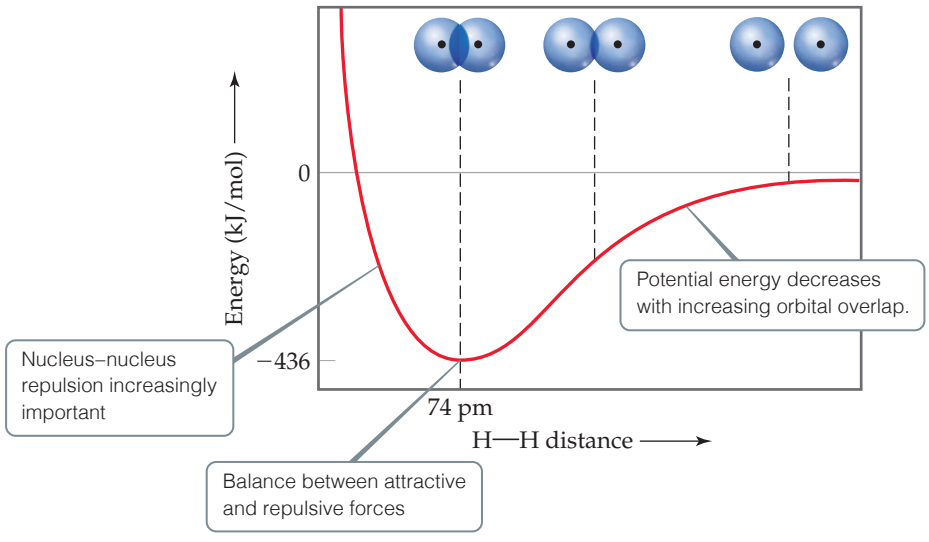
In Lewis theory, covalent bonding occurs when atoms share electrons because the sharing concentrates electron density between the nuclei. In valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when a valence atomic orbital of one atom shares space, or *overlaps*, with a valence atomic orbital of another atom. The overlap of orbitals allows two electrons of opposite spin to share the space between the nuclei, forming a covalent bond.

Figure 9.12 shows three examples of how valence-bond theory describes the coming together of two atoms to form a molecule. In the example of the formation of H_2, each hydrogen atom has a single electron in a 1*s* orbital. As the orbitals overlap, electron density is concentrated between the nuclei. Because the electrons in the overlap region are simultaneously attracted to both nuclei, they hold the atoms together, forming a covalent bond.

The idea of orbital overlap producing a covalent bond applies equally well to other molecules. In HCl, for example, chlorine has the electron configuration $[Ne]3s^2 3p^5$. All the valence orbitals of chlorine are full except one 3*p* orbital, which contains a single electron. This 3*p* electron pairs with the single 1*s* electron of H to form the covalent bond that holds HCl together (Figure 9.12). Because the other two chlorine 3*p* orbitals are already each filled with a pair of electrons, they do not participate in the bonding to hydrogen. Likewise, we can explain the covalent bond in Cl_2 in terms of the overlap of the singly occupied 3*p* orbital of one Cl atom with the singly occupied 3*p* orbital of another.

There is always an optimum distance between the two nuclei in any covalent bond. **Figure 9.13** shows how the potential energy of a system consisting of two H atoms changes as the atoms come together to form an H_2 molecule. When the atoms are infinitely far apart, they do not "feel" each other and so the energy approaches zero. As the distance between the atoms decreases, the overlap between their 1*s* orbitals increases. Because of the resulting increase in electron density between the nuclei, the potential energy of the system decreases. That is, the strength of the bond increases, as shown by the decrease in

Go Figure From this graph, what are the bond length and bond strength in the H_2 molecule?



▲ **Figure 9.13** **Formation of the H_2 molecule as atomic orbitals overlap.**

the potential energy of the two-atom system. However, Figure 9.13 also shows that the energy increases sharply when the distance between the two hydrogen nuclei is less than 74 pm. The increase in potential energy of the system, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance at the minimum of the potential-energy curve (in this example, at 74 pm) corresponds to the bond length of the molecule. The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron–electron and nucleus–nucleus).

Self-Assessment Exercise

9.19 What atomic orbitals are expected to overlap in the bonding of F and Cl in FCl?

(a) F 2*s* and Cl 2*s*

(b) F 2*s* and Cl 3*s*

(c) F 2*p* and Cl 2*p*

(d) F 2*p* and Cl 3*p*

Exercises

9.20 Draw sketches illustrating the overlap between the following orbitals on two atoms: (**a**) the 2*s* orbital on each atom, (**b**) the $2p_z$ orbital on each atom (assume both atoms are on the *z*-axis), (**c**) the 2*s* orbital on one atom and the $2p_z$ orbital on the other atom.

Answers to Self-Assessment Exercise

9.19 (d)

9.5 Hybrid Orbitals



A hybrid car is one that has two different energy sources for its propulsion— electricity and petrol. These energy sources remain separable and distinct from one another. In biology, however, a hybrid is a blend of characteristics from two different species. For example, a mule is a cross between a donkey and a horse, having more strength than the

former and being smaller than the latter. In chemistry, when we talk of hybrid orbitals, we mean a blend that displays some of the shape and size characteristics of the contributing orbitals.

By the end of this section, you should be able to

- Determine the hybridization of atoms in molecules based on observed molecular structures.

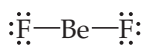
The VSEPR model, simple as it is, does a surprisingly good job at predicting molecular shape, despite the fact that it has no obvious relationship to the filling and shapes of atomic orbitals. For example, we would like to understand how to account for the tetrahedral arrangement of C—H bonds in methane in terms of the 2*s* and 2*p* orbitals of the central carbon atom, which are not directed toward the apices of a tetrahedron. How can we reconcile the notion that covalent bonds are formed from overlap of atomic orbitals with the molecular geometries that come from the VSEPR model?

To begin with, we recall that atomic orbitals are mathematical functions that come from the quantum-mechanical model for atomic structure. To explain molecular geometries, we often assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**. The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization**. The total number of atomic orbitals on an atom remains constant, so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

As we examine the common types of hybridization, notice the connection between the type of hybridization and some of the molecular geometries predicted by the VSEPR model: linear, bent, trigonal planar, and tetrahedral.

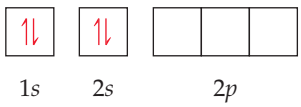
sp Hybrid Orbitals

To illustrate the process of hybridization, consider the BeF_2 molecule, which has the Lewis structure

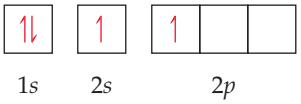


The VSEPR model predicts that BeF_2 is linear with two identical Be—F bonds, in accord with experiment. How can we use valence-bond theory to describe the bonding? The electron configuration of F ($1s^2 2s^2 2p^5$) indicates an unpaired electron in a 2*p* orbital. This electron can be paired with an unpaired Be electron to form a polar covalent bond. Which orbitals on the Be atom, however, overlap with those on the F atoms to form the Be—F bonds?

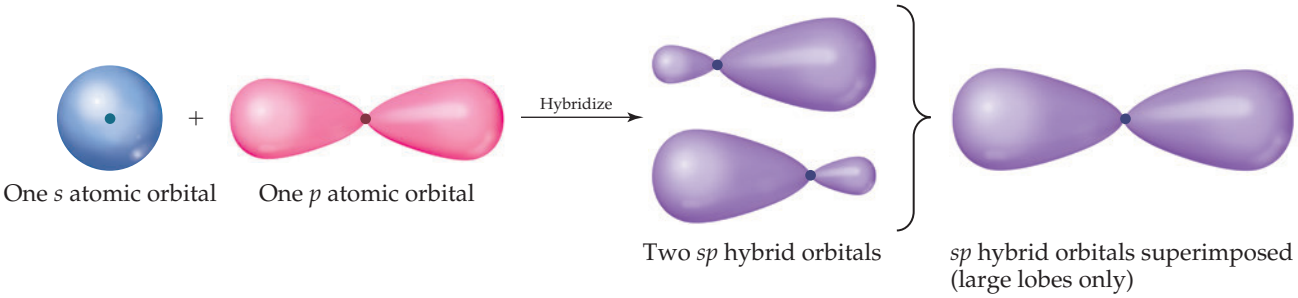
The orbital diagram for a ground-state Be atom is



Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by envisioning that we "promote" one of the 2*s* electrons to a 2*p* orbital:



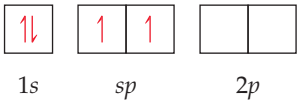
The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms. The two bonds would not be identical, however, because a Be 2*s* orbital would be used to form one of the bonds and a 2*p* orbital would be used to form the other. Therefore, although the promotion of an electron allows two Be—F bonds to form, we still have not explained the structure of BeF_2.



▲ **Figure 9.14** **Formation of *sp* hybrid orbitals.**

We can solve this dilemma by "mixing" the 2*s* orbital with one 2*p* orbital to generate two new orbitals, as shown in **Figure 9.14**. Like *p* orbitals, each new orbital has two lobes. Unlike *p* orbitals, however, one lobe is much larger than the other. The two new orbitals are identical in shape, but their large lobes point in opposite directions. These two new orbitals, which are shown in purple in Figure 9.14, are hybrid orbitals. Because we have hybridized one *s* and one *p* orbital, we call each hybrid an *sp* hybrid orbital. *According to the valence-bond model, a linear arrangement of electron domains implies* sp *hybridization.*

For the Be atom of BeF_2, we write the orbital diagram for the formation of two *sp* hybrid orbitals as

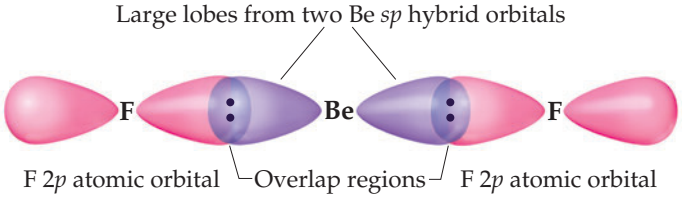


The electrons in the *sp* hybrid orbitals can form bonds with the two fluorine atoms (**Figure 9.15**). Because the *sp* hybrid orbitals are equivalent but point in opposite directions, BeF_2 has two identical bonds and a linear geometry. We have used one of the 2*p* orbitals in making the hybrids; the remaining two 2*p* atomic orbitals of Be remain unhybridized and are vacant. Remember also that each fluorine atom has two other valence *p* atomic orbitals, each containing one nonbonding electron pair. Those atomic orbitals are omitted from Figure 9.15 to keep the illustration simpler.

sp^2 and sp^3 Hybrid Orbitals

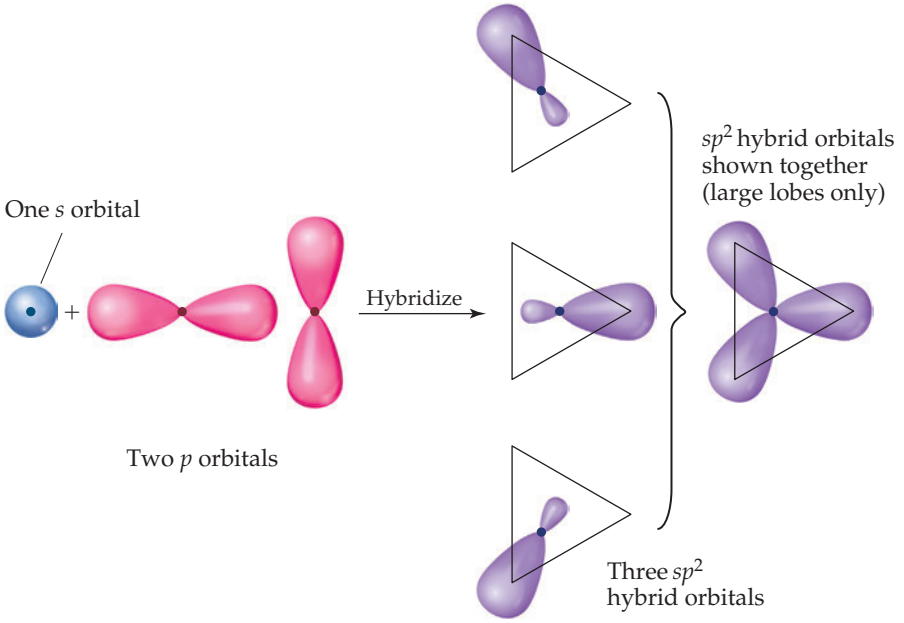
Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each hybrid orbital is equivalent to the others but points in a different direction. Thus, mixing one 2*s* and one 2*p* atomic orbital yields two equivalent *sp* hybrid orbitals that point in opposite directions (Figure 9.14). Other combinations of atomic orbitals can be hybridized to obtain different geometries, such as sp^2 and sp^3.

In BF_3, for example, mixing the 2*s* and two of the 2*p* atomic orbitals yields three equivalent sp^2 (pronounced "*s*-*p*-two") hybrid orbitals (**Figure 9.16**). The three sp^2 hybrid orbitals lie in the same plane, 120° apart from one another. They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar molecular geometry of BF_3. Notice that an unfilled 2*p* atomic orbital remains unhybridized; it is oriented perpendicular to the plane defined by the three sp^2 hybrid orbitals, with one lobe above and one below the plane. This unhybridized orbital will be important when we discuss double bonds in Section 9.6.



◀ **Figure 9.15** **Formation of two equivalent Be—F bonds in BeF_2.**

Go Figure What is the angle formed between the large lobes of the three sp^2 hybrid orbitals?



▲ **Figure 9.16** **Formation of sp^2 hybrid orbitals.**

An *s* atomic orbital can mix with all three *p* atomic orbitals in the same subshell. For example, the carbon atom in CH_4 forms four equivalent bonds with the four hydrogen atoms. We envision this process as resulting from the mixing of the 2*s* and all three 2*p* atomic orbitals of carbon to create four equivalent sp^3 (pronounced "*s*-*p*-three") hybrid orbitals. Each sp^3 hybrid orbital has a large lobe that points toward one vertex of a tetrahedron (**Figure 9.17**). These hybrid orbitals can be used to form two-electron bonds by overlap with the atomic orbitals of another atom, such as H. Using valence-bond theory, we can describe the bonding in CH_4 as the overlap of four equivalent sp^3 hybrid orbitals on C with the 1*s* orbitals of the four H atoms to form four equivalent bonds.

The idea of hybridization is also used to describe the bonding in molecules containing nonbonding pairs of electrons. In H_2O, for example, the electron-domain geometry around the central O atom is approximately tetrahedral (**Figure 9.18**). Thus, the four electron pairs can be envisioned as occupying sp^3 hybrid orbitals. Two of the hybrid orbitals contain nonbonding pairs of electrons, and the other two form bonds with the hydrogen atoms.

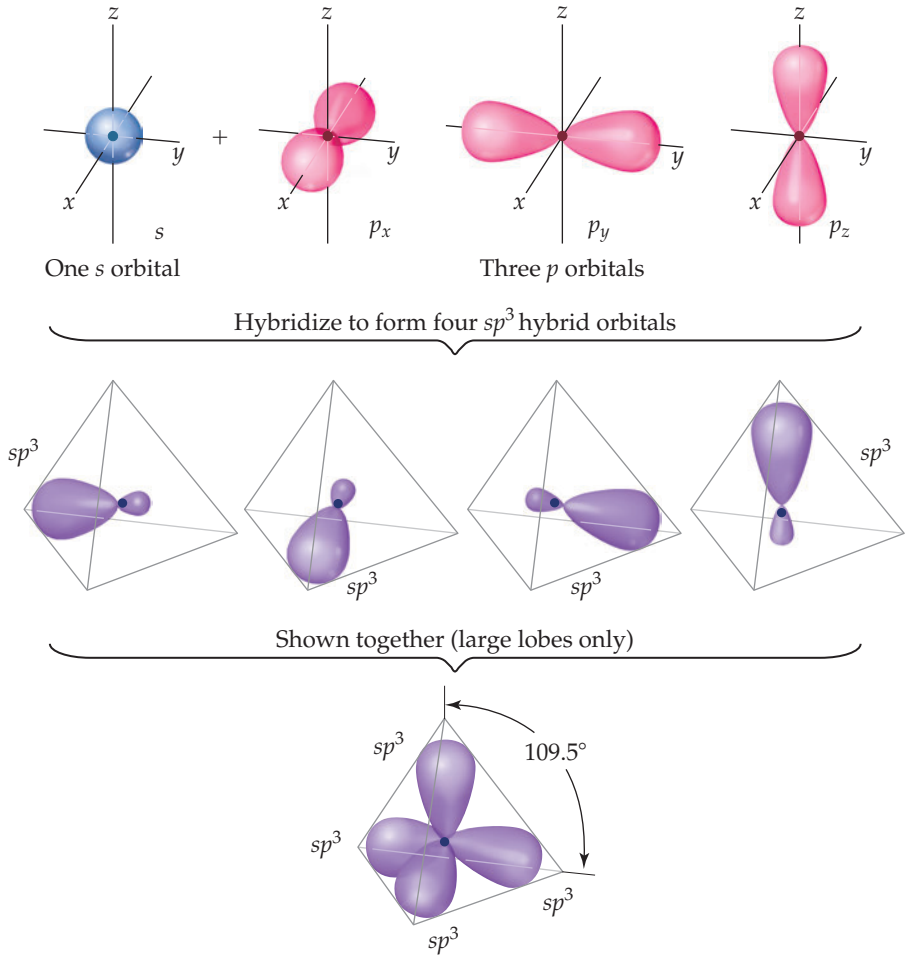
Hypervalent Molecules

So far our discussion of hybridization has extended only to Period 2 elements, specifically carbon, nitrogen, and oxygen. The elements of Period 3 and beyond introduce a new consideration because in many of their compounds these elements are **hypervalent**—they have more than an octet of electrons around the central atom. We saw in Section 9.2 that the VSEPR model works well to predict the geometries of hypervalent molecules such as PCl_5, SF_6, or BrF_5. But can we extend the use of hybrid orbitals to describe the bonding in these molecules? In short, the answer is no; hybrid orbitals should not be used for hypervalent molecules. Let's examine the reasons.

The valence-bond model we developed for Period 2 elements works well for compounds of Period 3 elements so long as we have no more than an octet of electrons in the valence-shell orbitals. Thus, for example, it is appropriate to discuss the bonding in PF_3 or H_2Se in terms of hybridized *s* and *p* orbitals on the central atom.

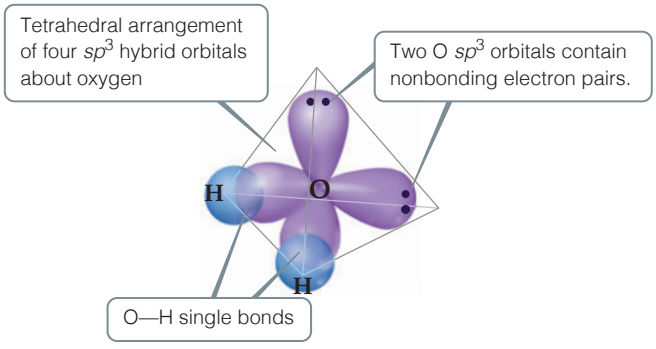
For compounds with more than an octet, we could imagine increasing the number of hybrid orbitals formed by including valence-shell *d* orbitals. For example, for SF_6 we

Go Figure Which of the *p* orbitals do you think contributes the most in the mixing that leads to the right-most sp^3 hybrid orbital in the second row of the figure?



▲ **Figure 9.17** **Formation of sp^3 hybrid orbitals.**

Go Figure Does it matter which of the two sp^3 hybrid orbitals are used to hold the two nonbonding electron pairs?



▲ **Figure 9.18** **Hybrid orbital description of H_2O.**

could envision mixing in two sulfur *3d* orbitals in addition to the *3s* and three *3p* orbitals to make a total of six hybrid orbitals. However, the sulfur *3d* orbitals are substantially higher in energy than the *3s* and *3p* orbitals, so the amount of energy needed to form the six hybrid orbitals is greater than the amount returned by forming bonds with the six fluorine atoms. Theoretical calculations suggest that the sulfur *3d* orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms, and that it would not be valid to describe the bonding in SF_6 in terms of six hybrid orbitals. The more detailed bonding model needed to discuss the bonding in SF_6 and other hypervalent molecules requires a treatment beyond the scope of a general chemistry text. Fortunately, the VSEPR model, which explains the geometrical properties of such molecules in terms of electrostatic repulsions, does a good job of predicting their geometries.

This discussion reminds us that models in science are not reality but rather are our attempts to describe aspects of reality that we have been able to measure, such as bond distances, bond energies, molecular geometries, and so on. A model may work well up to a certain point but not beyond it, as is the case for hybrid orbitals. The hybrid orbital model for Period 2 elements has proven very useful and is an essential part of any modern discussion of bonding and molecular geometry in organic chemistry. When it comes to molecules such as SF_6, however, we encounter the limitations of the model.

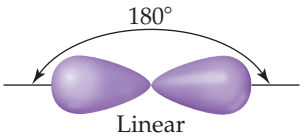
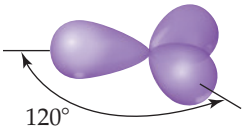
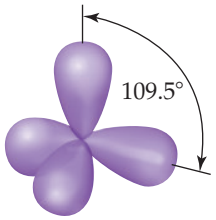
Hybrid Orbital Summary

Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules that have an octet or less of electrons around the central atom and in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. While the concept of hybrid orbitals has limited predictive value, when we know the electron-domain geometry, we can employ hybridization to describe the atomic orbitals used by the central atom in bonding.

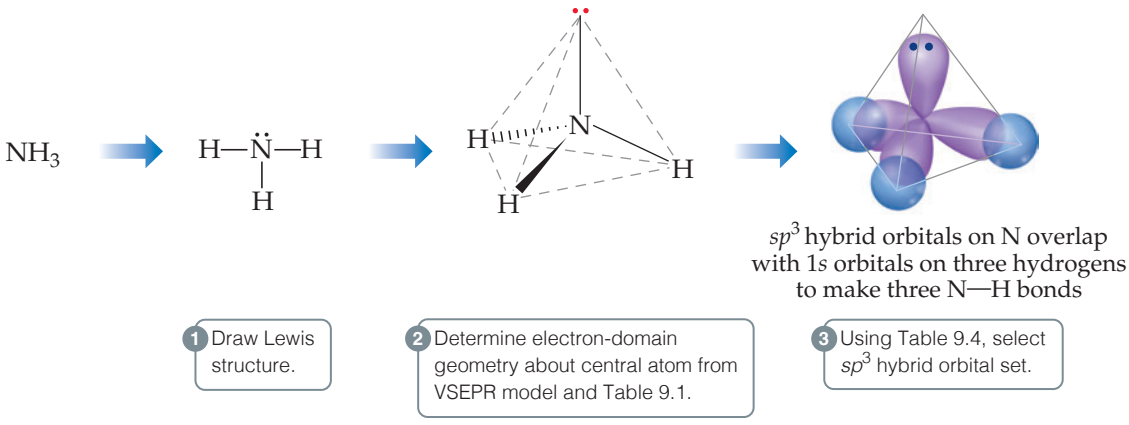
How to Describe the Hybrid Orbitals Used by an Atom in Bonding

1. Draw the *Lewis structure* for the molecule or ion.
2. Use the VSEPR model to determine the electron-domain geometry around the central atom.
3. Specify the *hybrid orbitals* needed to accommodate the electron pairs based on their geometric arrangement (**Table 9.4**).

TABLE 9.4 Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two *sp*	 Linear	BeF_2, $HgCl_2$
s,p,p	Three sp^2	 Trigonal planar	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Go Figure How would we modify the figure if we were looking at PH_3 rather than NH_3?



▲ **Figure 9.19 Hybrid orbital description of bonding in NH_3.** Note the comparison with Figure 9.6. Here we focus on the hybrid orbitals used to make bonds and to hold nonbonding electron pairs.

These steps are illustrated in **Figure 9.19**, which shows how the hybridization at N in NH_3 is determined.

Sample Exercise 9.5

Describing the Hybridization of a Central Atom

Describe the orbital hybridization around the central atom in NH_2^-.

SOLUTION

Analyze We are given the chemical formula for a polyatomic anion and asked to describe the type of hybrid orbitals surrounding the central atom.

Plan To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.

Solve The Lewis structure is

$$\left[\mathrm{H{:}\ddot{N}{:}H}\right]^-$$

Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.

Practice Exercise

For which of the following molecules or ions does the following description apply? "The bonding can be explained using a set of sp^2 hybrid orbitals on the central atom, with one of the hybrid orbitals holding a nonbonding pair of electrons."

(**a**) CO_2
(**b**) H_2S
(**c**) O_3
(**d**) CO_3^{2-}
(**e**) More than one of these

Self-Assessment Exercise

9.21 What is the orbital hybridization around boron in BH_4^-?

(a) sp
(b) sp^2
(c) sp^3

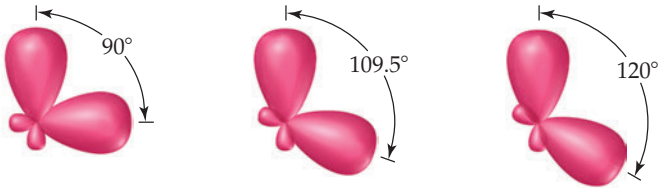
Exercises

9.22 For each statement, indicate whether it is true or false. (**a**) The greater the orbital overlap in a bond, the weaker the bond. (**b**) The greater the orbital overlap in a bond, the shorter the bond. (**c**) To create a hybrid orbital, you could use the *s* orbital on one atom with a *p* orbital on another atom. (**d**) Nonbonding electron pairs cannot occupy a hybrid orbital.

9.23 Consider the molecule BF_3. (**a**) What is the electron configuration of an isolated B atom? (**b**) What is the electron configuration of an isolated F atom? (**c**) What hybrid orbitals should be constructed on the B atom to make the B–F bonds in BF_3? (**d**) What valence orbitals, if any, remain unhybridized on the B atom in BF_3?

9.24 Indicate the hybridization of the central atom in (**a**) H_2S, (**b**) SeF_6, (**c**) $P(OH)_3$, (**d**) AlI_3.

9.25 Shown here are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type of hybridization, if any, that could lead to hybrid orbitals at the specified angle.



Answers to Self-Assessment Exercise

9.21 (c)

9.6 Multiple Bonds



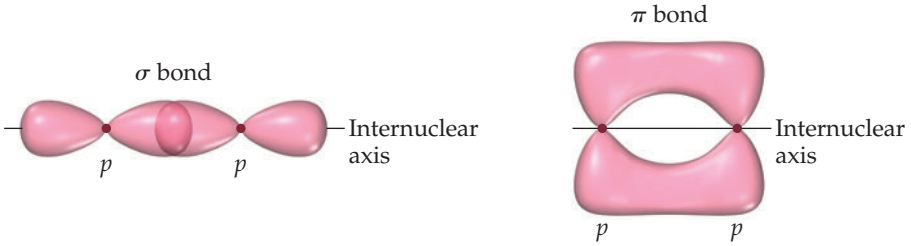
Vision begins when light is focused by the lens of the eye onto the retina, the layer of cells lining the interior of the eyeball. The retina contains photoreceptor cells called rods and cones. The rods are sensitive to dim light and are used in night vision. The cones are sensitive to colors. The tops of the rods and cones contain a molecule called *rhodopsin*, which consists of a protein, *opsin*, bonded to a reddish purple pigment called *retinal*.

Our vision depends on the rigidity of double bonds in retinal. In its normal form, retinal is held rigid by its double bonds. Light entering the eye is absorbed by rhodopsin, and it is the energy of that light that is used to break the π-bond portion of the double bond. Breaking the double bond allows rotation around the bond axis, changing the geometry of the retinal molecule. The retinal then separates from the opsin, triggering the reactions that produce a nerve impulse that the brain interprets as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus, only five photons of light are necessary to stimulate the eye.

At the end of this section, you should be able to

- Recognize orbital arrangements in single, double, and triple bonds.
- Identify where delocalization of π-electrons occurs.

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the *internuclear axis*). The line joining the



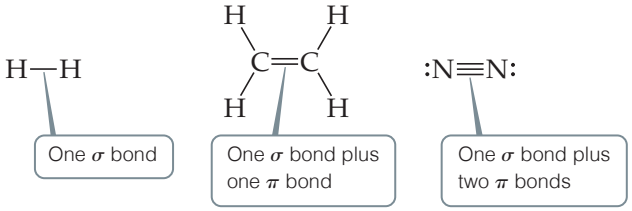
▲ **Figure 9.20 Comparison of σ and π bonds.** Note that the *two* regions of overlap in the π bond, above and below the internuclear axis, constitute a single π bond.

two nuclei passes through the middle of the overlap region, forming a type of covalent bond called a **sigma (σ) bond**. Examples of sigma bond formation include:

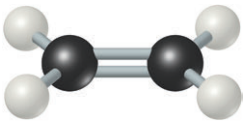
- the overlap of two *s* orbitals; one from each H in H_2 (Figure 9.12),
- the overlap of an H *s* orbital and a Cl *p* orbital in HCl (Figure 9.12),
- the overlap of two *p* orbitals; one from each Cl in Cl_2 (Figure 9.12),
- the overlap of an F *p* orbital and a Be *sp* hybrid orbital in BeF_2 (Figure 9.15).

To describe multiple bonding, we must consider a second kind of bond, this one the result of overlap between two *p* orbitals oriented perpendicularly to the internuclear axis (**Figure 9.20**). The sideways overlap of *p* orbitals produces what is called a **pi (π) bond**. A π bond is one in which the overlap regions lie above and below the internuclear axis. Unlike a σ bond, in a π bond the electron density is not concentrated on the internuclear axis. Although it is not evident in Figure 9.20, the sideways orientation of *p* orbitals in a π bond makes for weaker overlap. As a result, π bonds are generally weaker than σ bonds.

In almost all cases, single bonds are σ bonds. A double bond consists of one σ bond and one π bond, and a triple bond consists of one σ bond and two π bonds:



Consider ethene (C_2H_4), which has a C=C double bond. As illustrated by the ball-and-stick model of **Figure 9.21**, the three bond angles about each carbon are all approximately 120°, suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.16) to form σ bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after sp^2 hybridization one electron in each carbon remains in the *unhybridized* 2*p* orbital. Note that this unhybridized 2*p* orbital is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals.



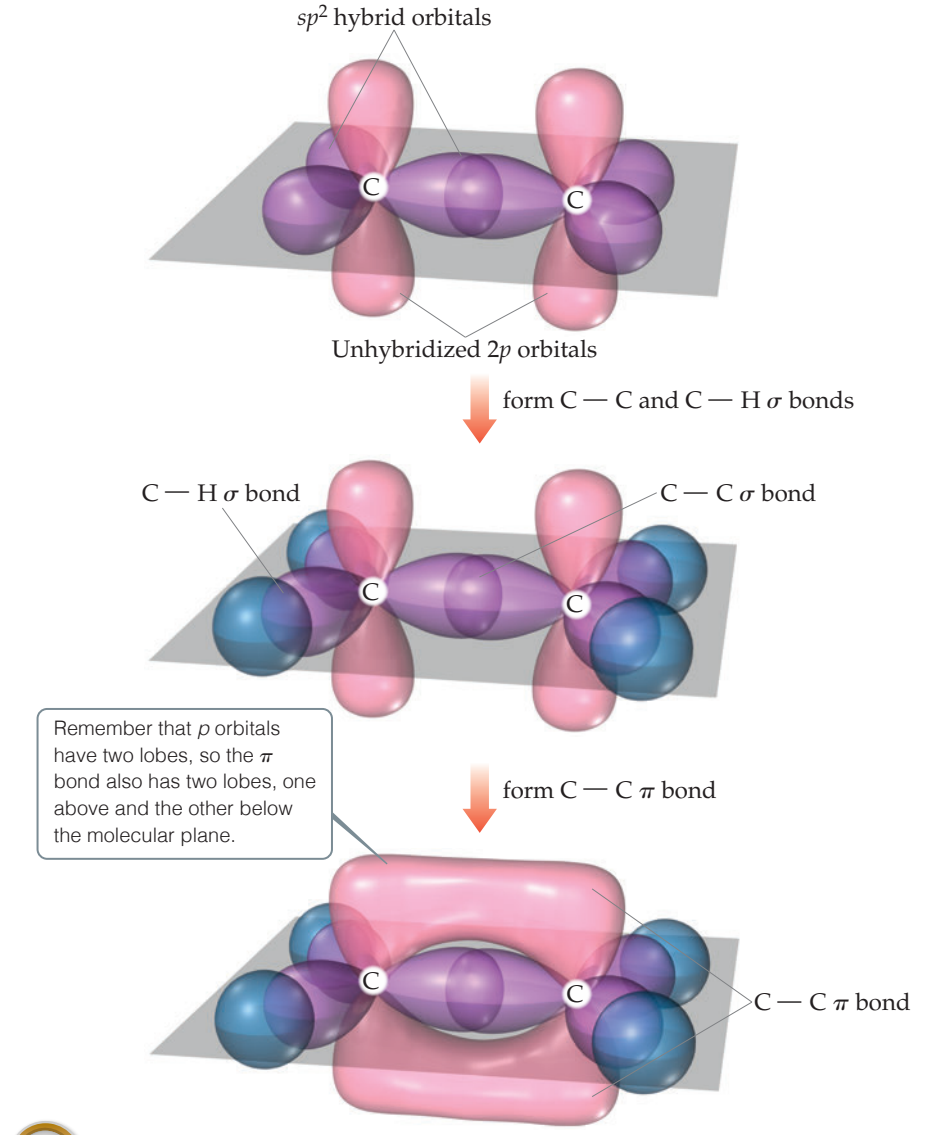
▲ **Figure 9.21 Trigonal-planar molecular geometry of ethene.** The double bond is made up of one C—C σ bond and one C—C π bond.

Let's go through the steps of building the bonds in the ethene molecule. Each sp^2 hybrid orbital on a carbon atom contains one electron. **Figure 9.22** shows how we can first envision forming the C—C σ bond by the overlap of two sp^2 hybrid orbitals, one on each carbon atom. Two electrons are used in forming the C—C σ bond. Next, the C—H σ bonds are formed by overlap of the remaining sp^2 hybrid orbitals on the C atoms with the 1*s* orbitals on each H atom. We use eight more electrons to form these four C—H bonds. Thus, 10 of the 12 valence electrons in the C_2H_4 molecule are used to form five σ bonds.

The remaining two valence electrons reside in the unhybridized 2*p* orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other, as shown in Figure 9.22. The resulting electron density is concentrated above and below the C—C bond axis: It is a π bond (Figure 9.20). Thus, the C=C double bond in ethene consists of one σ bond and one π bond.

Although we cannot experimentally observe a π bond directly (all we can observe are the positions of the atoms), the structure of ethene provides strong support for

Go Figure Why is it important that the sp^2 hybrid orbitals of the two carbon atoms lie in the same plane?



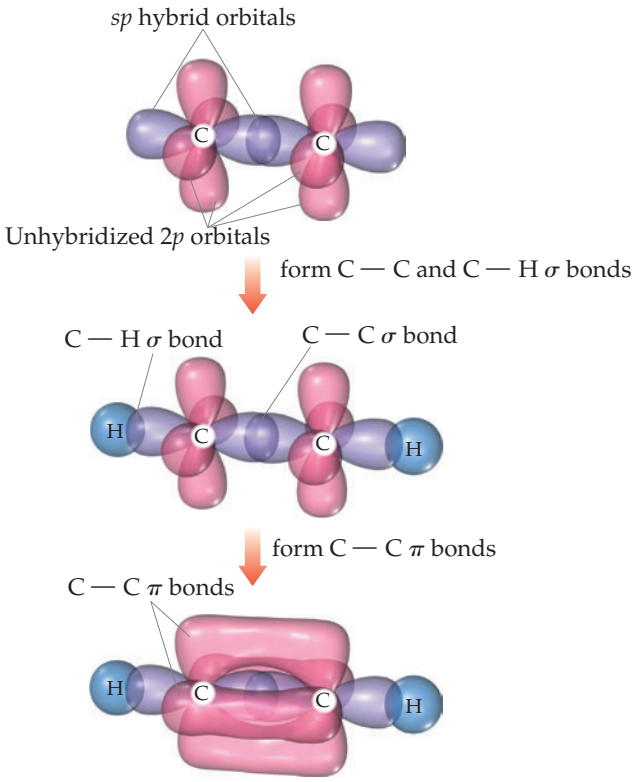
▲ **Figure 9.22** **Hybrid orbital bonding in ethene.**

its presence. First, the C—C bond length in ethene (134 pm) is much shorter than in compounds with C—C single bonds (154 pm), consistent with the presence of a stronger C═C double bond. Second, all six atoms in C_2H_4 lie in the same plane. The p orbitals on each C atom that make up the π bond can achieve a good overlap only when the two CH_2 fragments lie in the same plane. Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

Triple bonds can also be explained using hybrid orbitals. Ethyne (C_2H_2), for example, is a linear molecule containing a triple bond: H—C≡C—H. The linear geometry suggests that each carbon atom uses sp hybrid orbitals to form σ bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized 2p orbitals at right angles to each other and to the axis of the sp hybrid set (**Figure 9.23**). Thus, there are *two* p orbitals remaining on an sp-hybridized carbon atom. These p orbitals overlap to form a pair of π bonds. The triple bond in ethyne therefore consists of one σ bond and two π bonds.

Although it is possible to make π bonds from d orbitals, the only π bonds we will consider are those formed by the overlap of p orbitals. These π bonds can form only if

Go Figure Based on the models of bonding in ethene and ethyne, which molecule should have the greater carbon—carbon bond strength?



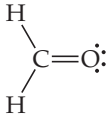
▲ **Figure 9.23** **Formation of two π bonds in ethyne, C_2H_2.**

unhybridized *p* orbitals are present on the bonded atoms. Therefore, only atoms having *sp* or sp^2 hybridization can form π bonds. Further, double and triple bonds (and hence π bonds) are more common in molecules made up of Period 2 atoms, especially C, N, and O. Larger atoms, such as S, P, and Si, form π bonds less readily.

Sample Exercise 9.6

Describing σ and π Bonds in a Molecule

Methanal has the Lewis structure



Describe how the bonds in methanal are formed in terms of overlaps of hybrid and unhybridized orbitals.

SOLUTION

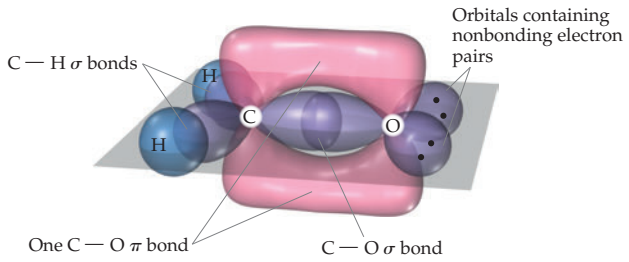
Analyze We are asked to describe the bonding in methanal in terms of hybrid orbitals.

Plan Single bonds are σ bonds, and double bonds consist of one σ bond and one π bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

Solve The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120°. This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C—H and one C—O σ bonds to C. There remains an unhybridized 2*p* orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

The O atom also has three electron domains around it, and so we assume it has sp^2 hybridization as well. One of these hybrid orbitals participates in the C—O σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has a *p* orbital that is perpendicular to the plane of the molecule. The two *p* orbitals overlap to form a C—O π bond (**Figure 9.24**).

Continued



▲ **Figure 9.24** **Formation of σ and π bonds in methanal, H_2CO.**

Practice Exercise

We have just arrived at a bonding description for the methanal molecule. Which of the following statements about the molecule is or are true?

(i) Two of the electrons in the molecule are used to make the π bond in the molecule.

(ii) Six of the electrons in the molecule are used to make the σ bonds in the molecule.

(iii) The C—O bond length in methanal should be shorter than that in methanol, H_3COH.

(a) Only one of the statements is true.

(b) Statements (i) and (ii) are true.

(c) Statements (i) and (iii) are true.

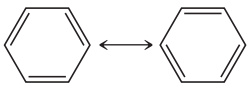
(d) Statements (ii) and (iii) are true.

(e) All three statements are true.

Resonance Structures, Delocalization, and π Bonding

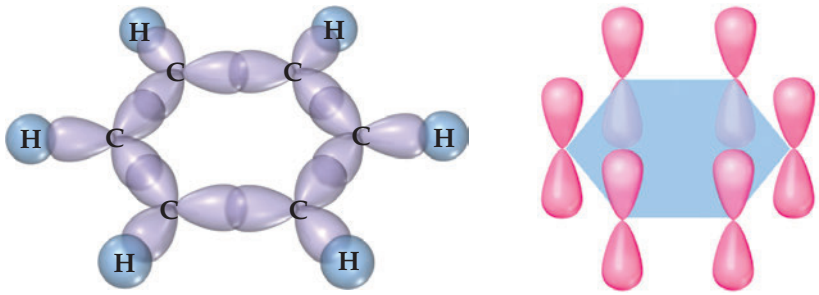
In the molecules we have discussed thus far in this section, the bonding electrons are *localized*. By this we mean that the σ and π electrons are associated totally with the two atoms that form the bond. In many molecules, however, we cannot adequately describe the bonding as being entirely localized. This situation arises particularly in molecules that have two or more resonance structures involving π bonds.

One molecule that cannot be described with localized π bonds is benzene (C_6H_6), which has two resonance structures:



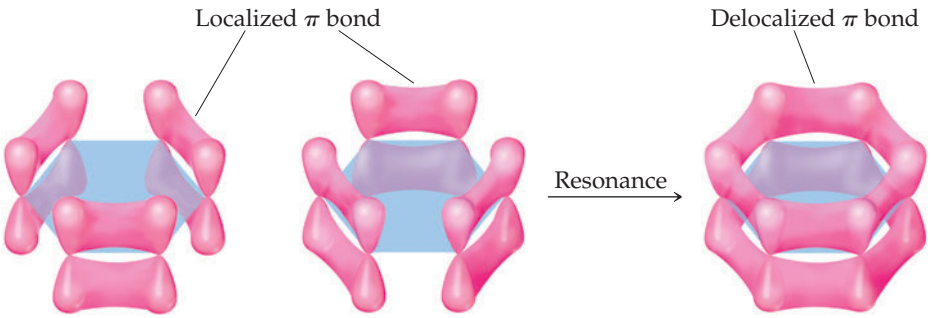
Benzene has a total of 30 valence electrons. To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at 120° angles, the appropriate hybrid set is sp^2. Six localized C—C σ bonds and six localized C—H σ bonds are formed from the sp^2 hybrid orbitals, as shown in **Figure 9.25**(**a**). Thus, 24 of the valence electrons are used to form the σ bonds in the molecule.

Go Figure What are the two kinds of σ bonds found in benzene?



(a) σ bonds **(b)** p orbitals

▲ **Figure 9.25** **σ and π bond networks in benzene, C_6H_6.** (**a**) The σ bond framework. (**b**) The π bonds are formed from overlap of the unhybridized $2p$ orbitals on the six carbon atoms.



◀ **Figure 9.26** **Delocalized π bonds in benzene.**

Because the hybridization at each C atom is sp^2, there is one *p* orbital on each C atom, each oriented perpendicular to the plane of the molecule. The situation is very much like that in ethene except we now have six *p* orbitals arranged in a ring [**Figure 9.25**(**b**)]. The remaining six valence electrons occupy these six *p* orbitals, one per orbital.

We could envision using the *p* orbitals to form three localized π bonds. As shown in **Figure 9.26**, there are two equivalent ways to make these localized bonds, each corresponding to one resonance structure. However, a representation that reflects *both* resonance structures has the six π electrons "smeared out" among all six carbon atoms, as shown on the right in Figure 9.26.

This model leads us to predict that all the carbon–carbon bond lengths will be identical, with a bond length between that of a C—C single bond (154 pm) and that of a C=C double bond (134 pm). This prediction is consistent with the observed carbon–carbon bond length in benzene (140 pm).

Because we cannot describe the π bonds in benzene as individual bonds between neighboring atoms, we say that benzene has a six-electron π system **delocalized** among the six carbon atoms. Delocalization of the electrons in its π bonds gives benzene a special stability. Electron delocalization in π bonds is also responsible for the color of many organic molecules. A final important point to remember about delocalized π bonds is the constraint they place on the geometry of a molecule. For optimal overlap of the *p* orbitals, all the atoms involved in a delocalized π bonding network should lie in the same plane. This restriction imparts a certain rigidity to the molecule that is absent in molecules containing only σ bonds (see the "Chemistry and Life" box on vision).

Sample Exercise 9.7

Delocalized Bonding

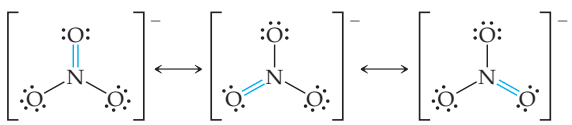
Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

SOLUTION

Analyze Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized π bonds.

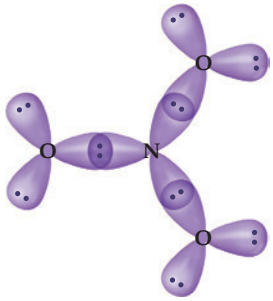
Plan Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations would suggest that the π component of the double bonds is delocalized.

Solve In Section 8.6 we saw that NO_3^- has three resonance structures:



In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. It is helpful when considering delocalized π bonding to consider atoms with lone pairs that are bonded to the central atom to be sp^2 hybridized as well. Thus, we can envision that each of the O atoms in the anion has three sp^2 hybrid orbitals in the plane of the ion. Each of the four atoms has an unhybridized *p* orbital oriented perpendicular to the plane of the ion.

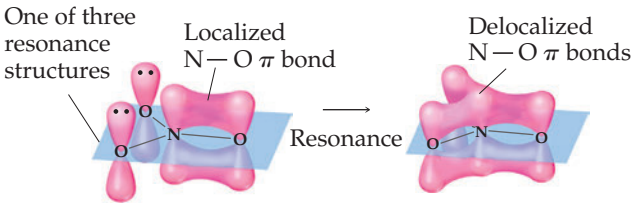
The NO_3^- ion has 24 valence electrons. We can first use the sp^2 hybrid orbitals on the four atoms to construct the three N—O σ bonds. That uses all of the sp^2 hybrids on the N atom and one sp^2 hybrid on each O atom. Each of the two remaining sp^2 hybrids on each O atom is used to hold a nonbonding pair of electrons. Thus, for any of the resonance structures, we have the following arrangement in the plane of the ion:



Continued

Notice that we have accounted for a total of 18 electrons—6 in the three N—O σ bonds, and 12 as nonbonding pairs on the O atoms. The remaining six electrons will reside in the π system of the ion.

The four p orbitals—one on each of the four atoms—are used to build the π system. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the p orbital on N and a p orbital on one of the O atoms. The remaining two O atoms have nonbonding pairs in their p orbitals. Thus, for each of the resonance structures, we have the situation shown in **Figure 9.27**. Because each resonance structure contributes equally to the observed structure of NO_3^-, however, we represent the π bonding as delocalized over the three N—O bonds, as shown in the figure. We see that the NO_3^- ion has a six-electron π system delocalized among the four atoms in the ion.



▲ **Figure 9.27** **Localized and delocalized representations of the six-electron π system in NO_3^-.**

Practice Exercise

How many electrons are in the π system of the ozone molecule, O_3?

(**a**) 2 (**b**) 4 (**c**) 6 (**d**) 14 (**e**) 18

General Conclusions about σ and π Bonding

On the basis of the examples we have seen, we can draw a few helpful conclusions for using hybrid orbitals to describe molecular structures:

- Every pair of bonded atoms shares one or more pairs of electrons. Each bond line we draw in a Lewis structures represents two shared electrons. In every σ bond one pair of electrons is localized in the space between the atoms. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule. The correlation between the set of hybrid orbitals and the geometry about an atom is given in Table 9.4.
- Because the electrons in σ bonds are localized in the region between two bonded atoms, they do not make a significant contribution to the bonding between any other two atoms.
- When atoms share more than one pair of electrons, one pair is used to form a σ bond; the additional pairs form π bonds. The centers of charge density in a π bond lie above and below the internuclear axis.
- Molecules can have π systems that extend over more than two bonded atoms. Electrons in extended π systems are said to be "delocalized." We can determine the number of electrons in the π system of a molecule using the procedures we discussed in this section.

Self-Assessment Exercises

9.26 Draw one resonance structure of the carbonate ion, CO_3^{2-}. How many σ- and π-bonds are present in CO_3^{2-}?

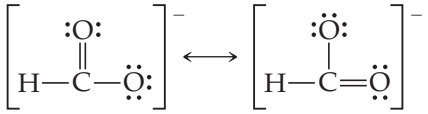
(a) 3σ bonds

(b) 3σ bonds and 1π bond

(c) 3σ bonds and 2π bonds

(d) 4σ bonds

9.27 Is the π-bond in the HCO_2^- ion shown here localized or delocalized?



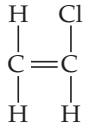
(a) Localized

(b) Delocalized

Exercises

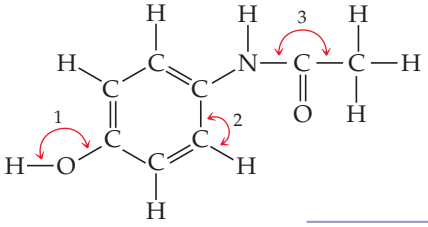
9.28 (**a**) Draw a picture showing how two *p* orbitals on two different atoms can be combined to make a σ bond. (**b**) Sketch a π bond that is constructed from *p* orbitals. (**c**) Which is generally stronger, a σ bond or a π bond? Explain. (**d**) Can two *s* orbitals combine to form a π bond? Explain.

9.29 Vinyl chloride, C_2H_3Cl, is a gas that is used to form the important polymer called polyvinyl chloride (PVC). Its Lewis structure is



(**a**) What is the total number of valence electrons in the vinyl chloride molecule? (**b**) How many valence electrons are used to make σ bonds in the molecule? (**c**) How many valence electrons are used to make π bonds in the molecule? (**d**) How many valence electrons remain in nonbonding pairs in the molecule? (**e**) What is the hybridization at each carbon atom in the molecule?

9.30 Acetaminophen, better known as paracetamol, has the following Lewis structure:



(**a**) What are the approximate values of the bond angles labelled 1, 2, and 3? (**b**) What hybrid orbitals are used about the central atom of each of these angles? (**c**) How many σ bonds are in the molecule?

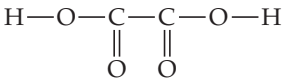
9.31 (**a**) What is the difference between a localized π bond and a delocalized one? (**b**) How can you determine whether a molecule or ion will exhibit delocalized π bonding? (**c**) Is the π bond in NO_2^- localized or delocalized?

9.32 In the sulfate ion, SO_4^{2-}, the sulfur atom is the central atom with the other 4 oxygen atoms attached to it. (**a**) Draw a Lewis structure for the sulfate ion. (**b**) What hybridization is exhibited by the S atom? (**c**) Are there multiple equivalent resonance structures for the ion? (**d**) How many electrons are in the π system of the ion?

9.33 Predict the molecular geometry of each of the following molecules:

(a) H—C≡C—C≡C—C≡N

(b)



(c) H—N=N—H

Answers to Self-Assessment Exercises (b) **9.26** (b) **9.27**

9.7 | Molecular Orbitals



At the very northern tip of Denmark lies the city of Skagen and Grenen beach, a long sandbar that reaches into the sea. What is remarkable is that it lies at the meeting of two seas—the Skagerrak (part of the North Sea) and the Kattegat (part of the Baltic sea). Where these two seas meet, the water is 'confused', the waves of one sea meeting those of the other, sometimes to reinforce one another, sometimes to cancel one another.

In this section, we look at a model of bonding in which the electrons are treated as waves that can interact, reinforce, or cancel one another.

By the end of this section, you should be able to

- Understand the molecular orbitals formed from two 1s atomic orbitals.

While valence-bond theory helps explain some of the relationships among Lewis structures, atomic orbitals, and molecular geometries, it does not explain all aspects of bonding. It is not successful, for example, in describing the excited states of molecules, which we must understand to explain how molecules absorb light, giving them color.

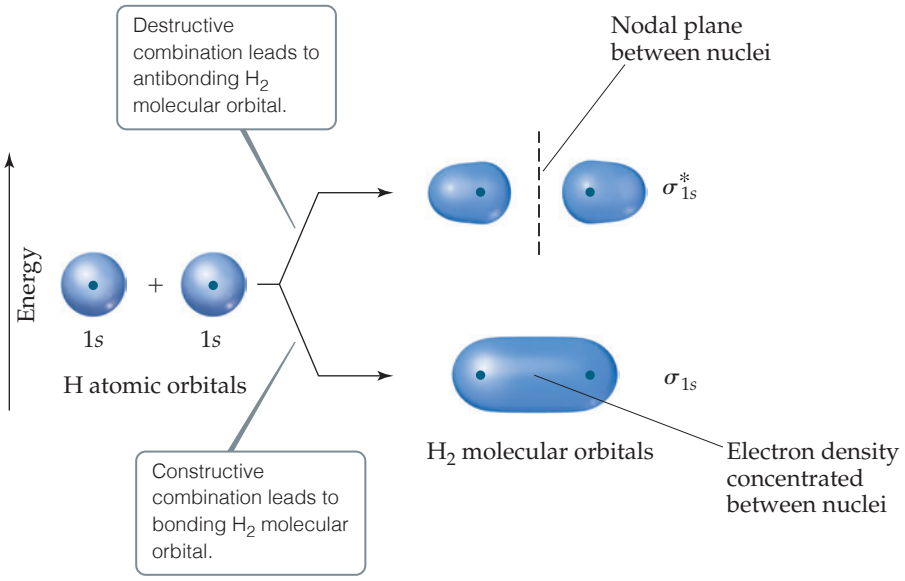
Some aspects of bonding are better explained by a more sophisticated model called **molecular orbital theory**. In Chapter 6, we saw that electrons in atoms can be described by wave functions, which we call atomic orbitals. In a similar way, molecular orbital theory describes the electrons in molecules by using specific wave functions, each of which is called a **molecular orbital (MO)**.

Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did with atomic orbitals. Unlike atomic orbitals, however, MOs are associated with an entire molecule, not with a single atom.

Molecular Orbitals of the Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule, H_2. We will use the two 1*s* atomic orbitals (one on each H atom) to construct molecular orbitals for H_2. *Whenever two atomic orbitals overlap, two molecular orbitals form.* Thus, the overlap of the 1*s* orbitals of two hydrogen atoms to form H_2 produces two MOs. The first MO, which is shown at the bottom right of **Figure 9.28**, is formed by adding the wave functions for the two 1*s* orbitals. We refer to this as *constructive combination*. The energy of the resulting MO is lower

Go Figure What is the probability of finding an electron at the nodal plane in the antibonding orbital?



▲ **Figure 9.28** **The two molecular orbitals of H_2, one a bonding MO and one an antibonding MO.**

in energy than the two atomic orbitals from which it was made. It is called the **bonding molecular orbital**.

The second MO is formed by what is called *destructive combination:* combining the two atomic orbitals in a way that causes the electron density to be canceled in the central region where the two overlap. The process is discussed more fully in the "Closer Look" box later in the chapter. The energy of the resulting MO, referred to as the **antibonding molecular orbital**, is higher than the energy of the atomic orbitals. The antibonding MO of H_2 is shown at the top right in Figure 9.28.

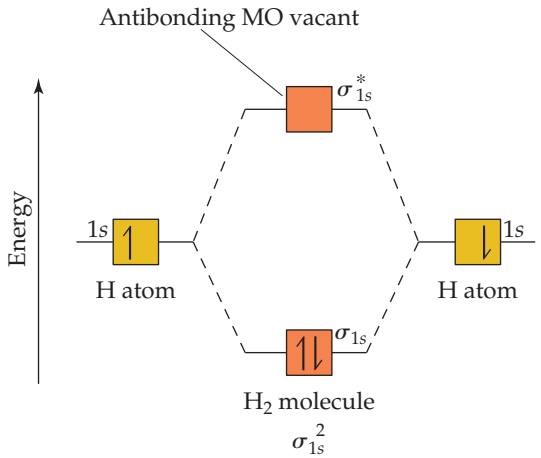
As illustrated in Figure 9.28, in the bonding MO electron density is concentrated in the region between the two nuclei. This sausage-shaped MO results from summing the two atomic orbitals so that the atomic orbital wave functions combine in the region between the two nuclei. Because an electron in this MO is attracted to both nuclei, the electron is more stable (it has lower energy) than it is in the 1*s* atomic orbital of an isolated hydrogen atom. Further, because this bonding MO concentrates electron density between the nuclei, it holds the atoms together in a covalent bond.

By contrast, the antibonding MO has very little electron density between the nuclei. Instead of combining in the region between the nuclei, the atomic orbital wave functions cancel each other in this region, leaving the greatest electron density on opposite sides of the two nuclei. Thus, an antibonding MO excludes electrons from the very region in which a bond must be formed. Antibonding orbitals invariably have a *plane* in the region between the nuclei where the electron density is zero. This plane is called a **nodal plane** of the MO. (The nodal plane is shown as a dashed line in Figure 9.28 and subsequent figures.) An electron in an antibonding MO is repelled from the bonding region and is therefore less stable (it has higher energy) than it is in the 1*s* atomic orbital of a hydrogen atom.

Notice from Figure 9.28 that the electron density in both the bonding MO and the antibonding MO of H_2 is centered about the internuclear axis. MOs of this type are called **sigma (σ) molecular orbitals** (by analogy to σ bonds). The bonding sigma MO of H_2 is labeled σ_{1s}; the subscript indicates that the MO is formed from two 1*s* orbitals. The antibonding sigma MO of H_2 is labeled σ^*_{1s} (read "sigma-star-one-*s*"); the asterisk denotes that the MO is antibonding.

The relative energies of two 1*s* atomic orbitals and the molecular orbitals formed from them are represented by an **energy-level diagram** (also called a **molecular orbital diagram**). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle, as shown in **Figure 9.29**. Like atomic orbitals, each MO can accommodate two electrons with their spins paired (Pauli exclusion principle).

Go Figure What would happen to the energy of the σ_{1s} MO if the H atoms in H_2 were pulled apart to a distance twice as long as its normal bond length?



▲ **Figure 9.29** Energy-level diagram and electron configuration for H_2.

As the MO diagram for H_2 in Figure 9.29 shows, each H atom has one electron, so there are two electrons in H_2. These two electrons occupy the lower-energy bonding (σ_{1s}) MO, and their spins are paired. Electrons occupying a bonding molecular orbital are called *bonding electrons*. Because the σ_{1s} MO is lower in energy than the H 1*s* atomic orbitals, the H_2 molecule is more stable than the two separate H atoms.

By analogy with atomic electron configurations, the electron configurations for molecules can be written with superscripts to indicate electron occupancy. The electron configuration for H_2, then, is σ_{1s}^2.

Bond Order

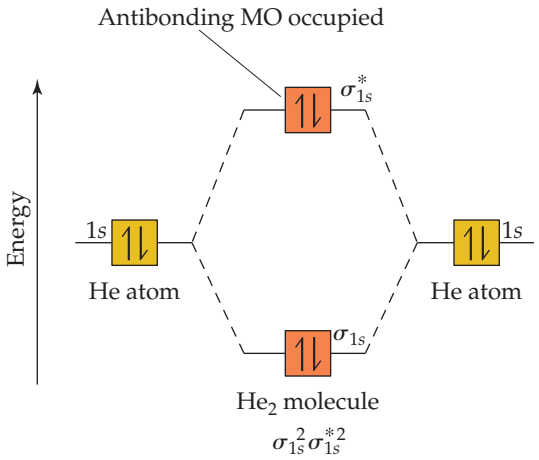
In molecular orbital theory, the stability of a covalent bond is related to its **bond order**, defined as half the difference between the number of bonding electrons and the number of antibonding electrons:

$$\text{Bond order} = \tfrac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons}) \quad [9.1]$$

We take half the difference because we are used to thinking of bonds as pairs of electrons. *A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond.* Because MO theory also treats molecules containing an odd number of electrons, bond orders of 1/2, 3/2, or 5/2 are possible.

Let's now consider the bond order in H_2 and He_2, referring to Figures 9.29 and 9.30. H_2 has two bonding electrons and zero antibonding electrons, so it has a bond order of 1.

Figure 9.30 shows the energy-level diagram for the hypothetical He_2 molecule, which requires four electrons to fill its molecular orbitals. Because only two electrons can go in the σ_{1s} MO, the other two electrons must go in the σ_{1s}^* MO. The electron configuration of He_2 is thus $\sigma_{1s}^2\sigma_{1s}^{*2}$. The energy decrease realized in going from He atomic orbitals to the He bonding MO is offset by the energy increase realized in going from the atomic orbitals to the He antibonding MO.* Because He_2 has two bonding electrons and two antibonding electrons, it has a bond order of 0. A bond order of 0 means that no bond exists. Molecular orbital theory correctly predicts that hydrogen forms diatomic molecules but helium does not.



▶ **Figure 9.30** **Energy-level diagram and electron configuration for He_2.**

*Antibonding MOs are slightly more energetically unfavorable than bonding MOs are energetically favorable. Thus, whenever there is an equal number of electrons in bonding and antibonding orbitals, the energy of the molecule is slightly higher than that for the separated atoms. As a result, no bond is formed.

Sample Exercise 9.8

Bond Order

What is the bond order of the He_2^+ ion? Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

SOLUTION

Analyze We will determine the bond order for the He_2^+ ion and use it to predict whether the ion is stable.

Plan To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1*s* orbital, and the 1*s* orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.30). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.

Solve The energy-level diagram for the He_2^+ ion is shown in Figure 9.31. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \tfrac{1}{2}(2 - 1) = \tfrac{1}{2}$$

Because the bond order is greater than 0, we predict the He_2^+ ion to be stable relative to the separated He and He^+. Formation of He_2^+ in the gas phase has been demonstrated in laboratory experiments.

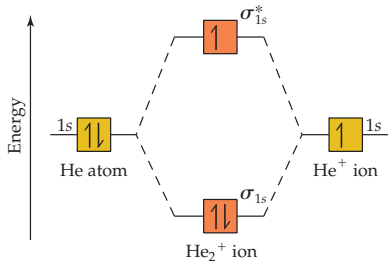
Practice Exercise

How many of the following molecules and ions have a bond order of $\frac{1}{2}$: H_2, H_2^+, H_2^-, and He_2^{2+}?

(a) 0 **(b)** 1 **(c)** 2 **(d)** 3 **(e)** 4

Go Figure

What is the electron configuration of the He_2^+ ion?



▲ **Figure 9.31** **Energy-level diagram for the He_2^+ ion.**

Self-Assessment Exercise

9.34 What is the bond order of H_2^{2+}?

(a) 0

(b) ½

(c) 1

Exercises

9.35 (**a**) What is the difference between hybrid orbitals and molecular orbitals? (**b**) How many electrons can be placed into each MO of a molecule? (**c**) Can antibonding molecular orbitals have electrons in them?

9.36 Consider the H_2^+ ion. (**a**) Sketch the molecular orbitals of the ion and draw its energy-level diagram. (**b**) How many electrons are there in the H_2^+ ion? (**c**) Write the electron configuration of the ion in terms of its MOs. (**d**) What is the bond order in H_2^+? (**e**) Suppose that the ion is excited by light so that an electron moves from a lower-energy to a higher-energy MO. Would you expect the excited-state H_2^+ ion to be stable or to fall apart? (**f**) Which of the following statements about part (e) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

Answers to Self-Assessment Exercise

9.34 (a)

9.8 | Bonding in Period 2 Diatomic Molecules



Some diatomic molecules are harmless to us, for example N_2, others are harmful, for example CO and CN-, yet others are essential for life—O_2 and NO. Even simple molecules may play a central role in our physiology!

Take the NO molecule. It controls several important human physiological functions. Our bodies use it to relax muscles, kill foreign cells, and reinforce memory. The 1998 Nobel Prize in Physiology or Medicine was awarded to three scientists for their research that uncovered the importance of NO as a "signaling" molecule in the cardiovascular system. NO also functions as a neurotransmitter and is implicated in many other biological pathways. That NO plays such an important role in human metabolism was unsuspected before 1987, because NO has an odd number of electrons and is highly reactive. In 1992, it was named 'Molecule of the Year'. Leafy greens and beetroot are rich in nitrates which can be metabolized to NO in the body.

In this section, we will focus on a molecular orbital approach to bonding in diatomic molecules. By the end, you should be able to

- Use MO diagrams to describe the bonding in Period 2 diatomic molecules.

In considering the MO description of diatomic molecules other than H_2, we will initially restrict our discussion to *homonuclear* diatomic molecules (those composed of two identical atoms) of Period 2 elements.

Period 2 atoms have valence 2*s* and 2*p* orbitals, and we need to consider how they interact to form MOs. The following rules summarize some of the guiding principles for the formation of MOs and for how they are populated by electrons:

1. The number of MOs formed equals the number of atomic orbitals combined.
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy.
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap. That is, as the overlap increases, the energy of the bonding MO is lowered and the energy of the antibonding MO is raised.
4. Each MO can accommodate, at most, two electrons, with their spins paired (Pauli exclusion principle).
5. When MOs of the same energy are populated, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund's rule).

Molecular Orbitals for Li_2 and Be_2

Lithium has the electron configuration $1s^2 2s^1$. When lithium metal is heated above its boiling point (1342 °C), Li_2 molecules are found in the vapor phase. The Lewis structure for Li_2 indicates a Li—Li single bond. We will now use MOs to describe the bonding in Li_2.

Figure 9.32 shows that the Li 1*s* and 2*s* atomic orbitals have substantially different energy levels. From this, we can assume that the 1*s* orbital on one Li atom interacts only with the 1*s* orbital on the other atom (rule 2). Likewise, the 2*s* orbitals interact only with each other. Notice that combining four atomic orbitals produces four MOs (rule 1).

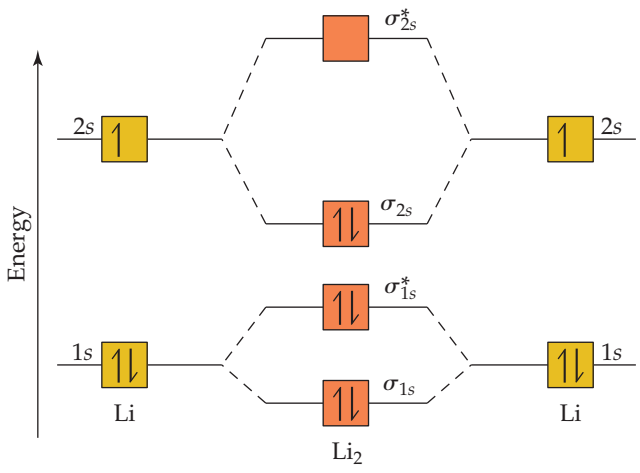
The Li 1*s* orbitals combine to form σ_{1s} and σ^*_{1s} bonding and antibonding MOs, as they did for H_2. The 2*s* orbitals interact with one another in exactly the same way, producing bonding (σ_{2s}) and antibonding (σ^*_{2s}) MOs. In general, the separation between bonding and antibonding MOs depends on the extent to which the constituent atomic orbitals overlap. Because the Li 2*s* orbitals extend farther from the nucleus than the 1*s* orbitals do, the 2*s* orbitals overlap more effectively. As a result, the energy difference between the σ_{2s} and σ^*_{2s} orbitals is greater than the energy difference between the σ_{1s} and σ^*_{1s} orbitals. The 1*s* orbitals of Li are much lower in energy than the 2*s* orbitals; therefore, the energy of the σ^*_{1s} antibonding MO is much lower than the energy of the σ_{2s} bonding MO.

Each Li atom has three electrons, so six electrons must be placed in Li_2 MOs. As shown in Figure 9.32, these electrons occupy the σ_{1s}, σ^*_{1s}, and σ_{2s} MOs, each with two electrons. The electron configuration of Li2 is therefore $\sigma_{1s}{}^2\,\sigma^*_{1s}{}^2\,\sigma_{2s}{}^2$. There are four electrons in bonding orbitals and two in antibonding orbitals, so the bond order is $\frac{1}{2}(4 - 2) = 1$. The molecule has a single bond, in agreement with its Lewis structure.

Because both the σ_{1s} and σ^*_{1s} MOs of Li_2 are completely filled, the 1*s* orbitals contribute almost nothing to the bonding. The single bond in Li_2 is due essentially to the interaction of the valence 2*s* orbitals on the Li atoms. This example illustrates the general rule that *core electrons usually do not contribute significantly to bonding in molecules*. The rule is equivalent to using only the valence electrons when drawing Lewis structures. Thus, we need not consider further the 1*s* orbitals while discussing the other Period 2 diatomic molecules.

The MO description of Be_2 follows readily from the energy-level diagram for Li_2. Each Be atom has four electrons ($1s^2 2s^2$), so we must place eight electrons in molecular orbitals. Therefore, we completely fill the σ_{1s}, σ^*_{1s}, σ_{2s}, and σ^*_{2s} MOs. With equal numbers of bonding and antibonding electrons, the bond order is zero; thus, Be_2 does not exist.

Go Figure Which of the MOs in the diagram will have nodal planes?



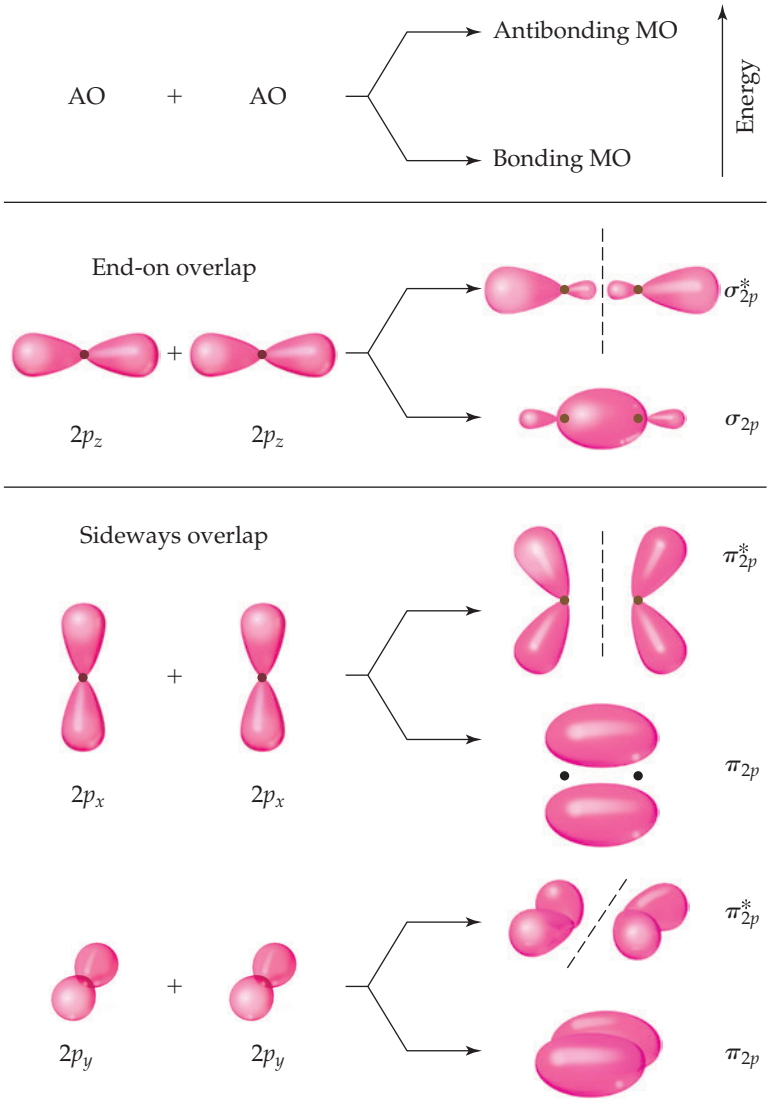
▲ **Figure 9.32** **Energy-level diagram for the Li_2 molecule.**

Molecular Orbitals from 2*p* Atomic Orbitals

Before we can consider the remaining Period 2 diatomic molecules, we must look at the MOs that result from combining 2*p* atomic orbitals. The interactions between *p* orbitals are shown in **Figure 9.33**, where we have arbitrarily chosen the internuclear axis to be the *z*-axis. The $2p_z$ orbitals face each other head to head. Just as with *s* orbitals, we can combine $2p_z$ orbitals in two ways. One combination concentrates electron density between the nuclei and is, therefore, a bonding molecular orbital. The other combination excludes electron density from the bonding region and so is an antibonding molecular orbital. In both MOs, the electron density lies along the internuclear axis, so they are σ molecular orbitals: σ_{2p} and σ^*_{2p}.

The other 2*p* orbitals overlap sideways and thus concentrate electron density above and below the internuclear axis. MOs of this type are called **pi (π) molecular orbitals** by analogy to π bonds. We get one π bonding MO by combining the $2p_x$ atomic orbitals and another from the $2p_y$ atomic orbitals. These two π_{2p} molecular orbitals have the same energy; in other words, they are degenerate. Likewise, we get two degenerate π^*_{2p} antibonding MOs that are perpendicular to each other like the 2*p* orbitals from which

Go Figure In which MO is the overlap of atomic orbitals greater, a σ_{2p} or a π_{2p}?



▲ **Figure 9.33** **Contour representations of the molecular orbitals formed by 2*p* orbitals.**

they were made. These π^*_{2p} orbitals have four lobes, pointing away from the two nuclei, as shown in Figure 9.33.

The $2p_z$ orbitals on two atoms point directly at each other. Hence, overlap of two $2p_z$ orbitals is greater than that of two $2p_x$ or $2p_y$ orbitals. We therefore expect the σ_{2p} MO to be lower in energy (more stable) than the π_{2p} MOs. Similarly, the σ^*_{2p} MO should be higher in energy (less stable) than the π^*_{2p} MOs.

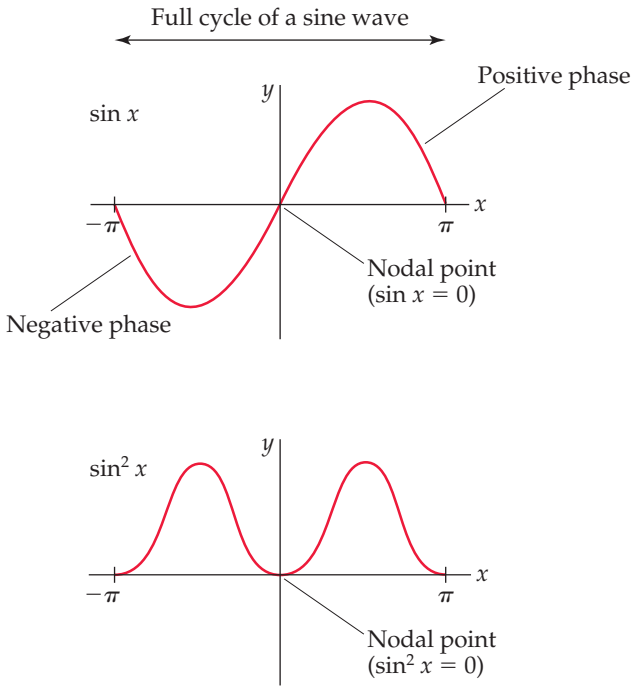
A CLOSER LOOK Phases in Atomic and Molecular Orbitals

Our discussion of atomic orbitals in Chapter 6 and molecular orbitals in this chapter highlights some of the most important applications of quantum mechanics in chemistry. In the quantum-mechanical treatment of electrons in atoms and molecules, we are mainly interested in determining two characteristics of the electrons—their energies and their distribution in space. Recall that solving Schrödinger's wave equation yields the electron's energy, E, and wave function, ψ, but that ψ does not have a direct physical meaning. The contour representations of atomic and molecular orbitals we have presented thus far are based on ψ^2 (the *probability density*), which gives the probability of finding the electron at a given point in space.

Because probability densities are squares of functions, their values must be nonnegative (zero or positive) at all points in space. However, the functions themselves can have negative values. The situation is like that of the sine function plotted in **Figure 9.34**. In the top graph, the sine function is negative for x between 0 and $-\pi$ and positive for x between 0 and $+\pi$. We say that the *phase* of the sine function is negative between 0 and $-\pi$ and positive between 0 and $+\pi$. If we square the sine function (bottom graph), we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. In other words, *we lose the phase information of the function upon squaring it.*

Like the sine function, the more complicated wave functions for atomic orbitals can also have phases. Consider, for example, the representations of the 1*s* orbital in Figure 9.35. Note that here we plot this orbital a bit differently from what is shown in Section 6.6. The origin is the point where the nucleus resides, and the wave function for the 1*s* orbital extends from the origin out into space. The plot shows the value of ψ for a slice taken along the *z*-axis. A contour representation of the 1*s* orbital is shown after the plot. Notice that the value of the 1*s* wave function is always a positive number (we show positive values in red in Figure 9.35). Thus, it has only one phase. Notice also that the wave function approaches zero only at a long distance from the nucleus. It therefore has no nodes, as we saw in Figure 6.21.

In the graph for the $2p_z$ orbital in Figure 9.35, the wave function changes sign when it passes through $z = 0$. Notice that the two halves of the wave have the same shape except that one has positive (red) values and the other negative (blue) values. Analogously to the sine function, the wave function changes phase when it passes through the origin. Mathematically, the $2p_z$ wave function is equal to zero whenever $z = 0$. This corresponds to any point on the *xy* plane, so we say that the *xy* plane is a *nodal plane* of the $2p_z$ orbital. The wave function for a *p* orbital is much like a sine function because it has two equal parts that have opposite phases. Figure 9.35 gives a typical representation used by chemists of the wave function for a p_z orbital.* The red and blue lobes indicate the different phases of the orbital.



▲ **Figure 9.34** **Graphs for a sine function and the same function squared.**

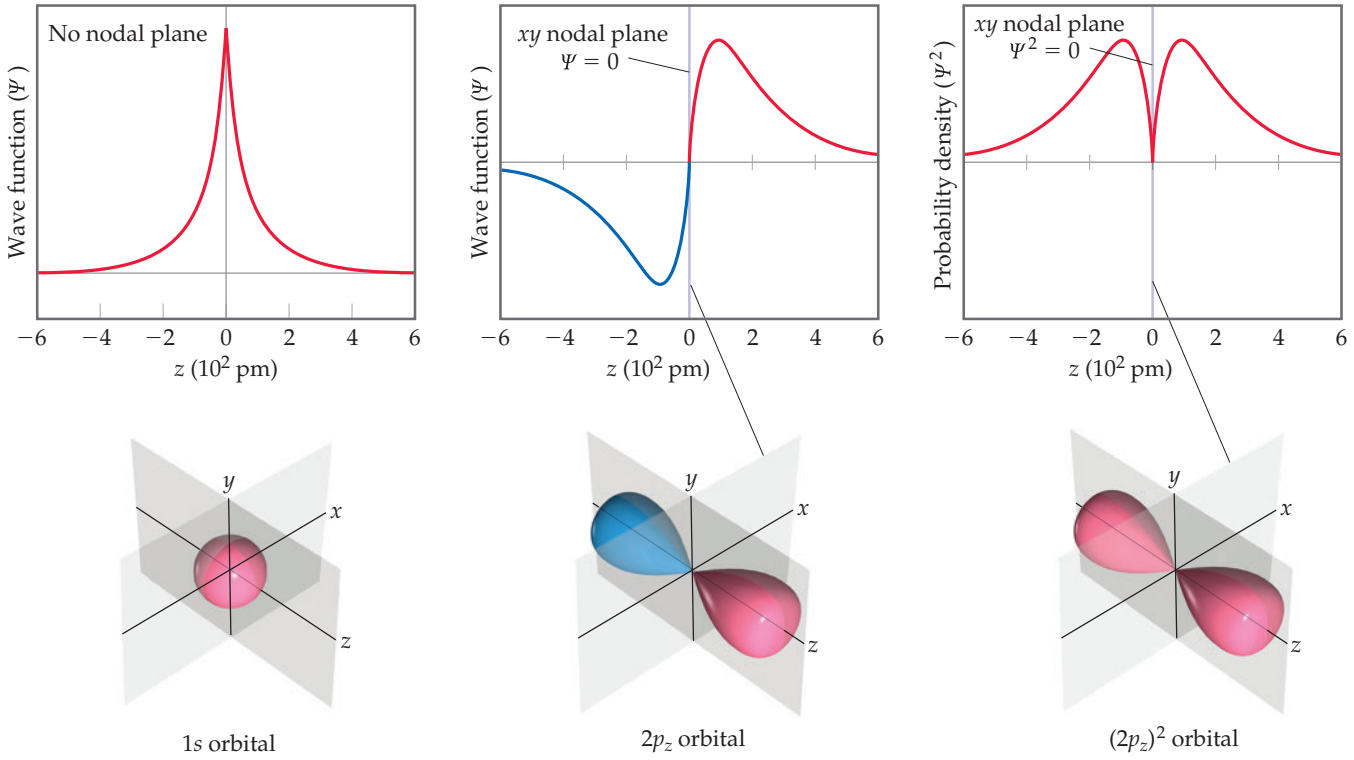
(Note: The colors do *not* represent charge, as they did in the plots in Figures 9.10 and 9.11.) As with the sine function, the origin is a node.

The third graph in Figure 9.35 shows that when we square the wave function of the $2p_z$ orbital, we get two peaks that are symmetrical about the origin. Both peaks are positive because squaring a negative number produces a positive number. Thus, *we lose the phase information of the function upon squaring it* just as we did for the sine function. When we square the wave function for the p_z orbital, we get the probability density for the orbital, which is given as a contour representation in Figure 9.35. This is what we saw in the earlier presentation of *p* orbitals. For this squared wave function, both lobes have the same phase and therefore the same sign. We use this representation throughout most of this book because it has a simple physical interpretation: The square of the wave function at any point in space represents the electron density at that point.

The lobes of the wave functions for the *d* orbitals also have different phases. For example, the wave function for a d_{xy} orbital has four lobes, with the phase of each lobe opposite the phase of its nearest neighbors (**Figure 9.36**). The wave functions for the

*The mathematical development of this three-dimensional function (and its square) is beyond the scope of this book, and, as is typically done by chemists, we have used lobes that are the same shape as in Figure 9.35.

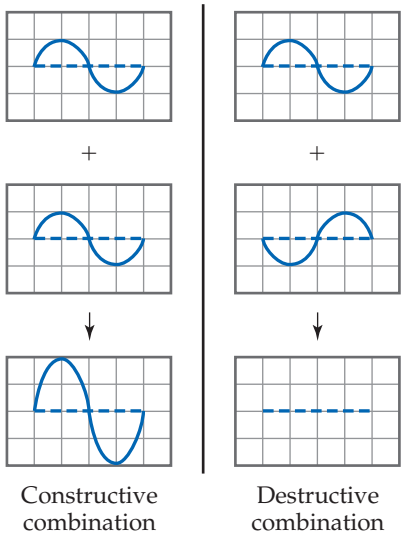
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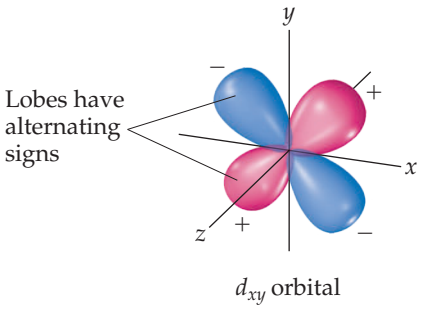


▲ **Figure 9.35 Phases in wave functions of *s* and *p* atomic orbitals.** Red shading means a positive value for the wave function, and blue shading means a negative value.

other *d* orbitals likewise have lobes in which the phase in one lobe is opposite that in an adjacent lobe.

Why do we need to consider the complexity introduced by considering the phase of the wave function? While it is true that the phase is not necessary to visualize the shape of an atomic orbital in an isolated atom, it does become important when we consider overlap of orbitals in molecular orbital theory. Let's use the sine function as an example again. If you add two sine functions having the same phase, they add *constructively,* resulting in increased amplitude:

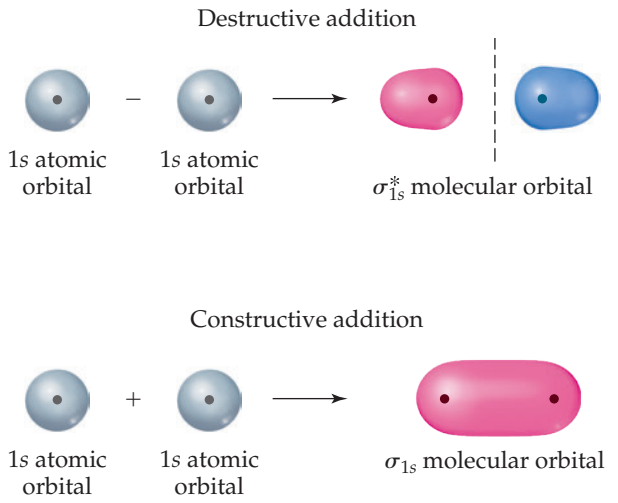




▲ **Figure 9.36 Phases in *d* orbitals.**

but if you add two sine functions having opposite phases, they add *destructively* and cancel each other.

The idea of constructive and destructive interactions of wave functions is key to understanding the origin of bonding and antibonding molecular orbitals. For example, the wave function of the σ_{1s} MO of H_2 is generated by adding the wave function for the 1*s* orbital on one atom to the wave function for the 1*s* orbital on the other atom, with both orbitals having the same phase. The atomic wave functions overlap *constructively* in this case to increase the electron density between the two atoms (**Figure 9.37**). The wave function of the σ^*_{1s} MO of H_2 is generated by subtracting the wave function for a 1*s* orbital on one atom from the wave function for a 1*s* orbital on the other atom. The result is that the atomic orbital wave functions overlap *destructively* to create a region of zero electron density between the two atoms—a node. Notice the similarity between this figure and Figure 9.29. In Figure 9.37, we use red and blue shading to denote positive and negative phases in the H atomic orbitals.



▲ **Figure 9.37** **Molecular orbitals from atomic orbital wave functions.**

However, chemists may alternatively draw contour representations in different colors, or with one phase shaded and one unshaded, to denote the two phases.

When we square the wave function of the σ^*_{1s} MO, we get the electron density representation which we saw earlier, in Figure 9.29. Notice once again that we lose the phase information when we look at the electron density.

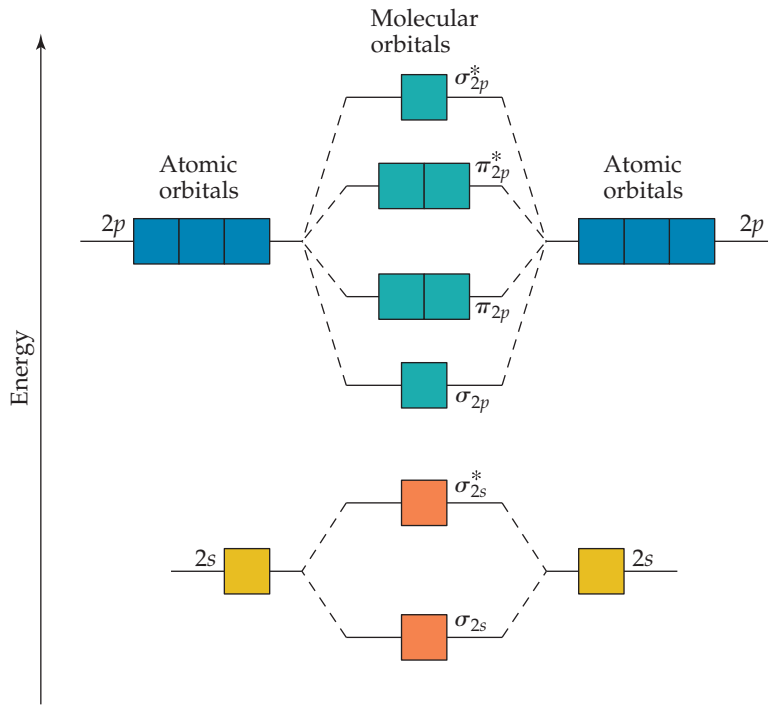
The wave functions of atomic and molecular orbitals are used by chemists to understand many aspects of chemical bonding, spectroscopy, and reactivity.

Related Exercises: 9.116, 9.127, 9.129

Electron Configurations for B_2 through Ne_2

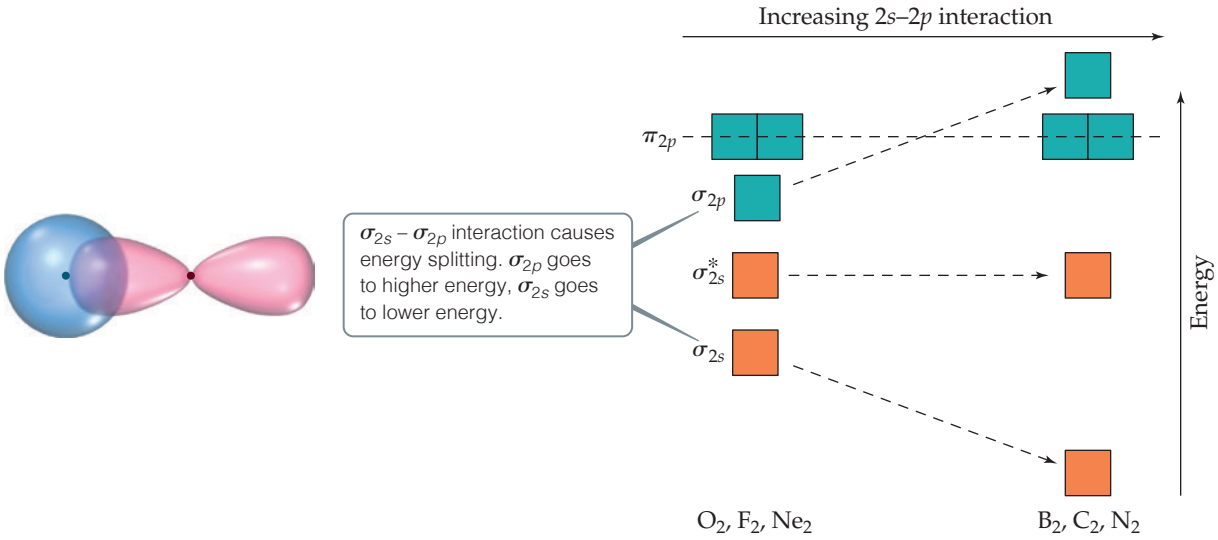
We can combine our analyses of MOs formed from *s* orbitals (Figure 9.29) and from *p* orbitals (Figure 9.33) to construct an energy-level diagram (**Figure 9.38**) for homonuclear diatomic molecules of the elements boron through neon, all of which have valence 2*s* and 2*p* atomic orbitals. The following features of the diagram are notable:

- The 2*s* atomic orbitals are substantially lower in energy than the 2*p* atomic orbitals. Consequently, both MOs formed from the 2*s* orbitals are lower in energy than the lowest-energy MO derived from the 2*p* atomic orbitals.
- The overlap of the two $2p_z$ orbitals is greater than that of the two $2p_x$ or $2p_y$ orbitals. As a result, the bonding σ_{2p} MO is lower in energy than the π_{2p} MOs, and the antibonding σ^*_{2p} MO is higher in energy than the π^*_{2p} MOs.
- Both the π_{2p} and π^*_{2p} MOs are *doubly degenerate*; that is, there are two degenerate MOs of each type.



◀ **Figure 9.38** **Energy-level diagram for MOs of Period 2 homonuclear diatomic molecules.** The diagram assumes no interaction between the 2*s* atomic orbital on one atom and the 2*p* atomic orbitals on the other atom, and experiment shows that it fits only for O_2, F_2, and Ne_2.

Go Figure Which molecular orbitals have switched relative energy in the group on the right as compared with the group on the left?



▲ **Figure 9.39** **The effect of interactions between 2*s* and 2*p* atomic orbitals.**

Before we can add electrons to Figure 9.38, we must consider one more effect. We have constructed the diagram assuming no interaction between the 2*s* orbital on one atom and the 2*p* orbitals on the other. In fact, such interactions can and do take place. **Figure 9.39** shows the overlap of a 2*s* orbital on one of the atoms with a 2*p* orbital on the other. These interactions increase the energy difference between the σ_{2s} and σ_{2p} MOs, with the σ_{2s} energy decreasing and the σ_{2p} energy increasing (Figure 9.39). These 2*s*–2*p* interactions can be strong enough that the energetic ordering of the MOs can be altered: For B_2, C_2, and N_2, the σ_{2p} MO is above the π_{2p} MOs in energy. For O_2, F_2, and Ne_2, the σ_{2p} MO is below the π_{2p} MOs.

Given the energy ordering of the molecular orbitals, it is a simple matter to determine the electron configurations for the diatomic molecules B_2 through Ne_2. For example, a boron atom has three valence electrons. (Remember that we are ignoring the core 1*s* electrons.) Thus, for B_2 we must place six electrons in MOs. Four of them fill the σ_{2s} and σ^*_{2s} MOs, leading to no net bonding. The fifth electron goes in one π_{2p} MO, and the sixth goes in the other π_{2p} MO, with the two electrons having the same spin. Therefore, B_2 has a bond order of 1.

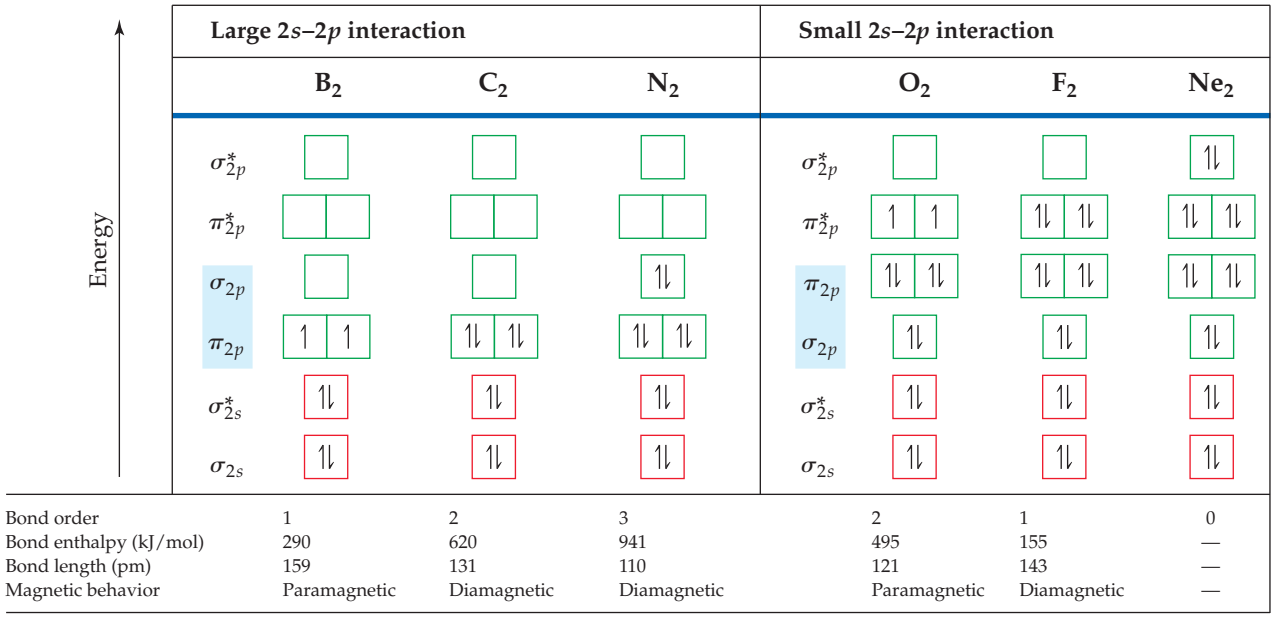
Each time we move one element to the right in Period 2, two more electrons must be placed in the energy-level diagram. For example, on moving to C_2, we have two more electrons than in B_2, and these electrons are placed in the π_{2p} MOs, completely filling them. The electron configurations and bond orders for B_2 through Ne_2 are given in **Figure 9.40**.

Electron Configurations and Molecular Properties

The way a substance behaves in a magnetic field can in some cases provide insight into the arrangements of its electrons. Molecules with one or more unpaired electrons are attracted to a magnetic field. The more unpaired electrons in a species, the stronger the attractive force. This type of magnetic behavior is called **paramagnetism**.

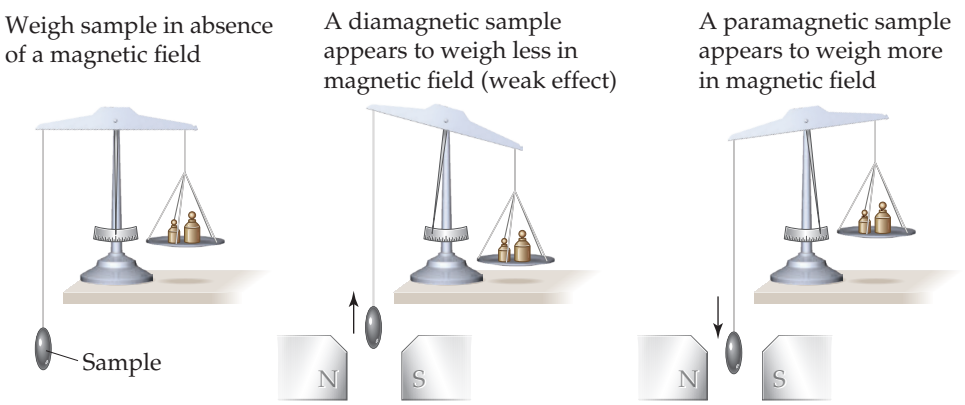
Substances with no unpaired electrons are weakly repelled by a magnetic field. This property is called **diamagnetism**. The distinction between paramagnetism and diamagnetism is nicely illustrated in an older method for measuring magnetic properties (**Figure 9.41**). It involves weighing the substance in the presence and absence of a magnetic field. A paramagnetic substance appears to weigh more in the magnetic field; a diamagnetic substance appears to weigh less. The magnetic behaviors observed for the Period 2 diatomic molecules agree with the electron configurations shown in Figure 9.40.

Go Figure Which stable molecules have their highest-energy electrons in antibonding orbitals?



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (pm)	159	131	110	121	143	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

▲ **Figure 9.40** **Molecular orbital electron configurations and some experimental data for Period 2 diatomic molecules.**



◀ **Figure 9.41** **Determining the magnetic properties of a sample.**

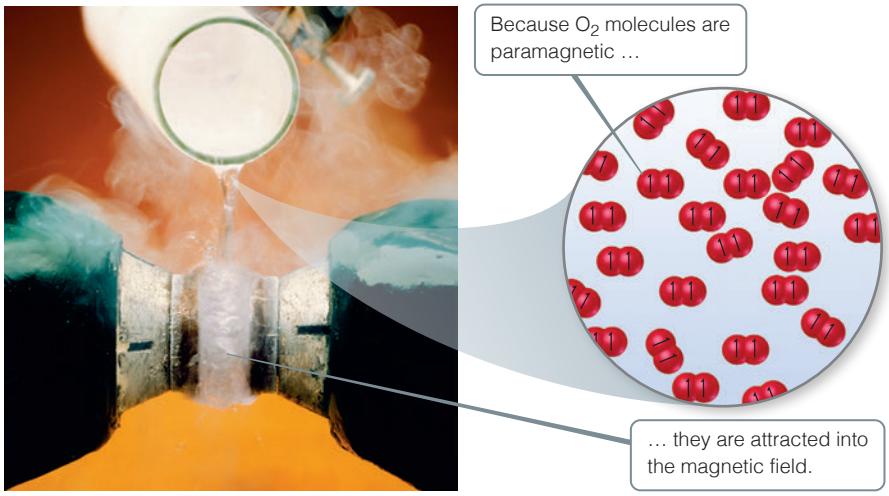
Electron configurations in molecules can also be related to bond distances and bond enthalpies. As bond order increases, bond distances decrease and bond enthalpies increase. N_2, for example, whose bond order is 3, has a short bond distance and a large bond enthalpy. The N_2 molecule does not react readily with other substances to form nitrogen compounds. The high bond order of the molecule helps explain its exceptional stability. We should also note, however, that molecules with the same bond orders do *not* have the same bond distances and bond enthalpies. Bond order is only one factor influencing these properties. Other factors include nuclear charge and extent of orbital overlap.

Bonding in O_2 provides an interesting test case for molecular orbital theory. The Lewis structure for this molecule shows a double bond and complete pairing of electrons:



The short O—O bond distance (121 pm) and relatively high bond enthalpy (495 kJ/mol) are in agreement with the presence of a double bond. However, Figure 9.40 tells us that

Go Figure What would you expect to see if liquid nitrogen were poured between the poles of the magnet?



▲ **Figure 9.42 Paramagnetism of O_2.** When liquid oxygen is poured through a magnet, it "sticks" to the poles.

the molecule contains two unpaired electrons and should therefore be paramagnetic, a detail not discernible in the Lewis structure. The paramagnetism of O_2 is demonstrated in **Figure 9.42**, which confirms the prediction from MO theory. The MO description also correctly predicts a bond order of 2 as did the Lewis structure.

Going from O_2 to F_2, we add two electrons, completely filling the π^*_{2p} MOs. Thus, F_2 is expected to be diamagnetic and have an F—F single bond, in accord with its Lewis structure. Finally, the addition of two more electrons to make Ne_2 fills all the bonding and antibonding MOs. Therefore, the bond order of Ne_2 is zero, and the molecule is not expected to exist.

Sample Exercise 9.9

Molecular Orbitals of a Period 2 Diatomic Ion

For the O_2^+ ion predict (**a**) number of unpaired electrons, (**b**) bond order, (**c**) bond enthalpy and bond length.

SOLUTION

Analyze Our task is to predict several properties of the cation O_2^+.

Plan We will use the MO description of O_2^+ to determine the desired properties. We must first determine the number of electrons in O_2^+ and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use Figure 9.40 to estimate the bond enthalpy and bond length.

Solve

(**a**) The O_2^+ ion has 11 valence electrons, one fewer than O_2. The electron removed from O_2 to form O_2^+ is one of the two unpaired π^*_{2p} electrons (see Figure 9.40). Therefore, O_2^+ has one unpaired electron.

(**b**) The molecule has eight bonding electrons (the same as O_2) and three antibonding electrons (one fewer than O_2). Thus, its bond order is

$$\tfrac{1}{2}(8 - 3) = 2\tfrac{1}{2}$$

(**c**) The bond order of O_2^+ is between that for O_2 (bond order 2) and N_2 (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O_2 and N_2, approximately 700 kJ/mol and 115 pm. (The experimentally measured values are 625 kJ/mol and 112.3 pm.)

Practice Exercise

Place the following molecular ions in order from smallest to largest bond order: C_2^{2+}, N_2^-, O_2^-, and F_2^-.

(**a**) $C_2^{2+} < N_2^- < O_2^- < F_2^-$
(**b**) $F_2^- < O_2^- < N_2^- < C_2^{2+}$
(**c**) $O_2^- < C_2^{2+} < F_2^- < N_2^-$
(**d**) $C_2^{2+} < F_2^- < O_2^- < N_2^-$
(**e**) $F_2^- < C_2^{2+} < O_2^- < N_2^-$

Heteronuclear Diatomic Molecules

The principles we have used in developing an MO description of homonuclear diatomic molecules can be extended to *heteronuclear* diatomic molecules—those in which the two atoms in the molecule are not the same. We conclude this section with a fascinating heteronuclear diatomic molecule—nitric oxide, NO.

The NO molecule has 11 valence electrons, and two possible Lewis structures can be drawn. The Lewis structure with the lower formal charges places the odd electron on the N atom:

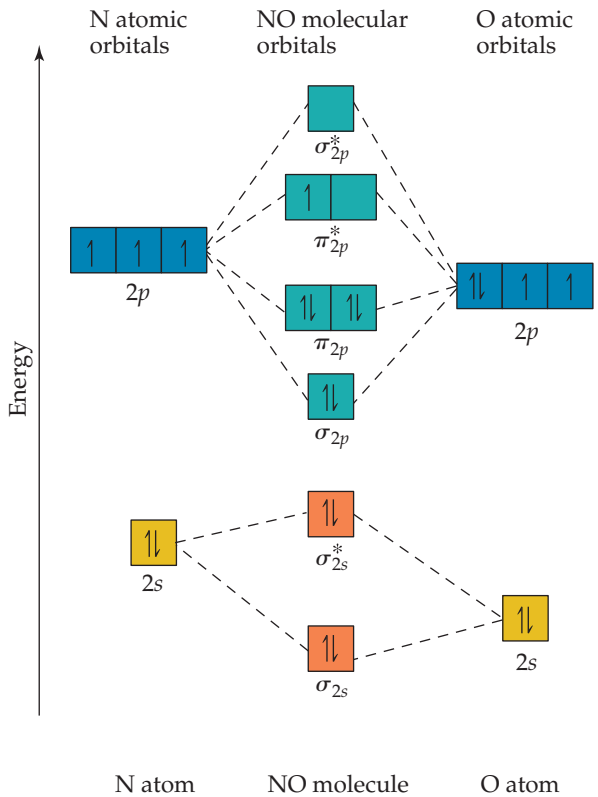


Both structures indicate the presence of a double bond, but when compared with the molecules in Figure 9.40, the experimental bond length of NO (115 pm) suggests a bond order greater than 2. How do we treat NO using the MO model?

If the atoms in a heteronuclear diatomic molecule do not differ too greatly in electronegativities, their MOs resemble those in homonuclear diatomics, with one important modification: The energy of the atomic orbitals of the more electronegative atom is lower than that of the atomic orbitals of the less electronegative element. In **Figure 9.43**, you see that the 2*s* and 2*p* atomic orbitals of oxygen are slightly lower than those of nitrogen because oxygen is more electronegative than nitrogen. The MO energy-level diagram for NO is much like that of a homonuclear diatomic molecule—because the 2*s* and 2*p* orbitals on the two atoms interact, the same types of MOs are produced.

There is one other important difference in the MOs of heteronuclear molecules. The MOs are still a mix of atomic orbitals from both atoms, but in general an *MO in a heteronuclear diatomic molecule has a greater contribution from the atomic orbital to which it is closer in energy*. In the case of NO, for example, the σ_{2s} bonding MO is closer in energy to the

Go Figure How many valence-shell electrons are there in NO?



▲ **Figure 9.43** **The energy-level diagram for atomic and molecular orbitals in NO.**

O 2*s* atomic orbital than to the N 2*s* atomic orbital. As a result, the σ_{2s} MO has a slightly greater contribution from O than from N—the orbital is no longer an equal mixture of the two atoms, as was the case for the homonuclear diatomic molecules. Similarly, the σ^*_{2s} antibonding MO is weighted more heavily toward the N atom because that MO is closest in energy to the N 2*s* atomic orbital.

We complete the MO diagram for NO by filling the MOs in Figure 9.43 with the 11 valence electrons. Eight bonding and three antibonding electrons give a bond order of $\frac{1}{2}(8 - 3) = 2\frac{1}{2}$, which agrees better with experiment than the Lewis structures do. The unpaired electron resides in one of the π^*_{2p} MOs, which have a greater contribution from the N atom. (We could have placed this electron in either the left or right π^*_{2p} MO.) Thus, the Lewis structure that places the unpaired electron on nitrogen (the one preferred on the basis of formal charge) is the more accurate description of the true electron distribution in the molecule.

CHEMISTRY PUT TO WORK Orbitals and Energy

Asked to identify the major technological challenge for the twenty-first century, you might say "energy," reasoning that development of sustainable energy sources is crucial to meet the needs of future generations of people on our planet. One of the most remarkable sources of clean energy is the Sun, which sends enough energy to power the world for millions of years. Our challenge is to capture enough of this energy in a form that allows us to use it as needed. *Photovoltaic solar cells* convert the light from the Sun into usable electricity, and the development of more efficient solar cells is one way to address Earth's future energy needs.

How does solar energy conversion work? Fundamentally, we need to be able to use photons from the Sun, especially from the visible portion of the spectrum, to excite electrons in molecules and materials to different energy levels. The brilliant colors around you—those of your clothes, the photographs in this book, the foods you eat—are due to the selective absorption of visible light by chemicals. It is helpful to think of this process in the context of molecular orbital theory: Light excites an electron from a filled molecular orbital to an empty one at higher energy. Because MOs have definite energies, only light of the proper wavelengths can excite electrons.

In discussing light absorption by molecules, we can focus on the two MOs shown in **Figure 9.44**. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. In N_2, for example, the HOMO is the σ_{2p} MO and the LUMO is the π^*_{2p} MO (Figure 9.40).

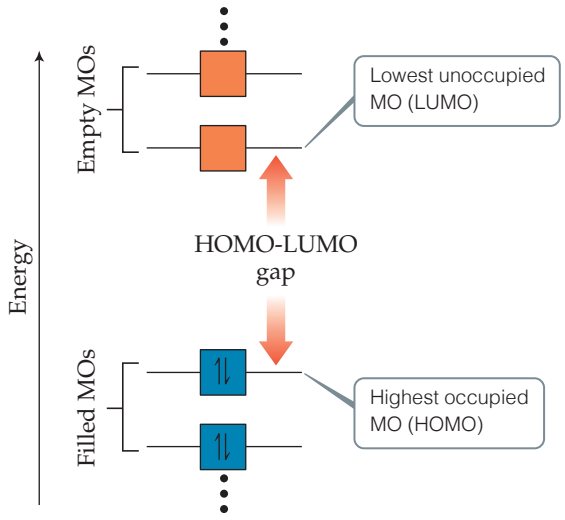
The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the minimum energy needed to excite an electron in the molecule. Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to the higher level. The minimum energy needed to excite an electron from the HOMO to the LUMO in N_2 corresponds to light with a wavelength of less than 200 nm, which is far into the ultraviolet part of the spectrum. As a result, N_2 cannot absorb visible light and is therefore colorless.

The magnitude of the energy gap between filled and empty electronic states is critical for solar energy conversion. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy. Titanium dioxide is a readily available material that can be reasonably efficient at converting light directly into electricity. However, TiO_2 is white and absorbs only a small amount of the Sun's radiant energy. Scientists are working to make solar cells in which TiO_2 is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum. If the HOMO of these molecules is higher in energy than the HOMO of TiO_2, the excited electrons will flow from the molecules into the TiO_2, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world's energy portfolio.

Related Exercises: 9.113, 9.118, 9.128

Design an Experiment



▲ **Figure 9.44 Definitions of the highest occupied and lowest unoccupied molecular orbitals**. The energy difference between these is the HOMO-LUMO gap.

Sample Integrative Exercise

Putting Concepts Together

Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is a puckered, eight-membered ring (see Figure 7.26). Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:

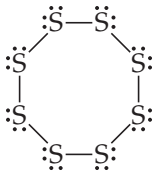
$$S_8(s) \longrightarrow 4\,S_2(g)$$

(a) The electron configuration of which Period 2 element is most similar to that of sulfur? (b) Use the VSEPR model to predict the S—S—S bond angles in S_8 and the hybridization at S in S_8. (c) Use MO theory to predict the sulfur–sulfur bond order in S_2. Do you expect this molecule to be diamagnetic or paramagnetic? (d) Use average bond enthalpies (Table 8.3) to estimate the enthalpy change for this reaction. Is the reaction exothermic or endothermic?

SOLUTION

(**a**) Sulfur is a Group 16 element with an $[Ne]3s^2 3p^4$ electron configuration. It is expected to be most similar electronically to oxygen (electron configuration, $[He]2s^2 2p^4$), which is immediately above it in the periodic table.

(**b**) The Lewis structure of S_8 is



There is a single bond between each pair of S atoms and two nonbonding electron pairs on each S atom. Thus, we see four electron domains around each S atom and expect a tetrahedral electron-domain geometry corresponding to sp^3 hybridization. Because of the nonbonding pairs, we expect the S—S—S angles to be somewhat less than 109.5°, the tetrahedral angle. Experimentally, the S—S—S angle in S_8 is 108°, in good agreement with this prediction. Interestingly, if S_8 were a planar ring, it would have S—S—S angles of 135°. Instead, the S_8 ring puckers to accommodate the smaller angles dictated by sp^3 hybridization.

(**c**) The MOs of S_2 are analogous to those of O_2, although the MOs for S_2 are constructed from the 3*s* and 3*p* atomic orbitals of sulfur. Further, S_2 has the same number of valence electrons as O_2. Thus, by analogy with O_2, we expect S_2 to have a bond order of 2 (a double bond) and to be paramagnetic with two unpaired electrons in the π^*_{3p} molecular orbitals of S_2.

(**d**) We are considering the reaction in which an S_8 molecule falls apart into four S_2 molecules. From parts (b) and (c), we see that S_8 has S—S single bonds and S_2 has S=S double bonds. During the reaction, therefore, we are breaking eight S—S single bonds and forming four S=S double bonds. We can estimate the enthalpy of the reaction by using Equation 5.33 and the average bond enthalpies in Table 8.3:

$$\begin{aligned}\Delta H_{rxn} &= 8\,D(S{-}S) - 4\,D(S{=}S)\\ &= 8(266\text{ kJ}) - 4(418\text{ kJ}) = +456\text{ kJ}\end{aligned}$$

Recall that $D(X{-}Y)$ represents the X—Y bond enthalpy. Because $\Delta H_{rxn} > 0$, the reaction is endothermic (Section 5.3). The very positive value of ΔH_{rxn} suggests that high temperatures are required to cause the reaction to occur.

Self-Assessment Exercise

9.37 What is the bond order of CO?

(a) 1

(b) 2

(c) 3

Exercises

9.38 Draw a picture that shows all three 2*p* orbitals on one atom and all three 2*p* orbitals on another atom. (**a**) Imagine the atoms coming close together to bond. How many σ bonds can the two sets of 2*p* orbitals make with each other? (**b**) How many π bonds can the two sets of 2*p* orbitals make with each other? (**c**) How many antibonding orbitals, and of what type, can be made from the two sets of 2*p* orbitals?

9.39 (**a**) What are the relationships among bond order, bond length, and bond energy? (**b**) According to molecular orbital theory, would either Be_2 or Be_2^+ be expected to exist? Explain.

9.40 How would we describe a substance that contains only paired electrons and is weakly repelled by a magnetic field? Which of the following ions would you expect to possess similar characteristics: H_2^-, Ne_2^+, F_2, O_2^{2+}?

9.41 Using Figures 9.32 and 9.40 as guides, draw the molecular orbital electron configuration for (**a**) B_2^+, (**b**) Li_2^+, (**c**) N_2^+, (**d**) Ne_2^{2+}. In each case indicate whether the addition of an electron to the ion would increase or decrease the bond order of the species.

9.42 Determine the electron configurations for CN^+, CN, and CN^-. (**a**) Which species has the strongest C—N bond? (**b**) Which species, if any, has unpaired electrons?

9.43 Consider the molecular orbitals of the P_2 molecule. Assume that the MOs of diatomics from the third row of the periodic

table are analogous to those from the second row. (**a**) Which valence atomic orbitals of P are used to construct the MOs of P_2? (**b**) The figure that follows shows a sketch of one of the MOs for P_2. What is the label for this MO? (**c**) For the P_2 molecule, how many electrons occupy the MO in the figure? (**d**) Is P_2 expected to be diamagnetic or paramagnetic?



Answers to Self-Assessment Exercise

9.37 (c)

Chapter Summary and Key Terms

MOLECULAR SHAPES (INTRODUCTION AND SECTION 9.1) The three-dimensional shapes and sizes of molecules are determined by their **bond angles** and bond lengths. Molecules with a central atom A surrounded by n atoms B, denoted AB_n, adopt a number of different geometric shapes, depending on the value of n and on the particular atoms involved. In the overwhelming majority of cases, these geometries are related to five basic shapes (linear, trigonal pyramidal, tetrahedral, trigonal bipyramidal, and octahedral).

THE VSEPR MODEL (SECTION 9.2) The **valence-shell electron-pair repulsion (VSEPR) model** rationalizes molecular geometries based on the repulsions between **electron domains**, which are regions about a central atom in which electrons are likely to be found. **Bonding pairs** of electrons, which are those involved in making bonds, and **nonbonding pairs** of electrons, also called **lone pairs**, both create electron domains around an atom. According to the VSEPR model, electron domains orient themselves to minimize electrostatic repulsions; that is, they remain as far apart as possible.

Electron domains from nonbonding pairs exert slightly greater repulsions than those from bonding pairs, which leads to certain preferred positions for nonbonding pairs and to the departure of bond angles from idealized values. Electron domains from multiple bonds exert slightly greater repulsions than those from single bonds. The arrangement of electron domains around a central atom is called the **electron-domain geometry**; the arrangement of atoms is called the **molecular geometry**.

MOLECULAR POLARITY (SECTION 9.3) The dipole moment of a polyatomic molecule depends on the vector sum of the dipole moments associated with the individual bonds, called the **bond dipoles**. Certain molecular shapes, such as linear AB_2 and trigonal planar AB_3, lead to cancellation of the bond dipoles, producing a nonpolar molecule, which is one whose overall dipole moment is zero. In other shapes, such as bent AB_2 and trigonal pyramidal AB_3, the bond dipoles do not cancel and the molecule will be polar (that is, it will have a nonzero dipole moment).

COVALENT BONDING AND ORBITAL OVERLAP (SECTION 9.4) **Valence-bond theory** is an extension of Lewis's notion of electron-pair bonds. In valence-bond theory, covalent bonds are formed when atomic orbitals on neighboring atoms overlap one another. The overlap region is one of greater stability for the two electrons because of their simultaneous attraction to two nuclei. The greater the overlap between two orbitals, the stronger the bond that is formed.

HYBRID ORBITALS (SECTION 9.5) To extend the ideas of valence-bond theory to polyatomic molecules, we must envision mixing s and p orbitals to form **hybrid orbitals**. The process of **hybridization** leads to hybrid atomic orbitals that have a large lobe directed to overlap with orbitals on another atom to make a bond. Hybrid orbitals can also accommodate nonbonding pairs. A particular mode of hybridization can be associated with each of three common electron-domain geometries (linear = sp; trigonal planar = sp^2; tetrahedral = sp^3). The bonding in **hypervalent** molecules—those with more than an octet of electrons—is not as readily discussed in terms of hybrid orbitals.

MULTIPLE BONDS (SECTION 9.6) Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called **sigma (σ) bonds**. Bonds can also be formed from the sideways overlap of p orbitals. Such a bond is called a **pi (π) bond**. A double bond, such as that in C_2H_4, consists of one σ bond and one π bond; each carbon atom has an unhybridized ***p* orbital**, and these are the orbitals that overlap to form π bonds. A triple bond, such as that in C_2H_2, consists of one σ and two π bonds. The formation of a π bond requires that molecules adopt a specific orientation; the two CH_2 groups in C_2H_4, for example, must lie in the same plane. As a result, the presence of π bonds introduces rigidity into molecules. In molecules that have multiple bonds and more than one resonance structure, such as C_6H_6, the π bonds are **delocalized**; that is, the π bonds are spread among several atoms.

MOLECULAR ORBITALS (SECTION 9.7) **Molecular orbital theory** is another model used to describe the bonding in molecules. In this model, the electrons exist in allowed energy states called **molecular orbitals (MOs)**. An MO can extend over all the atoms of a molecule. Like an atomic orbital, a molecular orbital has a definite energy and can hold two electrons of opposite spin. We can build molecular orbitals by combining atomic orbitals on different atomic centers. In the simplest case, the combination of two atomic orbitals leads to the formation of two MOs, one at lower energy and one at higher energy relative to the energy of the atomic orbitals. The lower-energy MO concentrates charge density in the region between the nuclei and is called a **bonding molecular orbital**. The higher-energy MO excludes electrons from the region between the nuclei and is called an **antibonding molecular orbital**. Antibonding MOs exclude electron density from the region between the nuclei and have a **nodal plane**—a place at which the electron density is zero—between the nuclei. Occupation of bonding MOs favors bond formation, whereas occupation of antibonding MOs is unfavorable. The bonding and antibonding MOs formed by the combination of s orbitals are **sigma (σ) molecular orbitals**; they lie on the internuclear axis.

The combination of atomic orbitals and the relative energies of the molecular orbitals are shown by an **energy-level** (or **molecular orbital**) **diagram**. When the appropriate number of electrons is put into the MOs, we can calculate the **bond order** of a bond, which is half the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of 1 corresponds to a single bond, and so forth. Bond orders can be fractional numbers.

BONDING IN PERIOD 2 DIATOMIC MOLECULES (SECTION 9.8)

Electrons in core orbitals do not contribute to the bonding between atoms, so a molecular orbital description usually needs to consider only electrons in the outermost electron subshells. To describe the MOs of Period 2 homonuclear diatomic molecules, we need to consider the MOs that can form by the combination of *p* orbitals. The *p* orbitals that point directly at one another can form σ bonding and σ^* antibonding MOs. The *p* orbitals that are oriented perpendicular to the internuclear axis combine to form **pi (π) molecular orbitals**. In diatomic molecules, the π molecular orbitals occur as a pair of degenerate (same energy) bonding MOs and a pair of degenerate antibonding MOs. The σ_{2p} bonding MO is expected to be lower in energy than the π_{2p} bonding MOs because of larger orbital overlap of the *p* orbitals directed along the internuclear axis. However, this ordering is reversed in B_2, C_2, and N_2 because of interaction between the 2*s* and 2*p* atomic orbitals of different atoms.

The molecular orbital description of Period 2 diatomic molecules leads to bond orders in accord with the Lewis structures of these molecules. Further, the model predicts correctly that O_2 should exhibit **paramagnetism**, which leads to attraction of a molecule into a magnetic field due to the influence of unpaired electrons. Molecules in which all the electrons are paired exhibit **diamagnetism**, which leads to weak repulsion from a magnetic field. The molecular orbitals of heteronuclear diatomic molecules are often closely related to those of homonuclear diatomic molecules.

Learning Outcomes After studying this chapter, you should be able to:

- Draw and name the predicted three-dimensional shapes of molecules using the VSEPR model. (Section 9.2) *Related Exercises*: *9.10, 9.63*
- Determine whether a molecule is polar or nonpolar based on its geometry and the individual bond dipole moments. (Section 9.3) *Related Exercises*: *9.17, 9.71*
- Explain the role of orbital overlap in the formation of covalent bonds. (Section 9.4) *Related Exercises*: *9.22, 9.74*
- Determine the hybridization of atoms in molecules based on observed molecular structures. (Section 9.5) *Related Exercises*: *9.24, 9.76*
- Sketch how orbitals overlap to form sigma (σ) and pi (π) bonds. (Section 9.6) *Related Exercises*: *9.28, 9.78*
- Explain the existence of delocalized π bonds in molecules such as benzene. (Section 9.6) *Related Exercises*: *9.31, 9.83*
- Count the number of electrons in a delocalized π system. (Section 9.6) *Related Exercises*: *9.32, 9.84*
- Explain the concept of bonding and antibonding molecular orbitals and draw examples of σ and π MOs. (Section 9.7) *Related Exercises*: *9.35, 9.86*
- Draw molecular orbital energy-level diagrams and place electrons into them to obtain the bond orders and electron configurations of diatomic molecules using molecular orbital theory. (Sections 9.7 and 9.8) *Related Exercises*: *9.36, 9.87*
- Correlate bond order, bond strength (bond enthalpy), bond length, and magnetic properties with molecular orbital descriptions of molecules. (Section 9.8) *Related Exercises*: *9.41, 9.91*

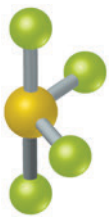
Key Equations

- Bond order $= \frac{1}{2}$ (number of bonding electrons $-$ number of antibonding electrons) [9.1]

Exercises

Visualizing Concepts

9.44 A certain AB_4 molecule has a "seesaw" shape

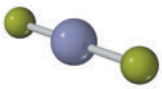


From which of the fundamental geometries shown in Figure 9.3 could you remove one or more atoms to create a molecule having this seesaw shape? [Section 9.1]

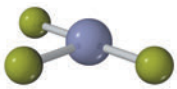
9.45 (**a**) If these three balloons are all the same size, what angle is formed between the red one and the green one? (**b**) If additional air is added to the blue balloon so that it gets larger, will the angle between the red and green balloons increase, decrease, or stay the same? (**c**) Which of the following aspects of the VSEPR model is illustrated by part (b): (i) The electron-domain geometry for four electron domains is tetrahedral. (ii) The electron domains for nonbonding pairs are larger than those for bonding pairs. (iii) The hybridization that corresponds to a trigonal planar electron-domain geometry is sp^2. [Section 9.2]



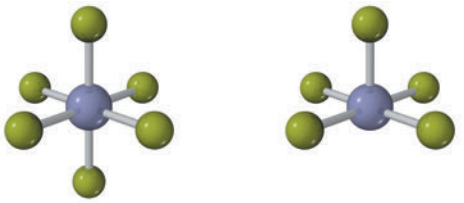
9.46 For each molecule (a)–(f), indicate how many different electron-domain geometries are consistent with the molecular geometry shown. [Section 9.2]



(a)

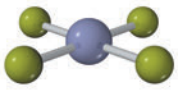


(b)

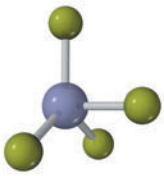


(c)

(d)

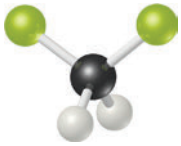


(e)

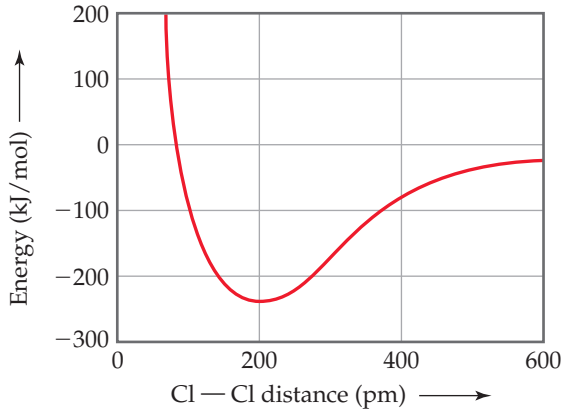


(f)

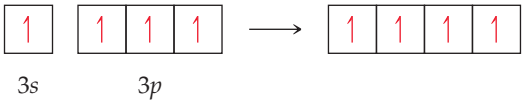
9.47 The molecule shown here is *difluoromethane* (CH_2F_2), which is used as a refrigerant called R-32. (**a**) Based on the structure, how many electron domains surround the C atom in this molecule? (**b**) Would the molecule have a nonzero dipole moment? (**c**) If the molecule is polar, which of the following describes the direction of the overall dipole moment vector in the molecule: (i) from the carbon atom toward a fluorine atom, (ii) from the carbon atom to a point midway between the fluorine atoms, (iii) from the carbon atom to a point midway between the hydrogen atoms, or (iv) from the carbon atom toward a hydrogen atom? [Sections 9.2 and 9.3]



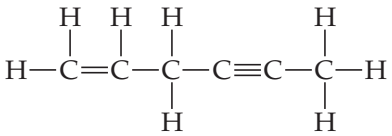
9.48 The following plot shows the potential energy of two Cl atoms as a function of the distance between them. (**a**) If the two atoms are very far away from each other, what is their potential energy of interaction? (**b**) We know that the Cl_2 molecule exists. What is the approximate bond length and bond strength for the Cl–Cl bond in Cl_2 from this graph? (**c**) If the Cl_2 molecule is compressed under higher and higher pressure, does the Cl–Cl bond become stronger or weaker?



9.49 The orbital diagram that follows presents the final step in the formation of hybrid orbitals by a silicon atom. (**a**) Which of the following best describes what took place before the step pictured in the diagram: (i) Two 3*p* electrons became unpaired, (ii) An electron was promoted from the 2*p* orbital to the 3*s* orbital, or (iii) An electron was promoted from the 3*s* orbital to the 3*p* orbital? (**b**) What type of hybrid orbital is produced in this hybridization? [Section 9.5]

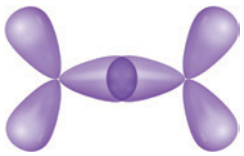


9.50 In the hydrocarbon



(**a**) What is the hybridization at each carbon atom in the molecule? (**b**) How many σ bonds are there in the molecule? (**c**) How many π bonds? (**d**) Identify all the 120° bond angles in the molecule. [Section 9.6]

9.51 This drawing shows the overlap of two hybrid orbitals to form a bond in a hydrocarbon. (**a**) Which of the following types of bonds is being formed: (i) C—C σ, (ii) C—C π, or (iii) C—H σ? (**b**) Which of the following could be the identity of the hydrocarbon: (i) CH_4, (ii) C_2H_6, (iii) C_2H_4, or (iv) C_2H_2? [Section 9.6]

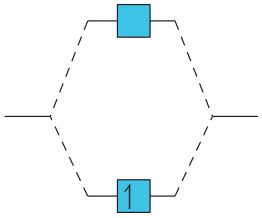


9.52 This molecule is called *furan*. It is represented in typical shorthand way for organic molecules, with hydrogen atoms not shown, and each of the 4 vertices representing a carbon atom.



(**a**) What is the molecular formula for furan? (**b**) How many valence electrons are there in the molecule? (**c**) What is the hybridization at each of the carbon atoms? (**d**) How many electrons are in the π system of the molecule? (**e**) The C—C—C bond angles in furan are much smaller than those in benzene. The likely reason is which of the following: (i) The hybridization of the carbon atoms in furan is different from that in benzene, (ii) Furan does not have another resonance structure equivalent to the one shown here, or (iii) The atoms in a five-membered ring are forced to adopt smaller angles than in a six-membered ring. [Section 9.5]

9.53 The following is part of a molecular orbital energy-level diagram for MOs constructed from 1*s* atomic orbitals.

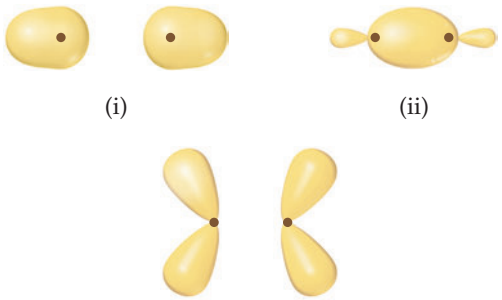


(**a**) What labels do we use for the two MOs shown? (**b**) For which of the following molecules or ions could this be the energy-level diagram:

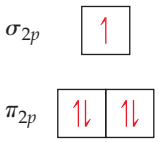
H_2, He_2, H_2^+, He_2^+, or H_2^-?

(**c**) What is the bond order of the molecule or ion? (**d**) If an electron is added to the system, into which of the MOs will it be added? [Section 9.7]

9.54 For each of these contour representations of molecular orbitals, identify (**a**) the atomic orbitals (*s* or *p*) used to construct the MO (**b**) the type of MO (σ or π), (**c**) whether the MO is bonding or antibonding, and (**d**) the locations of nodal planes. [Sections 9.7 and 9.8]



9.55 The diagram that follows shows the highest-energy occupied MOs of a neutral molecule CX, where element X is in the same row of the periodic table as C. (**a**) Based on the number of electrons, can you determine the identity of X? (**b**) Would the molecule be diamagnetic or paramagnetic? (**c**) Consider the π_{2p} MOs of the molecule. Would you expect them to have a greater atomic orbital contribution from C, have a greater atomic orbital contribution from X, or be an equal mixture of atomic orbitals from the two atoms? [Section 9.8]



Molecular Shapes; the VSEPR Model (Sections 9.1 and 9.2)

9.56 (**a**) Boron trichloride (BCl_3) and the carbonate ion (CO_3^{2-}) are both described as trigonal. What does this indicate about their bond angles? (**b**) The PCl_3 molecule is trigonal pyramidal, while ICl_3 is T-shaped. Which of these molecules is flat?

9.57 How does a trigonal pyramid differ from a tetrahedron so far as molecular geometry is concerned?

9.58 Describe the bond angles to be found in each of the following molecular structures: (**a**) trigonal planar, (**b**) tetrahedral, (**c**) octahedral, (**d**) linear.

9.59 Would you expect the nonbonding electron-pair domain in NCl_3 to be greater or smaller in size than the corresponding one in PCl_3?

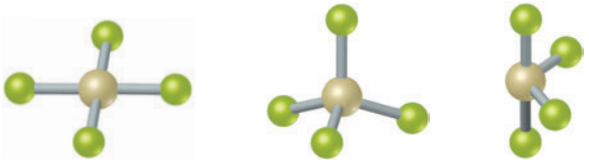
9.60 In which of the following molecules can you confidently predict the bond angles about the central atom, and for which would you be a bit uncertain? Explain in each case. (**a**) H_2S, (**b**) BCl_3, (**c**) CH_3I, (**d**) CBr_4, (**e**) $TeBr_4$.

9.61 How many electron domains are surrounding the central atoms which adopt the following geometries? (**a**) linear (**b**) trigonal planar (**c**) trigonal pyramidal (**d**) trigonal bipyramidal.

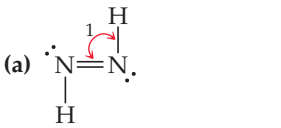
9.62 What are the electron-domain and molecular geometries of a molecule that has the following electron domains on its central atom? (**a**) Three bonding domains and no nonbonding domains, (**b**) three bonding domains and one nonbonding domain, (**c**) two bonding domains and two nonbonding domains.

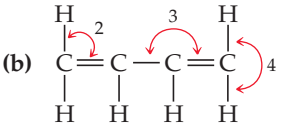
9.63 Draw the Lewis structure for each of the following molecules or ions, and predict their electron-domain and molecular geometries: (**a**) AsF_3, (**b**) CH_3^+, (**c**) BrF_3, (**d**) ClO_3^-, (**e**) XeF_2, (**f**) BrO_2^-.

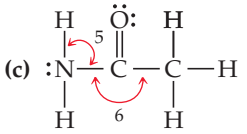
9.64 The figure that follows contains ball-and-stick drawings of three possible shapes of an AF_4 molecule. (**a**) For each shape, give the electron-domain geometry on which the molecular geometry is based. (**b**) For each shape, how many nonbonding electron domains are there on atom A? (**c**) Which of the following elements will lead to an AF_4 molecule with the shape in (iii): Be, C, S, Se, Si, Xe? (**d**) Name an element A that is expected to lead to the AF_4 structure shown in (i).

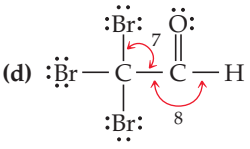


9.65 Give the approximate values for the indicated bond angles in the following molecules:









9.66 In which of the following AF_n molecules or ions is there more than one F—A—F bond angle: PF_6^-, SbF_5, SF_4?

9.67 Name the proper three-dimensional molecular shapes for each of the following molecules or ions, showing lone pairs as needed: (**a**) ClO_2^- (**b**) SO_4^{2-} (**c**) NF_3 (**d**) CCl_2Br_2 (**e**) SF_4^{2+}

Shapes and Polarity of Polyatomic Molecules (Section 9.3)

9.68 What is the distinction between a bond dipole and a molecular dipole moment?

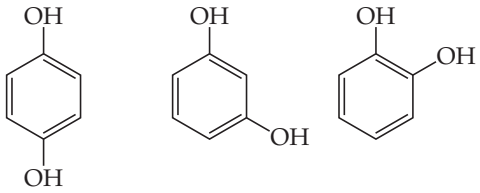
9.69 (**a**) The PH_3 molecule is polar. Does this offer experimental proof that the molecule cannot be planar? Explain. (**b**) It turns out that ozone, O_3, has a small dipole moment. How is this possible, given that all the atoms are the same?

9.70 (**a**) Consider the following two molecules: PCl_3 and BCl_3. Which molecule has a nonzero dipole moment? (**b**) Consider

the following two molecules: XeF_4 and SF_4. Which molecule has a zero dipole moment?

9.71 Predict whether each of the following molecules is polar or nonpolar: (**a**) CCl_4, (**b**) NH_3, (**c**) SF_4, (**d**) XeF_4, (**e**) CH_3Br, (**f**) GaH_3.

9.72 Dihydroxybenzene, $C_6H_6O_2$, exists in three forms (isomers) called *ortho, meta,* and *para*:



para *meta* *ortho*

Which of these has a nonzero dipole moment?

Orbital Overlap; Hybrid Orbitals (Sections 9.4 and 9.5)

9.73 For each statement, indicate whether it is true or false. (**a**) In order to make a covalent bond, the orbitals on each atom in the bond must overlap. (**b**) A *p* orbital on one atom cannot make a bond to an *s* orbital on another atom. (**c**) Lone pairs of electrons on an atom in a molecule influence the shape of a molecule. (**d**) The 1*s* orbital has a nodal plane. (**e**) The 2*p* orbital has a nodal plane.

9.74 How would you expect the extent of overlap of the bonding atomic orbitals to vary in the series IF, ICl, IBr, and I_2? Explain your answer.

9.75 Consider the SCl_2 molecule. (**a**) What is the electron configuration of an isolated S atom? (**b**) What is the electron configuration of an isolated Cl atom? (**c**) What hybrid orbitals should be constructed on the S atom to make the S-Cl bonds in SCl_2? (**d**) What valence orbitals, if any, remain unhybridized on the S atom in SCl_2?

9.76 What is the hybridization of the central atom in (**a**) PBr_5, (**b**) CH_2O, (**c**) O_3, (**d**) NO_2?

9.77 (**a**) Which geometry and central atom hybridization would you expect in the series BH_4^-, CH_4, NH_4^+? (**b**) What would you expect for the magnitude and direction of the bond dipoles in this series? (**c**) Write the formulas for the analogous species of the elements of Period 3; would you expect them to have the same hybridization at the central atom?

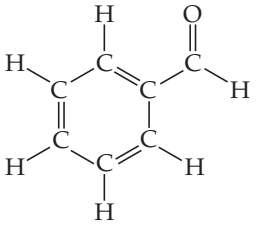
Multiple Bonds (Section 9.6)

9.78 (**a**) If the valence atomic orbitals of an atom are *sp* hybridized, how many unhybridized *p* orbitals remain in the valence shell? How many π bonds can the atom form? (**b**) Imagine that you could hold two atoms that are bonded together, twist them, and not change the bond length. Would it be easier to twist (rotate) around a single σ bond or around a double (σ plus π) bond, or would they be the same?

9.79 (**a**) Draw Lewis structures for chloromethane (CH_3Cl), chloroethene (C_2H_3Cl), and chloroethyne (C_2HCl). (**b**) What is the hybridization of the carbon atoms in each molecule? (**c**) Predict which molecules, if any, are planar. (**d**) How many σ and π bonds are there in each molecule?

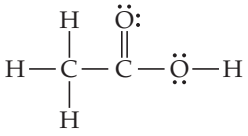
9.80 The oxygen atoms in O_2 participate in multiple bonding, whereas those in hydrogen peroxide, H_2O_2, do not. (**a**) Draw Lewis structures for both molecules. (**b**) What is the hybridization of the oxygen atoms in each molecule? (**c**) Which molecule has the stronger O—O bond?

9.81 Benzaldehyde, C_7H_6O, is a fragrant substance responsible for the aroma of almonds. Its Lewis structure is



(**a**) What is the hybridization at each of the carbon atoms of the molecule? (**b**) What is the total number of valence electrons in benzaldehyde? (**c**) How many of the valence electrons are used to make σ bonds in the molecule? (**d**) How many valence electrons are used to make π bonds? (**e**) How many valence electrons remain in nonbonding pairs in the molecule?

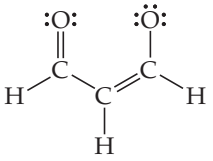
9.82 Consider the Lewis structure for acetic acid, which is known as vinegar:



(**a**) What are the approximate bond angles about each of the two carbon atoms, and what are the hybridizations of the orbitals on each of them? (**b**) What are the hybridizations of the orbitals on the two oxygen atoms, and what are the approximate bond angles at the oxygen that is connected to carbon and hydrogen? (**c**) What is the total number of σ bonds in the entire molecule, and what is the total number of π bonds?

9.83 (**a**) Write a single Lewis structure for N_2O, and determine the hybridization of the central N atom. (**b**) Are there other possible Lewis structures for the molecule? (**c**) Would you expect N_2O to exhibit delocalized π bonding?

9.84 Consider this Lewis structure.



(**a**) Does the Lewis structure depict a neutral molecule or an ion? If it is an ion, what is the charge on the ion? (**b**) What hybridization is exhibited by each of the carbon atoms? (**c**) Are there multiple equivalent resonance structures for the species? (**d**) How many electrons are in the π system of the species?

9.85 What hybridization do you expect for the atom that is underlined in each of the following species? (**a**) $\underline{I}O_2^-$; (**b**) $\underline{N}H_4^+$; (**c**) S$\underline{C}$N$^-$; (**d**) $\underline{Br}Cl_3$

Molecular Orbitals and Period 2 Diatomic Molecules (Sections 9.7 and 9.8)

9.86 (**a**) If you combine two atomic orbitals on two different atoms to make a new orbital, is this a hybrid orbital or a molecular orbital? (**b**) If you combine two atomic orbitals on *one* atom to make a new orbital, is this a hybrid orbital or a molecular orbital? (**c**) Does the Pauli exclusion principle (Section 6.7) apply to MOs? Explain.

9.87 (**a**) Sketch the molecular orbitals of the H_2^- ion and draw its energy-level diagram. (**b**) Write the electron configuration of

the ion in terms of its MOs. (**c**) Calculate the bond order in H_2^-. (**d**) Suppose that the ion is excited by light, so that an electron moves from a lower-energy to a higher-energy molecular orbital. Would you expect the excited-state H_2^- ion to be stable? (**e**) Which of the following statements about part (d) is correct: (i) The light excites an electron from a bonding orbital to an antibonding orbital, (ii) The light excites an electron from an antibonding orbital to a bonding orbital, or (iii) In the excited state there are more bonding electrons than antibonding electrons?

9.88 Indicate whether each statement is true or false. (**a**) *p* orbitals can only make σ or σ^* molecular orbitals. (**b**) The probability is always 0% for finding an electron in an antibonding orbital. (**c**) Molecules containing electrons that occupy antibonding orbitals must be unstable. (**d**) Electrons cannot occupy a nonbonding orbital.

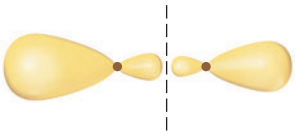
9.89 Explain the following: (**a**) The *peroxide* ion, O_2^{2-}, has a longer bond length than the *superoxide* ion, O_2^-. (**b**) The magnetic properties of B_2 are consistent with the π_{2p} MOs being lower in energy than the σ_{2p} MO. (**c**) The O_2^{2+} ion has a stronger O—O bond than O_2 itself.

9.90 (**a**) What does the term *paramagnetism* mean? (**b**) How can one determine experimentally whether a substance is paramagnetic? (**c**) Which of the following ions would you expect to be paramagnetic: O_2^+, N_2^{2-}, Li_2^+, O_2^{2-}? For those ions that are paramagnetic, determine the number of unpaired electrons.

9.91 If we assume that the energy-level diagrams for homonuclear diatomic molecules shown in Figure 9.40 can be applied to heteronuclear diatomic molecules and ions, predict the bond order and magnetic behavior of (**a**) CC^-, (**b**) NO^+, (**c**) HHe^+, (**d**) ClF.

9.92 (**a**) The nitric oxide molecule, NO, readily loses one electron to form the NO^+ ion. Which of the following is the best explanation of why this happens: (i) Oxygen is more electronegative than nitrogen, (ii) The highest energy electron in NO lies in a π_{2p}^* molecular orbital, or (iii) The π_{2p}^* MO in NO is completely filled. (**b**) Predict the order of the N—O bond strengths in NO, NO^+, and NO^-, and describe the magnetic properties of each. (**c**) With what neutral homonuclear diatomic molecules are the NO^+ and NO^- ions isoelectronic (same number of electrons)?

9.93 The iodine bromide molecule, IBr, is an *interhalogen compound*. Assume that the molecular orbitals of IBr are analogous to the homonuclear diatomic molecule F_2. (**a**) Which valence atomic orbitals of I and of Br are used to construct the MOs of IBr? (**b**) What is the bond order of the IBr molecule? (**c**) One of the valence MOs of IBr is sketched here. Why are the atomic orbital contributions to this MO different in size? (**d**) What is the label for the MO sketched here? (**e**) For the IBr molecule, how many electrons occupy the MO sketched here?



Additional Exercises

9.94 (**a**) What is the physical basis for the VSEPR model? (**b**) When applying the VSEPR model, we count a double or triple bond as a single electron domain. Why is this justified?

9.95 An AB_2 molecule is described as having a tetrahedral geometry. (**a**) How many nonbonding domains are on atom A? (**b**) Based on the information given, which of the following is the molecular geometry of the molecule: (i) linear, (ii) bent, (iii) trigonal planar, or (iv) tetrahedral?

9.96 Consider the following XF_4 ions: PF_4^-, BrF_4^-, ClF_4^+, and AlF_4^-. (**a**) Which of the ions have more than an octet of electrons around the central atom? (**b**) For which of the ions will the electron-domain and molecular geometries be the same? (**c**) Which of the ions will have an octahedral electron-domain geometry? (**d**) Which of the ions will exhibit a see-saw molecular geometry?

9.97 Consider the molecule PF_4Cl. (**a**) Draw a Lewis structure for the molecule, and predict its electron-domain geometry. (**b**) Which would you expect to take up more space, a P—F bond or a P—Cl bond? Explain. (**c**) Predict the molecular geometry of PF_4Cl. How did your answer for part (b) influence your answer here in part (c)? (**d**) Would you expect the molecule to distort from its ideal electron-domain geometry? If so, how would it distort?

9.98 The vertices of a tetrahedron correspond to four alternating corners of a cube. By using analytical geometry, demonstrate that the angle made by connecting two of the vertices to a point at the center of the cube is 109.5°, the characteristic angle for tetrahedral molecules.

9.99 Fill in the blank spaces in the following chart. If the molecule column is blank, find an example that fulfills the conditions of the rest of the row.

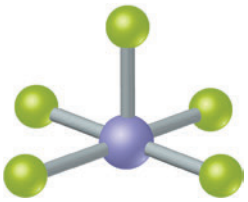
Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2			
		sp^3	Yes
		sp^3	No
	Trigonal planar		No
SF_4			
	Octahedral		No
		sp^2	Yes
	Trigonal bipyramidal		No
XeF_2			

9.100 From their Lewis structures, determine the number of σ and π bonds in each of the following molecules or ions: (**a**) hydrazine, N_2H_4; (**b**) hydrogen cyanide, HCN; (**c**) sulfur trioxide, SO_3; (**d**) ozone, O_3.

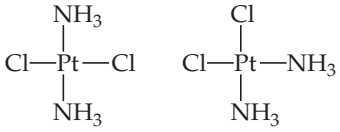
9.101 Ethyl propanoate, $CH_3CH_2COOCH_2CH_3$, gives a fruity pineapple-like smell. (**a**) Draw the Lewis structure for the molecule, assuming that carbon always forms four bonds in its stable compounds. (**b**) How many σ and how many π bonds are in the molecule? (**c**) Which CO bond is shortest in the molecule? (**d**) What is the hybridization of atomic orbitals around the carbon atom associated with that short bond? (**e**) What are the approximate bond angles around each carbon atom in the molecule?

9.102 An AB_5 molecule adopts the geometry shown here. (**a**) What is the name of this geometry? (**b**) Do you think there are any nonbonding electron pairs on atom A? (**c**) Suppose the

B atoms are halogen atoms. Of which group in the periodic table is atom A a member: (i) Group 15, (ii) Group 16, (iii) Group 17, (iv) Group 18, or (v) More information is needed?



9.103 There are two compounds of the formula $Pt(NH_3)_2Cl_2$:



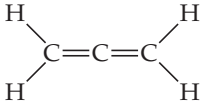
The compound on the right is called *cisplatin*, and the compound on the left is called *transplatin*. (**a**) Which compound has a nonzero dipole moment? (**b**) One of these compounds is an anticancer drug, and one is inactive. The anticancer drug works by its chloride ions undergoing a substitution reaction with nitrogen atoms in DNA that are close together, forming a N—Pt—N angle of about 90°. Which compound would you predict to be the anticancer drug?

9.104 The O—H bond lengths in the water molecule (H_2O) are 96 pm, and the H—O—H angle is 104.5°. The dipole moment of the water molecule is 6.17×10^{-30} C-m. (**a**) In what directions do the bond dipoles of the O—H bonds point? In what direction does the dipole moment vector of the water molecule point? (**b**) Calculate the magnitude of the bond dipole of the O—H bonds. (*Note:* You will need to use vector addition to do this.) (**c**) Compare your answer from part (b) to the dipole moments of the hydrogen halides (Table 8.3). Is your answer in accord with the relative electronegativity of oxygen?

9.105 (**a**) Predict the electron-domain geometry around the central S atom in SF_2, SF_4, and SF_6. (**b**) The anion IO_4^- has a tetrahedral structure: three oxygen atoms form double bonds with the central iodine atom and one oxygen atom which carries a negative charge forms a single bond. Predict the molecular geometry of IO_6^{5-}.

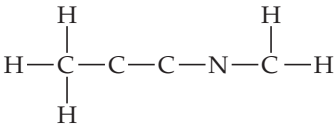
9.106 Which of the following statements about hybrid orbitals is or are true? (i) After an atom undergoes *sp* hybridization, there is one unhybridized *p* orbital on the atom, (ii) Under sp^2 hybridization, the large lobes point to the vertices of an equilateral triangle, and (iii) The angle between the large lobes of sp^3 hybrids is 109.5°.

9.107 The Lewis structure for allene is



Make a sketch of the structure of this molecule that is analogous to Figure 9.25. In addition, answer the following three questions: (**a**) Is the molecule planar? (**b**) Does it have a nonzero dipole moment? (**c**) Would the bonding in allene be described as delocalized? Explain.

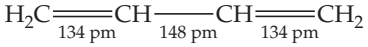
9.108 Consider the molecule C_4H_5N, which has the connectivity shown here. (**a**) After the Lewis structure for the molecule is completed, how many σ and how many π bonds are there in this molecule? (**b**) How many atoms in the molecule exhibit (i) *sp* hybridization, (ii) sp^2 hybridization, and (iii) sp^3 hybridization?



9.109 Sodium azide is a shock-sensitive compound that releases N_2 upon physical impact. The compound is used in automobile airbags. The azide ion is N_3^-. (**a**) Draw the Lewis structure of the azide ion that minimizes formal charge (it does not form a triangle). Is it linear or bent? (**b**) State the hybridization of the central N atom in the azide ion. (**c**) How many σ bonds and how many π bonds does the central nitrogen atom make in the azide ion?

9.110 In ozone, O_3, the two oxygen atoms on the ends of the molecule are equivalent to one another. (**a**) What is the best choice of hybridization scheme for the atoms of ozone? (**b**) For one of the resonance forms of ozone, which of the orbitals are used to make bonds and which are used to hold nonbonding pairs of electrons? (**c**) Which of the orbitals can be used to delocalize the π electrons? (**d**) How many electrons are delocalized in the π system of ozone?

9.111 Butadiene, C_4H_6, is a planar molecule that has the following carbon–carbon bond lengths:



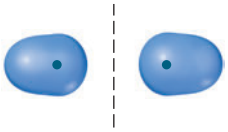
(**a**) Predict the bond angles around each of the carbon atoms and sketch the molecule. (**b**) From left to right, what is the hybridization of each carbon atom in butadiene? (**c**) The middle C—C bond length in butadiene (148 pm) is a little shorter than the average C—C single bond length (154 pm). Does this imply that the middle C—C bond in butadiene is weaker or stronger than the average C—C single bond? (**d**) Based on your answer for part (c), discuss what additional aspects of bonding in butadiene might support the shorter middle C—C bond.

9.112 The structure of *borazine*, $B_3N_3H_6$, is a six-membered ring of alternating B and N atoms. There is one H atom bonded to each B and to each N atom. The molecule is planar. (**a**) Write a Lewis structure for borazine in which the formal charge on every atom is zero. (**b**) Write a Lewis structure for borazine in which the octet rule is satisfied for every atom. (**c**) What are the formal charges on the atoms in the Lewis structure from part (b)? Given the electronegativities of B and N, do the formal charges seem favorable or unfavorable? (**d**) Do either of the Lewis structures in parts (a) and (b) have multiple resonance structures? (**e**) What are the hybridizations at the B and N atoms in the Lewis structures from parts (a) and (b)? Would you expect the molecule to be planar for both Lewis structures? (**f**) The six B—N bonds in the borazine molecule are all identical in length at 144 pm. Typical values for the bond lengths of B—N single and double bonds are 151 pm and 131 pm, respectively. Does the value of the B—N bond length seem to favor one Lewis structure over the other? (**g**) How many electrons are in the π system of borazine?

9.113 The highest occupied molecular orbital of a molecule is abbreviated as the HOMO. The lowest unoccupied molecular orbital in a molecule is called the LUMO. Experimentally, one can measure the difference in energy between the HOMO and LUMO by taking the electronic absorption (UV-visible) spectrum of the molecule. Peaks in the electronic absorption spectrum can be labeled as π_{2p}–π_{2p}^*, σ_{2s}–σ_{2s}^*, and so on, corresponding to electrons being promoted from one orbital to another. The HOMO-LUMO transition corresponds to molecules going from their ground

state to their first excited state. (**a**) Write out the molecular orbital valence electron configurations for the ground state and first excited state for N_2. (**b**) Is N_2 paramagnetic or diamagnetic in its first excited state? (**c**) The electronic absorption spectrum of the N_2 molecule has the lowest energy peak at 170 nm. To what orbital transition does this correspond? (**d**) Calculate the energy of the HOMO-LUMO transition in part (a) in terms of kJ/mol. (**e**) Is the N—N bond in the first excited state stronger or weaker compared to that in the ground state?

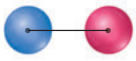
9.114 One of the molecular orbitals of the H_2^- ion is sketched here:



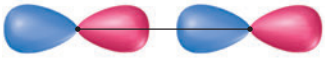
(**a**) Is the molecular orbital a σ or π MO? Is it bonding or antibonding? (**b**) In H_2^-, how many electrons occupy the MO shown here? (**c**) What is the bond order in the H_2^- ion? (**d**) Compared to the H—H bond in H_2, the H—H bond in H_2^- is expected to be which of the following: (i) Shorter and stronger, (ii) longer and stronger, (iii) shorter and weaker, (iv) longer and weaker, or (v) the same length and strength?

9.115 Place the following molecules and ions in order from smallest to largest bond order: N_2^{2+}, He_2^+, Cl_2 H_2^-, O_2^{2-}.

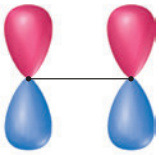
9.116 The following sketches show the atomic orbital wave functions (with phases) used to construct some of the MOs of a homonuclear diatomic molecule. For each sketch, determine the type of MO that will result from mixing the atomic orbital wave functions as drawn. Use the same labels for the MOs as in the "Closer Look" box on phases.



(a)



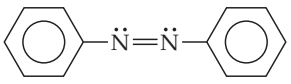
(b)



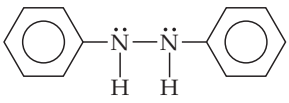
(c)

9.117 Molecules that are brightly colored have a small energy gap between filled and empty electronic states (the HOMO-LUMO gap; see Exercise 9.113). Suppose you have two samples, one is lycopene which is responsible for the red color in tomato, and the other is curcumin which is responsible for the yellow color in turmeric. Which one has the larger HOMO-LUMO gap?

9.118 *Azo dyes* are organic dyes that are used for many applications, such as the coloring of fabrics. Many azo dyes are derivatives of the organic substance *azobenzene,* $C_{12}H_{10}N_2$. A closely related substance is *hydrazobenzene,* $C_{12}H_{12}N_2$. The Lewis structures of these two substances are



Azobenzene



Hydrazobenzene

(Recall the shorthand notation used for benzene.) (**a**) What is the hybridization at the N atom in each of the substances? (**b**) How many unhybridized atomic orbitals are there on the N and the C atoms in each of the substances? (**c**) Predict the N—N—C angles in each of the substances. (**d**) Azobenzene is said to have greater delocalization of its π electrons than hydrazobenzene. Discuss this statement in light of your answers to (a) and (b). (**e**) All the atoms of azobenzene lie in one plane, whereas those of hydrazobenzene do not. Is this observation consistent with the statement in part (d)? (**f**) Azobenzene is an intense red-orange color, whereas hydrazobenzene is nearly colorless. Which molecule would be a better one to use in a solar energy conversion device? (See the "Chemistry Put to Work" box for more information about solar cells.)

9.119 (**a**) Using only the valence atomic orbitals of a hydrogen atom and a fluorine atom, and following the model of Figure 9.43, how many MOs would you expect for the HF molecule? (**b**) How many of the MOs from part (a) would be occupied by electrons? (**c**) It turns out that the difference in energies between the valence atomic orbitals of H and F are sufficiently different that we can neglect the interaction of the 1*s* orbital of hydrogen with the 2*s* orbital of fluorine. The 1*s* orbital of hydrogen will mix only with one 2*p* orbital of fluorine. Draw pictures showing the proper orientation of all three 2*p* orbitals on F interacting with a 1*s* orbital on H. Which of the 2*p* orbitals can actually make a bond with a 1*s* orbital, assuming that the atoms lie on the *z*-axis? (**d**) In the most accepted picture of HF, all the other atomic orbitals on fluorine move over at the same energy into the molecular orbital energy-level diagram for HF. These are called "nonbonding orbitals." Sketch the energy-level diagram for HF using this information and calculate the bond order. (Nonbonding electrons do not contribute to bond order.) (**e**) Look at the Lewis structure for HF. Where are the nonbonding electrons?

9.120 Carbon monoxide, CO, is isoelectronic to N_2. (**a**) Draw a Lewis structure for CO that satisfies the octet rule. (**b**) Assume that the diagram in Figure 9.43 can be used to describe the MOs of CO. What is the predicted bond order for CO? Is this answer in accord with the Lewis structure you drew in part (a)? (**c**) Experimentally, it is found that the highest energy electrons in CO reside in a σ-type MO. Is that observation consistent with Figure 9.43? If not, what modification needs to be made to the diagram? How does this modification relate to Figure 9.40? (**d**) Would you expect the π_{2p} MOs of CO to have equal atomic orbital contributions from the C and O atoms? If not, which atom would have the greater contribution?

9.121 The energy-level diagram in Figure 9.33 shows that the sideways overlap of a pair of *p* orbitals produces two molecular orbitals, one bonding and one antibonding. In ethene there is a pair of electrons in the bonding π orbital between the two carbons. Absorption of a photon of the appropriate wavelength can result in promotion of one of the bonding electrons from the π_{2p} to the π^*_{2p} molecular orbital. (**a**) Assuming this electronic transition corresponds to the HOMO-LUMO transition, what is the HOMO in ethene? (**b**) Assuming this electronic transition corresponds to the HOMO-LUMO transition, what is the LUMO in ethene? (**c**) Is the C—C bond in ethene stronger or weaker in the excited state than in the ground state? Why? (**d**) Is the C—C bond in ethene easier to twist in the ground state or in the excited state?

Integrative Exercises

9.122 A compound composed of 6.7% H, 40.0% C, and 53.3% O has a molar mass of approximately 60 g/mol. (**a**) What is the molecular formula of the compound? (**b**) What is its Lewis structure if the two O are bonded to C? (**c**) What is the geometry and hybridization of the C atom that is bonded to 2 O atoms? (**d**) How many σ and how many π bonds are there in the molecule?

9.123 Sulfur tetrafluoride (SF_4) reacts slowly with O_2 to form sulfur tetrafluoride monoxide (OSF_4) according to the following unbalanced reaction:

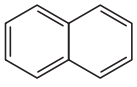
$$SF_4(g) + O_2(g) \longrightarrow OSF_4(g)$$

The O atom and the four F atoms in OSF_4 are bonded to a central S atom. (**a**) Balance the equation. (**b**) Write a Lewis structure of OSF_4 in which the formal charges of all atoms are zero. (**c**) Use average bond enthalpies (Table 8.3) to estimate the enthalpy of the reaction. Is it endothermic or exothermic? (**d**) Determine the electron-domain geometry of OSF_4, and write two possible molecular geometries for the molecule based on this electron-domain geometry. (**e**) For each of the molecules you drew in part (d), state how many fluorines are equatorial and how many are axial.

9.124 The phosphorus trihalides (PX_3) show the following variation in the bond angle X—P—X: PF_3, 96.3°; PCl_3, 100.3°; PBr_3, 101.0°; PI_3, 102.0°. The trend is generally attributed to the change in the electronegativity of the halogen. (**a**) Assuming that all electron domains are the same size, what value of the X—P—X angle is predicted by the VSEPR model? (**b**) What is the general trend in the X—P—X angle as the halide electronegativity increases? (**c**) Using the VSEPR model, explain the observed trend in X—P—X angle as the electronegativity of X changes. (**d**) Based on your answer to part (c), predict the structure of $PBrCl_4$.

9.125 (**a**) Compare the bond enthalpies (Table 8.3) of the carbon–carbon single, double, and triple bonds to deduce an average π-bond contribution to the enthalpy. What fraction of a single bond does this quantity represent? (**b**) Make a similar comparison of nitrogen–nitrogen bonds. What do you observe? (**c**) Write Lewis structures of N_2H_4, N_2H_2, and N_2, and determine the hybridization around nitrogen in each case. (**d**) Propose a reason for the large difference in your observations of parts (a) and (b).

9.126 (**a**) Use average bond enthalpies (Table 8.3) to estimate ΔH for the atomization of naphthalene, $C_{10}H_8$:

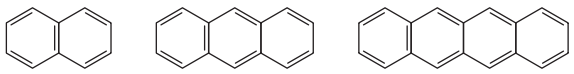


$$(g) \longrightarrow 10\,C(g) + 8\,H(g)$$

(**b**) Determine ΔH for the atomization of naphthalene using Hess's law and the data in Appendix C. (ΔH_f° of solid naphthalene is 77.1 kJ/mol and molar heat of sublimation of naphthalene is 72.9 kJ/mol.) (**c**) Explain the large discrepancy in the two values.

9.127 Many compounds of the transition-metal elements contain direct bonds between metal atoms. We will assume that the *z*-axis is defined as the metal–metal bond axis. (**a**) Which of the 3*d* orbitals (Figure 6.22) is most likely to make a σ bond between metal atoms? (**b**) Sketch the σ_{3d} bonding and σ^*_{3d} antibonding MOs. (**c**) With reference to the "Closer Look" box on the phases of orbitals, explain why a node is generated in the σ^*_{3d} MO. (**d**) Sketch the energy-level diagram for the Sc_2 molecule, assuming that only the 3*d* orbital from part (a) is important. (**e**) What is the bond order in Sc_2?

9.128 The organic molecules shown here are derivatives of benzene in which six-membered rings are "fused" at the edges of the hexagons.



Naphthalene Anthracene Tetracene

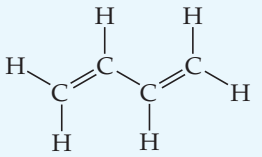
(**a**) Determine the empirical formula of benzene and of these three compounds. (**b**) Suppose you are given a sample of one of the compounds. Could combustion analysis be used to determine unambiguously which of the three it is? (**c**) Naphthalene, the active ingredient in mothballs, is a white solid. Write a balanced equation for the combustion of naphthalene to $CO_2(g)$ and $H_2O(g)$. (**d**) Using the Lewis structure for naphthalene and the average bond enthalpies in Table 8.3, estimate the heat of combustion of naphthalene in kJ/mol. (**e**) Benzene, naphthalene, and anthracene are colorless, but tetracene is orange. What does this imply about the relative HOMO–LUMO energy gaps in these molecules? See the "Chemistry Put to Work" box on orbitals and energy.

9.129 Antibonding molecular orbitals can be used to make bonds to other atoms in a molecule. For example, metal atoms can use appropriate *d* orbitals to overlap with the π^*_{2p} orbitals of the carbon monoxide molecule. This is called *d*-π backbonding. (**a**) Draw a coordinate axis system in which the *y*-axis is vertical in the plane of the paper and the *x*-axis horizontal. Write "M" at the origin to denote a metal atom. (**b**) Now, on the *x*-axis to the right of M, draw the Lewis structure of a CO molecule, with the carbon nearest the M. The CO bond axis should be on the *x*-axis. (**c**) Draw the CO π^*_{2p} orbital, with phases (see the "Closer Look" box on phases) in the plane of the paper. Two lobes should be pointing toward M. (**d**) Now draw the d_{xy} orbital of M, with phases. Can you see how they will overlap with the π^*_{2p} orbital of CO? (**e**) What kind of bond is being made with the orbitals between M and C, σ or π ? (**f**) Predict what will happen to the strength of the CO bond in a metal–CO complex compared to CO alone.

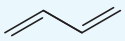
9.130 Methyl isocyanate, CH_3NCO, was made infamous in 1984 when an accidental leakage of this compound from a storage tank in Bhopal, India, resulted in the deaths of about 3800 people and severe and lasting injury to many thousands more. (**a**) Draw a Lewis structure for methyl isocyanate. (**b**) Draw a ball-and-stick model of the structure, including estimates of all the bond angles in the compound. (**c**) Predict all the bond distances in the molecule. (**d**) Do you predict that the molecule will have a dipole moment? Explain.

Design an Experiment

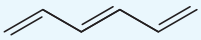
In this chapter, we have seen a number of new concepts, including the delocalization of π systems of molecules and the molecular orbital description of molecular bonding. A connection between these concepts is provided by the field of *organic dyes*, molecules with delocalized π systems that have color. The color is due to the excitation of an electron from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO). It is hypothesized that the energy gap between the HOMO and the LUMO depends on the length of the π system. Imagine that you are given samples of the following substances to test this hypothesis:



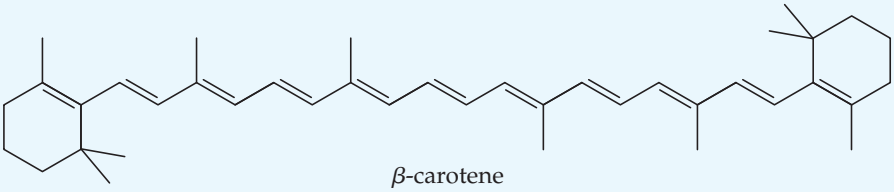
or, in shorthand notation for organic molecules



butadiene



hexatriene



β-carotene

β-Carotene is the substance chiefly responsible for the bright orange color of carrots. It is also an important nutrient for the body's production of retinal. (**a**) What experiments could you design to determine the amount of energy needed to excite an electron from the HOMO to the LUMO in each of these molecules? (**b**) How might you graph your data to determine whether a relationship exists between the length of the π system and the excitation energy? (**c**) What additional molecules might you want to procure to further test the ideas developed here? (**d**) How could you design an experiment to determine whether the delocalized systems and not some other molecular features, such as molecular length or the presence of bonds, are important in making the excitations occur in the visible portion of the spectrum? (*Hint*: You might want to test some additional molecules not shown here.)

WHAT'S AHEAD

10.1 ▶ Characteristics of Gases

10.2 ▶ Pressure

10.3 ▶ The Gas Laws

10.4 ▶ The Ideal Gas Equation

10.5 ▶ Gas Mixtures and Partial Pressures

10.6 ▶ The Kinetic-Molecular Theory of Gases

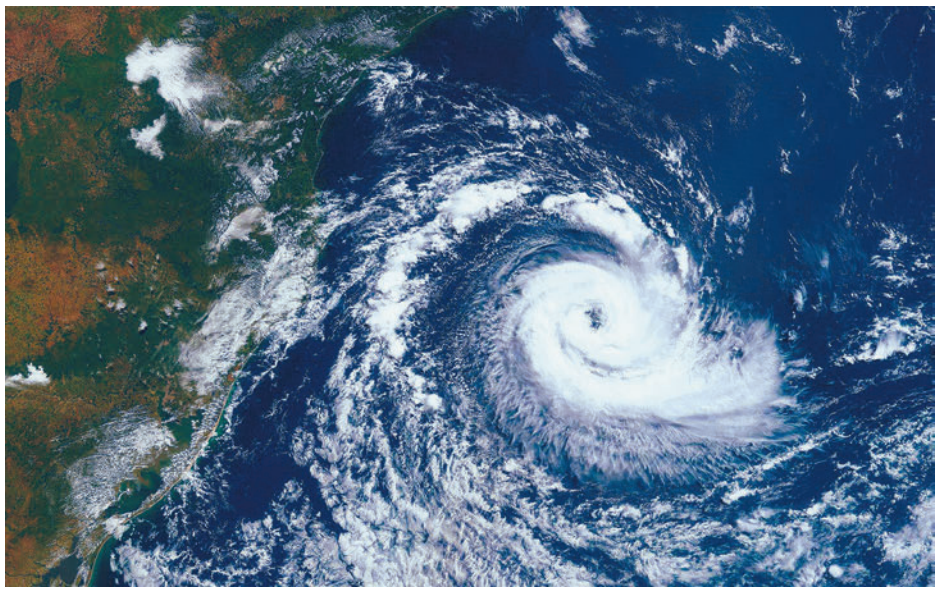
10.7 ▶ Molecular Effusion and Diffusion

10.8 ▶ Real Gases: Deviations from Ideal Behavior

10

GASES

10.1 | Characteristics of Gases



In this chapter, we examine the physical properties of gases—what is atmospheric pressure, how do gases respond to changes in pressure and temperature, and what does temperature measure at the molecular level? Because gases are the simplest state of matter, they serve as an excellent starting point for probing the behavior of large collections of atoms or molecules. Indeed, it is fairly straightforward to formulate a simple model for gases that explains their behavior under most common conditions. We gain further insight by then comparing how real gases differ from this ideal model as conditions change.

Thus, while we start with a description that treats all gases the same regardless of their chemical identity, we end by gaining an understanding of important aspects of the physical behavior of molecules.

By the end of this section, you should be able to

- Appreciate the fundamental differences between a gas and the condensed phases (liquid and solid) of a molecular compound.

Of the few elements that exist as gases at ordinary temperatures and pressures, He, Ne, Ar, Kr, and Xe are monatomic and H_2, N_2, O_2, F_2, and Cl_2 are diatomic. Many molecular compounds are gases, and Table 10.1 lists a few of them. Notice that all of these gases are composed entirely of nonmetallic elements. Furthermore, all have simple molecular formulas and, therefore, low molar masses.

Substances that are liquids or solids under ordinary conditions can also exist in the gaseous state, where they are often referred to as **vapors**. The substance H_2O, for example, can exist as liquid water, solid ice, or water vapor.

Even though different gaseous substances may have very different *chemical* properties, they behave quite similarly as far as their *physical* properties are concerned. For example, the N_2 and O_2 that account for approximately 99% of our atmosphere have very different chemical properties—O_2 supports human life but N_2 does not, to name just one difference—but these two components of air behave physically as one gaseous material because their physical properties are essentially identical.

The physical properties of gases differ significantly from those of solids and liquids. For example, a gas expands spontaneously to fill its container. Consequently, the volume of a gas equals the volume of its container. Gases also are highly compressible: When pressure is applied to a gas, its volume readily decreases. Solids and liquids, on the other hand, do not expand to fill their containers and are not readily compressible.

Two or more gases form a homogeneous mixture regardless of the identities or relative proportions of the gases; the atmosphere serves as an excellent example. Two or more liquids or two or more solids may or may not form homogeneous mixtures, depending on their chemical nature. For example, when water and gasoline are mixed, the two liquids remain as separate layers. In contrast, the water vapor and gasoline vapors above the liquids form a homogeneous gas mixture.

The characteristic properties of gases—expanding to fill a container, being highly compressible, forming homogeneous mixtures—arise because the molecules are relatively far apart. In any given volume of air, for example, the molecules take up only about 0.1% of the total volume with the rest being empty space. Thus, each molecule behaves largely as though the others were not present. As a result, different gases behave similarly even though they are made up of different molecules.

TABLE 10.1 Some Common Compounds That Are Gases at Room Temperature

Formula	Name	Characteristics
HCN	Hydrogen cyanide	Very toxic, slight odor of bitter almonds
H_2S	Hydrogen sulfide	Very toxic, odor of rotten eggs
CO	Carbon monoxide	Toxic, colorless, odorless
CO_2	Carbon dioxide	Colorless, odorless
CH_4	Methane	Colorless, odorless, flammable
C_2H_4	Ethene (Ethylene)	Colorless, ripens fruit
C_3H_8	Propane	Colorless, odorless, bottled gas
N_2O	Nitrous oxide	Colorless, sweet odor, laughing gas
NO_2	Nitrogen dioxide	Toxic, red-brown, irritating odor
NH_3	Ammonia	Colorless, pungent odor
SO_2	Sulfur dioxide	Colorless, irritating odor

Self-Assessment Exercise

10.1 True or false: All gases condense at the same temperature.

(a) True
(b) False

Exercises

10.2 Which of the following statements is false?

(**a**) Gases are far less dense than liquids.
(**b**) Gases are far more compressible than liquids.
(**c**) Because liquid water and liquid carbon tetrachloride do not mix, neither do their vapors.
(**d**) The volume occupied by a gas is determined by the volume of its container.

Answers to Self-Assessment Exercises

10.1 (b)

10.2 Pressure



What is the weather going to be like today or this week? Such knowledge not only helps us choose the clothing we wear during the day, but it also assists the farmer in planting and harvesting and the sailor in charting a course. The gases in our atmosphere, primarily N_2 and O_2 molecules, are heated by the Sun and moved here and there by pressure differences that create wind.

It is the behavior of gases that creates our weather—the gentle breezes, the violent storms, the humidity, and the rain. Tornadoes, like the one shown here, form when moist, warm air at lower elevations converges with cooler, dry air above. The resultant air flows produce winds that can approach speeds up to 500 km/hr.

By the end of this section, you should be able to

- Understand the molecular basis of pressure.

The molecules of a gas move chaotically, colliding with each other and with the walls of their container. The impacts with the container walls exert a force—an outward push against the walls. The **pressure**, P, that a gas exerts is defined as the force, F, divided by the area, A, of the surface on which the force is acting:

$$P = \frac{F}{A} \qquad [10.1]$$

Gases exert a pressure on any surface with which they are in contact. The gas in an inflated balloon, for example, exerts a pressure on the inside surface of the balloon.

Atmospheric Pressure and the Barometer

People, coconuts, and nitrogen molecules all experience an attractive gravitational force that pulls them toward the center of the Earth. When a coconut comes loose from a tree, for example, this force causes the coconut to be accelerated toward Earth, its speed increasing as its potential energy is converted into kinetic energy. The gas atoms and molecules of the atmosphere also experience a gravitational acceleration. Because these particles have such tiny masses, however, their thermal energies of motion (their kinetic energies) override the gravitational forces, so the particles that make up the atmosphere don't pile up at the Earth's surface. Nevertheless, the gravitational force does operate, and it causes the atmosphere as a whole to press down on the Earth's surface, creating *atmospheric pressure*, defined as the force exerted by the atmosphere on a given surface area.

You can demonstrate the existence of atmospheric pressure with an empty plastic water bottle. If you suck on the mouth of the empty bottle, chances are you can cause the bottle to partially cave in. When you break the partial vacuum you have created, the bottle pops out to its original shape. The bottle caves in because, once you've sucked out some of the air molecules, the air molecules in the atmosphere exert a force on the outside of the bottle that is greater than the force exerted by the lesser number of air molecules inside the bottle.

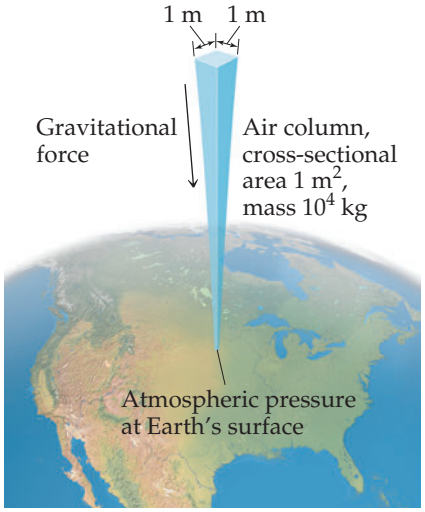
We can calculate the magnitude of the atmospheric pressure using Equation 10.1. The force, F, exerted by any object is the product of its mass, m, and its acceleration, a: $F = ma$. When applied to our atmosphere, the force is the gravitational force, which is also commonly called weight. The acceleration is that due to gravity, $g = 9.8\ \text{m/s}^2$. Thus, the gravitational force of the atmosphere on the Earth's surface (the weight of the atmosphere) is given by $F = mg$.

Now imagine a column of air, 1 m^2 in cross section, extending through the entire atmosphere (**Figure 10.1**). That column has a mass of roughly 10,000 kg. The downward gravitational force exerted on this column is

$$F = (10{,}000\ \text{kg})(9.8\ \text{m/s}^2) = 1 \times 10^5\ \text{kg m/s}^2 = 1 \times 10^5\ \text{N}$$

where N is the abbreviation for *newton*, the SI unit for force: $1\ \text{N} = 1\ \text{kg m/s}^2$.

The pressure exerted by the column is this force divided by the cross-sectional area, A, over which the force is applied. Because our air column has a cross-sectional area of 1 m^2, we have for the magnitude of atmospheric pressure at sea level



▲ **Figure 10.1** **Calculating atmospheric pressure.**

$$P = \frac{F}{A} = \frac{1 \times 10^5\ \text{N}}{1\ \text{m}^2} = 1 \times 10^5\ \text{N/m}^2 = 1 \times 10^5\ \text{Pa} = 1 \times 10^2\ \text{kPa}$$

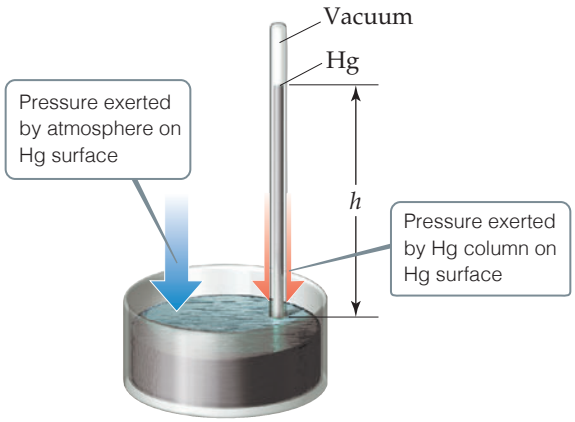
The SI unit of pressure is the **pascal** (Pa), named for Blaise Pascal (1623–1662), a French scientist who studied pressure: 1 Pa = 1 N/m^2. A related pressure unit is the **bar:** 1 bar = 10^5 Pa = 10^5 N/m^2. Thus, the atmospheric pressure at sea level we just calculated, 100 kPa, can be reported as 1 bar. (The actual atmospheric pressure at any location depends on weather conditions and altitude.) Another pressure unit is pounds per square inch (psi, lbs/in.^{2}). At sea level, atmospheric pressure is 14.7 psi.

In the seventeenth century, many scientists and philosophers believed that the atmosphere had no weight. Evangelista Torricelli (1608–1647), a student of Galileo's, proved this untrue. He invented the *barometer* (**Figure 10.2**), which is made from a glass tube more than 760 mm long that is closed at one end, completely filled with mercury, and inverted into a dish of mercury. (Care must be taken so that no air gets into the tube.) When the tube is inverted into the dish, some of the mercury flows out of the tube, but a column of mercury remains in the tube. Torricelli argued that the mercury surface in the dish experiences the full force of Earth's atmosphere, which pushes the mercury up the tube until the pressure exerted by the mercury column downward, due to gravity, equals the atmospheric pressure at the base of the tube. Therefore *the height,* h*, of the mercury column is a measure of atmospheric pressure and changes as atmospheric pressure changes.*

Standard atmospheric pressure, which corresponds to the typical pressure at sea level, is the pressure sufficient to support a column of mercury 760 mm high. In SI units, this pressure is 1.01325 × 10^5 Pa. Standard atmospheric pressure defines some common non-SI units used to express gas pressure, such as the **atmosphere** (atm) and the *millimeter of mercury* (mm Hg). The latter unit is also called the **torr**, after Torricelli: 1 torr = 1 mm Hg. Thus, we have

$$1\ \text{atm} = 760.\ \text{mm Hg} = 760.\ \text{torr} = 1.01325 \times 10^5\ \text{Pa} = 101.325\ \text{kPa} = 1.01325\ \text{bar}$$

Go Figure What happens to *h*, the height of the mercury column, if the atmospheric pressure increases?



▲ **Figure 10.2** **A mercury barometer.**

We use various devices to measure the pressures of enclosed gases. Tire gauges, for example, measure the pressure of air in car and bicycle tires. In laboratories, we sometimes use a *manometer*, which operates on a principle similar to that of a barometer, as shown in Sample Exercise 10.2.

Sample Exercise 10.1

Calculating Pressure

What is the pressure, in kilopascals, on the body of a diver if she is 31.0 m below the surface of the water when the atmospheric pressure on the surface is 98 kPa? Assume that the density of the water is 1.00 g/cm^3 $= 1.00 \times 10^3$ kg/m^3. The gravitational constant is 9.81 m/s^2, and 1 Pa $=$ 1 kg m s^2.

SOLUTION

Analyze We are asked to calculate the pressure on the diver given the atmospheric pressure (98 kPa) and the depth of the water (31.0 m).

Plan The total pressure on the diver equals that of the atmosphere plus that of the water. The pressure of the water can be calculated starting with Equation 10.1, $P = F/A$. The force, F, due to the water above the diver is given by its mass times the acceleration due to gravity, $F = mg$, where $g = 9.81$ m/s^2.

Solve The pressure caused by the water is

$$P = \frac{F}{A} = \frac{mg}{A}$$

The mass of the water is related to its density ($d = m/V$, so $m = d \times V$). We can treat the water as a column whose volume equals its cross-sectional area times its height: $V = A \times h$. When we make these substitutions for mass ($m = d \times V$) and volume ($V = A \times h$), we have

$$P = \frac{mg}{A} = \frac{dVg}{A} = \frac{d(Ah)g}{A} = dhg$$

Inserting SI quantities, we have

$$P = dhg = (1.00 \times 10^3 \text{ kg/m}^3)(31.0 \text{ m})(9.81 \text{ m/s}^2)$$

$$= 3.00 \times 10^5 \frac{\text{kg}}{\text{m s}^2} = 3.00 \times 10^5 \text{ Pa}$$

Thus, the total pressure on the diver is

$$P_{\text{total}} = 98 \text{ kPa} + 300 \text{ kPa} = 398 \text{ kPa}$$

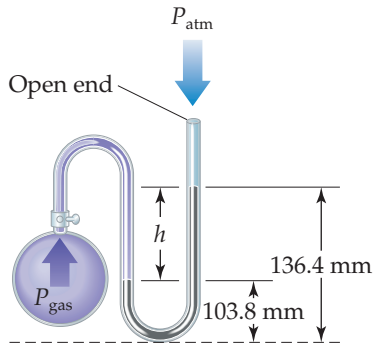
Practice Exercise

What would be the height of the column in a barometer if the external pressure was 101 kPa and water ($d = 1.00$ g/cm^3) was used in place of mercury?
(**a**) 0.0558 m (**b**) 0.760 m (**c**) 1.03×10^4 m
(**d**) 10.3 m (**e**) 0.103 m

Sample Exercise 10.2

Using a Manometer to Measure Gas Pressure

On a certain day, a laboratory barometer indicates that the atmospheric pressure is 764.7 torr. A sample of gas is placed in a flask attached to an open-end mercury manometer (Figure 10.3), and a meter stick is used to measure the height of the mercury in the two arms of the U tube. The height of the mercury in the open-ended arm is 136.4 mm, and the height in the arm in contact with the gas in the flask is 103.8 mm. What is the pressure of the gas in the flask (**a**) in atmospheres, (**b**) in kilopascals?



▲ **Figure 10.3** A mercury manometer.

SOLUTION

Analyze We are given the atmospheric pressure (764.7 torr) and the mercury heights in the two arms of the manometer and asked to determine the gas pressure in the flask. Recall that millimeters of mercury is a pressure unit. We know that the gas pressure from the flask must be greater than atmospheric pressure because the mercury level in the arm on the flask side (103.8 mm) is lower than the level in the arm open to the atmosphere (136.4 mm). Therefore, the gas from the flask is pushing mercury from the arm in contact with the flask into the arm open to the atmosphere.

Plan We will use the difference in height between the two arms (h in Figure 10.3) to obtain the amount by which the pressure of the gas exceeds atmospheric pressure. Because an open-end mercury manometer is used, the height difference directly measures the pressure difference in mm Hg or torr between the gas and the atmosphere.

Solve

(**a**) The pressure of the gas equals the atmospheric pressure plus h:

$$P_{\text{gas}} = P_{\text{atm}} + h$$
$$= 764.7 \text{ torr} + (136.4 \text{ torr} - 103.8 \text{ torr})$$
$$= 797.3 \text{ torr}$$

Continued

We convert the pressure of the gas to atmospheres:

$$P_{gas} = (797.3 \text{ torr})\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right) = 1.049 \text{ atm}$$

(b) To calculate the pressure in kPa, we employ the conversion factor between atmospheres and kPa:

$$1.049 \text{ atm}\left(\frac{101.3 \text{ kPa}}{1 \text{ atm}}\right) = 106.3 \text{ kPa}$$

Check The calculated pressure is a bit more than 1 atm, which is about 101 kPa. This makes sense because we anticipated that the pressure in the flask would be greater than the atmospheric pressure (764.7 torr = 1.01 atm) acting on the manometer.

Practice Exercise
If the pressure of the gas inside the flask were increased and the height of the column in the open-ended arm went up by 5.0 mm, what would be the new pressure of the gas in the flask, in kilopascals?

CHEMISTRY AND LIFE Blood Pressure

The human heart pumps blood to the parts of the body through arteries, and the blood returns to the heart through veins. When your blood pressure is measured, two values are reported, such as 120/80 (120 over 80), which is a normal reading. The first measurement is the *systolic pressure*, the maximum pressure when the heart is pumping. The second is the *diastolic pressure*, the pressure when the heart is in the resting part of its pumping cycle. The units associated with these pressure measurements are torr.

Blood pressure is measured using a pressure gauge attached to a closed, air-filled jacket or cuff that is applied like a tourniquet to the arm (Figure 10.4). The pressure gauge may be a mercury manometer or some other device. The air pressure in the cuff is increased using a small pump until it is above the systolic pressure and prevents the flow of blood. The air pressure inside the cuff is then slowly reduced until blood just begins to pulse through the artery, as detected by the use of a stethoscope. At this point the pressure in the cuff equals the pressure that the blood exerts inside the arteries. Reading the gauge gives the systolic pressure. The pressure in the cuff is then reduced further until the blood flows freely. The pressure at this point is the diastolic pressure.

Hypertension is the presence of abnormally high blood pressure. The usual criterion for hypertension is a blood pressure greater than 140/90, although recent studies suggest that health risks increase for systolic readings above 120. Hypertension significantly increases the workload on the heart and also places a stress on the walls of the blood vessels throughout the body. These effects increase the risk of aneurysms, heart attacks, and strokes.



▲ **Figure 10.4** Measuring blood pressure.

Self-Assessment exercise

10.3 An altimeter is an instrument used to measure the altitude of an aircraft and gives a reading in feet above a datum (usually ground level). It detects the atmospheric pressure outside the aircraft. As the reading on the altimeter increases, does the atmospheric pressure outside the aircraft:

(a) Increase
(b) Decrease

Exercises

10.4 A set of bookshelves rests on a hard floor surface on four legs, each having a cross-sectional dimension of 4.0 × 5.0 cm in contact with the floor. The total mass of the shelves plus the books stacked on them is 200 kg. Calculate the pressure in atmospheres exerted by the shelf footings on the surface.

10.5 (**a**) The compound 1-iodododecane is a nonvolatile liquid with a density of 1.20 g/mL. The density of mercury is 13.6 g/mL. What do you predict for the height of a barometer column based on 1-iodododecane, when the atmospheric pressure is 749 torr? (**b**) What is the pressure, in atmospheres, on the body of a diver if he is 21 ft below the surface of the water when the atmospheric *pressure* is 742 torr?

10.6 Perform the following conversions: (**a**) 0.912 atm to torr, (**b**) 0.685 bar to kilopascals, (**c**) 655 mm Hg to atmospheres, (**d**) 1.323×10^5 Pa to atmospheres, (**e**) 2.50 atm to psi.

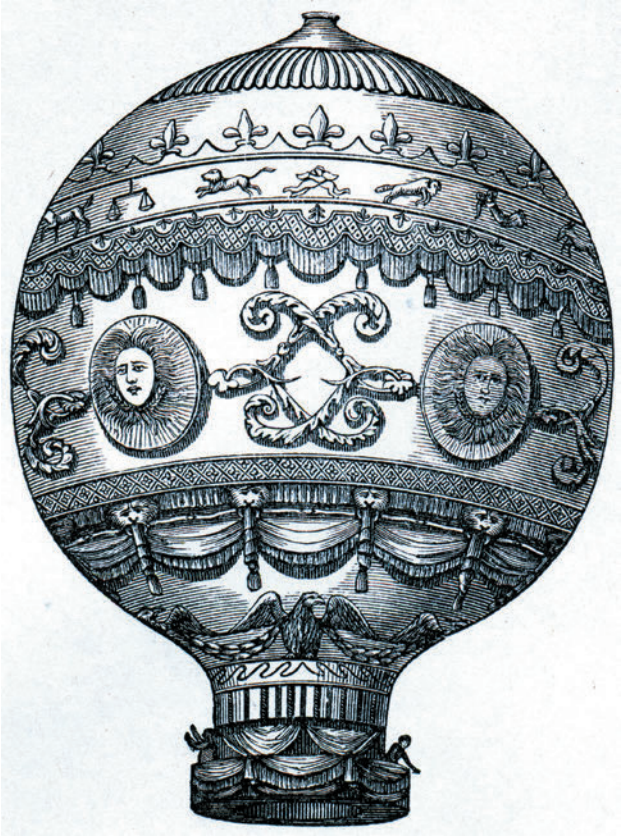
10.7 Hurricane Wilma of 2005 is the most intense hurricane on record in the Atlantic basin, with a low-pressure reading of 882 mbar (millibars). Convert this reading into (**a**) atmospheres, (**b**) torr, and (**c**) inches of Hg.

10.8 An open-end manometer containing mercury is connected to a container of gas, as depicted in Sample Exercise 10.2. What is the pressure of the enclosed gas in torr in each of the following situations? (**a**) The mercury in the arm attached to the gas is 15.4 mm higher than in the one open to the atmosphere; atmospheric pressure is 0.985 atm. (**b**) The mercury in the arm attached to the gas is 12.3 mm lower than in the one open to the atmosphere; atmospheric pressure is 0.99 atm.

Answers to Self-Assessment Exercises

10.3 (b)

10.3 The Gas Laws



It is said that Joseph Montgolfier first got the idea of a hot air balloon when he observed how laundry, drying over a fire, occasionally trapped air and billowed upwards. With the help of his brother Etienne, he built and tested an unmanned balloon using smoldering wool and hay as a heat source. This proved so successful that the balloon rose out of their control and crashed some 2 km away. On 19 September 1783, the brothers demonstrated their invention in front of King Louis XVI of France and Queen Marie Antoinette. The balloon had a basket attached to it carrying a sheep, a duck, and a rooster. All three animals survived the 3 km flight in which the balloon reached an estimated 1500 feet. Seeing this, the king sanctioned the first human flight in a hot air balloon. This was undertaken by Etienne in a tethered balloon with the first untethered flight being made in November of the same year.

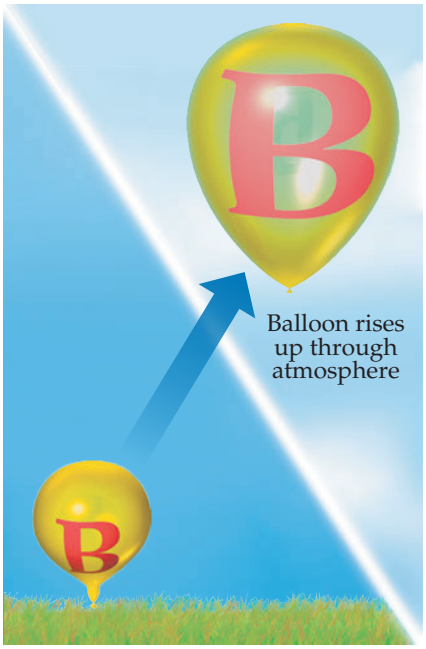
The bright colors of a hot air balloon can sometimes be seen in the still air of the early morning. In this section, we study some fundamental physical properties of gases. By the end of the section, you should be able to

- Understand the relationship between volume, temperature, and pressure of a gas.

Four variables are needed to define the physical condition, or *state*, of a gas: temperature, pressure, volume, and amount of gas, usually expressed as number of moles. The equations that express the relationships among these four variables are known as the *gas laws*. Because volume is easily measured, the first gas laws to be studied expressed the effect of one of the variables on volume, with the remaining two variables held constant.

Go Figure

Does atmospheric pressure increase or decrease as altitude increases? (Neglect changes in temperature.)



▲ **Figure 10.5** **As a balloon rises in the atmosphere, its volume increases.**

The Pressure–Volume Relationship: Boyle's Law

Gas volume increases as the pressure exerted on the gas decreases. Thus, an inflated weather balloon released at the Earth's surface expands as it rises (**Figure 10.5**) because the pressure of the atmosphere decreases with increasing elevation.

The British chemist Robert Boyle (1627–1691) was the first person to investigate the quantitative relationship between the pressure of a gas and its volume. He found, for example, that decreasing the pressure of a gas to half its original value causes the volume to double. Conversely, doubling the pressure causes the volume to decrease to half its original value.

Boyle's law, which summarizes these observations, states that:

The volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure.

When two measurements are inversely proportional, one gets smaller as the other gets larger. Boyle's law can be expressed mathematically as

$$V = \text{constant} \times \frac{1}{P} \quad \text{or} \quad PV = \text{constant} \qquad [10.2]$$

The value of the constant depends on temperature and on the amount of gas in the sample.

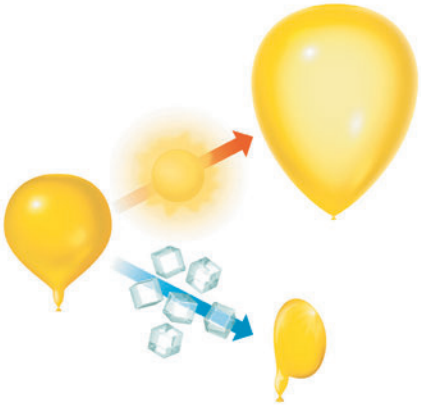
The graph of V versus P in **Figure 10.6** shows the curve obtained for a given quantity of gas at a fixed temperature. A linear relationship is obtained when V is plotted versus $1/P$ as shown on the right in Figure 10.6.

Boyle's law occupies a special place in the history of science because Boyle was the first to carry out experiments in which one variable was systematically changed to determine the effect on another variable. The data from the experiments were then employed to establish an empirical relationship—a "law."

We apply Boyle's law every time we breathe. The rib cage, which can expand and contract, and the diaphragm, a muscle beneath the lungs, govern the volume of the lungs. Inhalation occurs when the rib cage expands and the diaphragm moves downward. Both actions increase the volume of the lungs, thus decreasing the gas pressure inside the lungs. Atmospheric pressure then forces air into the lungs until the pressure in the lungs equals atmospheric pressure. Exhalation reverses the process—the rib cage contracts and the diaphragm moves up, decreasing the volume of the lungs. Air is forced out of the lungs by the resulting increase in pressure.

The Temperature–Volume Relationship: Charles's Law

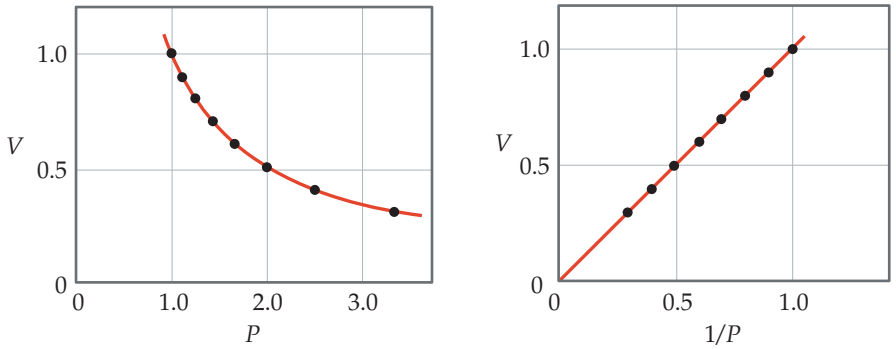
As **Figure 10.7** illustrates, the volume of an inflated balloon increases when the temperature of the gas inside the balloon increases and decreases when the temperature of the gas decreases. This relationship between gas volume and temperature was discovered in 1787 by French



▲ **Figure 10.7** **The effect of temperature on volume.**

Go Figure

What would a plot of P versus $1/V$ look like for a fixed quantity of gas at a fixed temperature?



▲ **Figure 10.6** **Boyle's Law.** For a fixed quantity of gas at constant temperature, the volume of the gas is inversely proportional to its pressure.

scientist Jacques Charles (1746–1823). Some typical volume–temperature data are shown in Figure 10.8. Notice that the extrapolated (dashed) line passes through −273 °C. Note also that the gas is predicted to have zero volume at this temperature. This condition is never realized, however, because all gases liquefy or solidify before reaching this temperature.

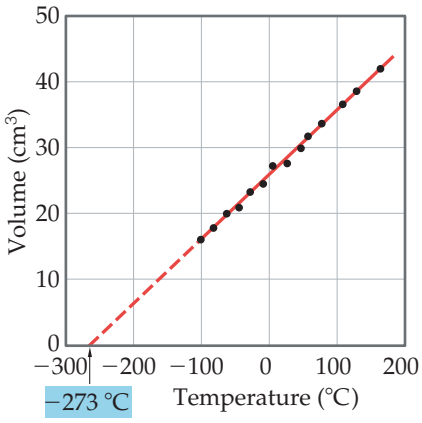
In 1848, William Thomson (1824–1907), a British physicist whose title was Lord Kelvin, proposed an absolute-temperature scale, now known as the Kelvin scale. On this scale, 0 K, called *absolute zero*, equals −273.15 °C. In terms of the Kelvin scale, **Charles's law** states:

The volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature.

Thus, doubling the absolute temperature causes the gas volume to double. Mathematically, Charles's law takes the form

$$V = \text{constant} \times T \quad \text{or} \quad \frac{V}{T} = \text{constant} \qquad [10.3]$$

with the value of the constant depending on the pressure and on the amount of gas.



▲ **Figure 10.8 Charles's Law.** For a fixed quantity of gas at constant pressure, the volume of the gas is proportional to its temperature.

The Quantity–Volume Relationship: Avogadro's Law

The relationship between the quantity of a gas and its volume follows from the work of Joseph Louis Gay-Lussac (1778–1823) and Amedeo Avogadro (1776–1856).

Gay-Lussac was one of those extraordinary figures in the history of science who could truly be called an adventurer. In 1804, he ascended to 7000 m in a hot air balloon—an exploit that held the altitude record for several decades. To better control the balloon, Gay-Lussac studied the properties of gases. In 1808, he observed the *law of combining volumes*: At a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. For example, two volumes of hydrogen gas react with one volume of oxygen gas to form two volumes of water vapor.

Three years later, Amedeo Avogadro interpreted Gay-Lussac's observation by proposing what is now known as **Avogadro's hypothesis**:

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

For example, 22.4 L of any gas at 0 °C and 101.3 kPa contain 6.02×10^{23} gas molecules (that is, 1 mol), as depicted in Figure 10.9.

Avogadro's law follows from Avogadro's hypothesis:

The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas.

Go Figure How many moles of gas are in each vessel?



	He	N_2	CH_4
Volume	22.4 L	22.4 L	22.4 L
Pressure	101.3 kPa	101.3 kPa	101.3 kPa
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

▲ **Figure 10.9 Avogadro's hypothesis.** At the same volume, pressure, and temperature, samples of different gases have the same number of molecules but different masses.

That is,

$$V = \text{constant} \times n \quad \text{or} \quad \frac{V}{n} = \text{constant} \qquad [10.4]$$

where n is number of moles. Thus, for instance, doubling the number of moles of gas causes the volume to double if T and P remain constant.

Sample Exercise 10.3

Evaluating the Effects of Changes in *P*, *V*, *n*, and *T* on a Gas

Suppose we have a gas confined to a cylinder with a movable piston that is sealed so there are no leaks. How will each of the following changes affect (i) the pressure of the gas, (ii) the number of moles of gas in the cylinder, (iii) the average distance between molecules: (**a**) Heating the gas while maintaining a constant pressure; (**b**) Reducing the volume while maintaining a constant temperature; (**c**) Injecting additional gas while keeping the temperature and volume constant.

SOLUTION

Analyze We need to think how each change affects (1) the pressure of the gas, (2) the number of moles of gas in the cylinder, and (3) the average distance between molecules.

Plan We can use the gas laws to evaluate the changes in pressure. The number of moles of gas in the cylinder will not change unless gas is either added or removed. Assessing the average distance between molecules is not quite as straightforward. For a given number of gas molecules, the average distance between molecules increases as the volume increases. Conversely, for constant volume, the average distance between molecules decreases as the number of moles increases. Thus, the average distance between molecules will be proportional to V/n.

Solve

(**a**) Because it is stipulated that the pressure remains constant, pressure is not a variable in this problem, and the total number of moles of gas will also remain constant. We know from Charles's law, however, that heating the gas while maintaining constant pressure will cause the piston to move and the volume to increase. Thus, the distance between molecules will increase.

(**b**) The reduction in volume causes the pressure to increase (Boyle's law). Compressing the gas into a smaller volume does not change the total number of gas molecules; thus, the total number of moles remains the same. The average distance between molecules, however, must decrease because of the smaller volume.

(**c**) Injecting more gas into the cylinder means that more molecules are present and there will be an increase in the number of moles of gas in the cylinder. Because we have added more molecules while keeping the volume constant, the average distance between molecules must decrease. Avogadro's law tells us that the volume of the cylinder should have increased when we added more gas, provided the pressure and temperature were held constant. Here the volume is held constant, as is the temperature, which means the pressure must change. Knowing from Boyle's law that there is an inverse relationship between volume and pressure ($PV = \text{constant}$), we conclude that if the volume does not increase on injecting more gas the pressure must increase.

Practice Exercise

An oxygen cylinder used in a hospital contains 35.4 L of oxygen gas at a pressure of 15.16 GPa. How much volume would the oxygen occupy if it were transferred to a container that maintained a pressure of 101.3 kPa if the temperature remains constant?

Self-Assessment Exercise

10.9 What happens to the pressure of a gas in a closed container if you double its volume while its temperature is held constant?

(a) The pressure is halved

(b) The pressure remains the same

(c) The pressure is doubled

Exercises

10.10 You have a gas at 25 °C confined to a cylinder with a movable piston. Which of the following actions would double the gas pressure? (**a**) Lifting up on the piston to double the volume while keeping the temperature constant; (**b**) Heating the gas so that its temperature rises from 25 °C to 50 °C, while keeping the volume constant; (**c**) Pushing down on the piston to halve the volume while keeping the temperature constant.

10.11 In the contact process, sulfur dioxide and oxygen gas react to form sulfur trioxide as follows:

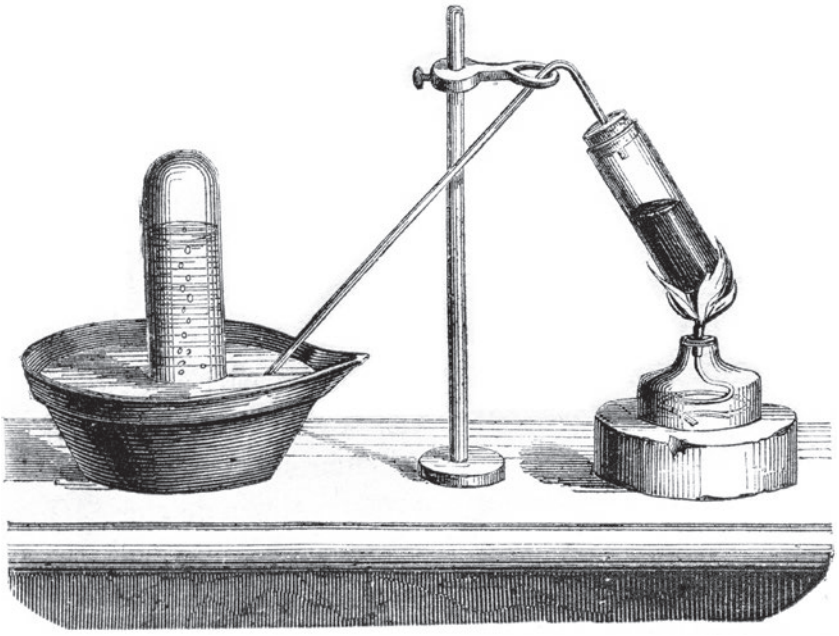
$$2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$$

At a certain temperature and pressure, 50 L of SO_2 reacts with 25 L of O_2. If all the SO_2 and O_2 are consumed, what volume of SO_3, at the same temperature and pressure, will be produced?

Answers to Self-Assessment Exercises

10.9 (a)

10.4 The Ideal Gas Equation



Early work on gases assumed that they were composed of individual atoms. This made them appealing to study as the interaction between atoms could be put on one side and the physical properties of the gas studied as a window onto the atomic world. There were some confusing observations, however. For example, the French chemist Gay-Lussac noticed that some reactions between gasses produced twice the volume of product than he expected. This was later explained by Amedeo Avogadro, a physics professor at the University of Turin in Italy, who suggested that gases were made of clusters of atoms; what we now call molecules. This breakthrough led to a new dawn of understanding of matter and chemical bonding.

By the end of this section, you should be able to

- Use the ideal gas equation to relate the amount of gas to its volume, pressure, and temperature.
- Calculate the molar mass of a gas from its density.

All three laws we just examined were obtained by holding two of the four variables *P, V, T,* and *n* constant and seeing how the remaining two variables affect each other. We can express each law as a proportionality relationship. Using the symbol $\propto$ for "is proportional to," we have

$$\begin{aligned} &\textit{Boyle's law}: && V \propto \frac{1}{P} && (\text{constant } n, T) \\ &\textit{Charles's law}: && V \propto T && (\text{constant } n, P) \\ &\textit{Avogadro's law}: && V \propto n && (\text{constant } P, T) \end{aligned}$$

We can combine these relationships into a general gas law:

$$V \propto \frac{nT}{P}$$

If we call the proportionality constant R, we obtain an equality:

$$V = R\left(\frac{nT}{P}\right)$$

which we can rearrange to

$$PV = nRT \qquad [10.5]$$

TABLE 10.2 Numerical Values of the Gas Constant R in Various Units

Units	Numerical Value
L atm/mol K	0.08206
J/mol K*	8.314
m^3 Pa/mol K*	8.314
L torr/mol K	62.36
L kPa/mol K	8.314

*SI unit

which is the **ideal gas equation** (also called the **ideal gas law**). An **ideal gas** is a hypothetical gas whose pressure, volume, and temperature relationships are described completely by the ideal gas equation.

In deriving the ideal gas equation, we make two assumptions:

- the molecules of an ideal gas do not interact with one another,
- the combined volume of the molecules is much smaller than the volume the gas occupies.

For these reasons, we consider the molecules as taking up no space in the container. In many cases, the small error introduced by these assumptions is acceptable. If more accurate calculations are needed, we can correct for the assumptions if we know something about the attraction molecules have for one another and the size of the molecules.

The term R in the ideal gas equation is the **gas constant**. The value and units of R depend on the units of P, V, n, and T. The value for T in the ideal gas equation must *always* be the absolute temperature (in kelvins instead of degrees Celsius). The quantity of gas, n, is normally expressed in moles. The units chosen for pressure are most often atmospheres or Pascals and the units of volume in liters. Table 10.2 shows the numerical value for R in various units. In working with the ideal gas equation, you must choose the form of R in which the units agree with the units of P, V, n, and T given in the problem.

Suppose we have 1.000 mol of an ideal gas at 101.325 kPa and 0.00 °C (273.15 K). According to the ideal gas equation, the volume of the gas is

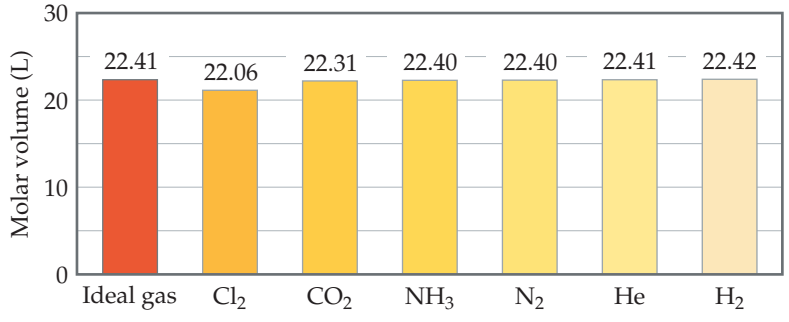
$$V = \frac{nRT}{P}$$

$$= \frac{(1.000\ \cancel{\text{mol}})(8.314\ \text{m}^3\ \text{Pa/mol K})(273.15\ \cancel{\text{K}})}{101.325 \times 10^3\ \text{Pa}} = 22.41\ \text{L}$$

The conditions 0 °C and 101.325 kPa are referred to as **standard temperature and pressure (STP)**. The volume occupied by 1 mol of ideal gas at STP, 22.41 L, is known as the *molar volume* of an ideal gas at STP.

The ideal gas equation accounts adequately for the properties of most gases under a variety of circumstances. The equation is not exactly correct, however, for any real gas. Thus, the measured volume for given values of P, n, and T might differ from the volume calculated from $PV = nRT$ (Figure 10.10). Although real gases do not always behave ideally, their behavior differs so little from ideal behavior that we can ignore any deviations for all but the most accurate work.

Go Figure Which gas deviates most from ideal behavior?



▲ **Figure 10.10** Comparison of molar volumes at STP.

Sample Exercise 10.4

Using the Ideal Gas Equation

Calcium carbonate, $CaCO_3(s)$, the principal compound in limestone, decomposes upon heating to $CaO(s)$ and $CO_2(g)$. A sample of $CaCO_3$ is decomposed, and the carbon dioxide is collected in a 250 mL flask. After decomposition is complete, the gas has a pressure of 131.72 kPa at a temperature of 31 °C. How many moles of CO_2 gas were generated?

SOLUTION

Analyze We are given the volume (250 mL), pressure (131.72 kPa), and temperature (31 °C) of a sample of CO_2 gas and asked to calculate the number of moles of CO_2 in the sample.

Plan Because we are given V, P, and T, we can solve the ideal gas equation for the unknown quantity, n.

Solve In analyzing and solving gas law problems, it is helpful to tabulate the information given in the problems and then to convert the values to units that are consistent with those for R (8.314 m^3 Pa/mol K). In this case, the given values are

$$V = 250\,\text{mL} = 0.250\,\text{L} = 2.5 \times 10^{-4}\,\text{m}^3$$
$$P = 131.72\,\text{kPa} = 131.72 \times 10^3\,\text{Pa}$$
$$T = 31\,^\circ\text{C} = (31 + 273)\,\text{K} = 304\,\text{K}$$

Remember: *Absolute temperature must always be used when the ideal gas equation is solved.*

We now rearrange the ideal gas equation (Equation 10.5) to solve for n

$$n = \frac{PV}{RT}$$

$$n = \frac{(131.72 \times 10^3\,\text{Pa})(2.5 \times 10^{-4}\,\text{m}^3)}{(8.314\,\text{m}^3\,\text{Pa/mol K})(304\,\text{K})}$$
$$= 0.013\,\text{mol CO}_2$$

Check Appropriate units cancel, thus ensuring that we have properly rearranged the ideal gas equation and have converted to the correct units.

Practice Exercise

Tennis balls are usually filled with either air or N_2 gas to a pressure above atmospheric pressure to increase their bounce. If a tennis ball has a volume of 144 cm^3 and contains 0.33 g of N_2 gas, what is the pressure inside the ball at 24 °C?

STRATEGIES FOR SUCCESS Calculations Involving Many Variables

In this chapter, we encounter a variety of problems based on the ideal gas equation, which contains four variables—P, V, n, and T—and one constant, R. Depending on the type of problem, we might need to solve for any of the four variables.

To extract the necessary information from problems involving more than one variable, we suggest the following steps:

1. **Tabulate information.** Read the problems carefully to determine which variable is the unknown and which variables have numeric values given. Every time you encounter a numerical value, jot it down. In many cases, constructing a table of the given information will be useful.
2. **Convert to consistent units.** Make certain that quantities are converted to the proper units. In using the ideal gas equation, for example, we usually use the value of R that has units of m^3 Pa/mol K.
3. **If a single equation relates the variables, solve the equation for the unknown.** For the ideal gas equation, these algebraic rearrangements will all be used at one time or another:

$$P = \frac{nRT}{V}, \quad V = \frac{nRT}{P}, \quad n = \frac{PV}{RT}, \quad T = \frac{PV}{nR}$$

4. **Use dimensional analysis.** Carry the units through your calculation. Using dimensional analysis enables you to check that you have solved an equation correctly. If the units in the equation cancel to give the units of the desired variable, you have probably used the equation correctly.

Sometimes you will not be given explicit values for several variables, making it look like a problem that cannot be solved. In these cases, however, you should look for information that can be used to determine the needed variables. For example, suppose you are using the ideal gas equation to calculate a pressure in a problem that gives a value for T but not for n or V. However, the problem states that "the sample contains 0.15 mol of gas per liter." You can turn this statement into the expression

$$\frac{n}{V} = 0.15\,\text{mol/L}$$

Solving the ideal gas equation for pressure yields

$$P = \frac{nRT}{V}$$

which we can rewrite as follows:

$$P = \left(\frac{n}{V}\right)RT$$

Thus, we can solve the equation even though we are not given values for n and V.

As we have continuously stressed, the most important thing you can do to become proficient at solving chemistry problems is to do the practice exercises, the end-of-section exercises and end-of-chapter exercises. By using systematic procedures, such as those described here, you should be able to minimize difficulties in solving problems involving many variables.

Relating the Ideal Gas Equation and the Gas Laws

The gas laws we discussed in Section 10.3 are special cases of the ideal gas equation. For example, when n and T are held constant, the product nRT contains three constants and so must itself be a constant:

$$PV = nRT = \text{constant} \quad \text{or} \quad PV = \text{constant} \qquad [10.6]$$

Note that this rearrangement gives Boyle's law. We see that if n and T are constant, the values of P and V can change, but the product PV must remain constant.

We can use Boyle's law to determine how the volume of a gas changes when its pressure changes. For example, if a cylinder fitted with a movable piston holds 50.0 L of O_2 gas at 1.875 MPa and 21 °C, what volume will the gas occupy if the temperature is maintained at 21 °C while the pressure is reduced to 101.3 kPa? Because the product PV is a constant when a gas is held at constant n and T, we know that

$$P_1V_1 = P_2V_2 \qquad [10.7]$$

where P_1 and V_1 are initial values and P_2 and V_2 are final values. Dividing both sides of this equation by P_2 gives the final volume, V_2:

$$V_2 = V_1 \times \frac{P_1}{P_2} = (50.0\text{ L})\left(\frac{1.875\text{ MPa}}{101.3\text{ kPa}}\right) = 925\text{ L}$$

The answer is reasonable because a gas expands as its pressure decreases.

In a similar way, we can start with the ideal gas equation and derive relationships between any other two variables, V and T (Charles's law), n and V (Avogadro's law), or P and T.

We are often faced with the situation in which P, V, and T all change for a fixed number of moles of gas. Because n is constant in this situation, the ideal gas equation gives

$$\frac{PV}{T} = nR = \text{constant}$$

Sample Exercise 10.5

Calculating the Effect of Temperature Changes on Pressure

The gas pressure in an aerosol can is 152 kPa at 25 °C. Assuming that the gas obeys the ideal gas equation, what is the pressure when the can is heated to 450 °C?

SOLUTION

Analyze We are given the initial pressure (152 kPa) and temperature (25 °C) of the gas and asked for the pressure at a higher temperature (450 °C).

Plan The volume and number of moles of gas do not change, so we must use a relationship connecting pressure and temperature. Converting temperature to the Kelvin scale and tabulating the given information, we have

	P	T
Initial	152 kPa	298 K
Final	P_2	723 K

Solve To determine how P and T are related, we start with the ideal gas equation and isolate the quantities that do not change (n, V, and R) on one side and the variables (P and T) on the other side.

$$\frac{P}{T} = \frac{nR}{V} = \text{constant}$$

Because the quotient P/T is a constant, we can write

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

(where the subscripts 1 and 2 represent the initial and final states, respectively). Rearranging to solve for P_2 and substituting the given data give

$$P_2 = (152\text{ kPa})\left(\frac{723\text{ K}}{298\text{ K}}\right) = 368.8\text{ kPa}$$

Check This answer is intuitively reasonable—increasing the temperature of a gas increases its pressure.

Comment It is evident from this example why aerosol cans carry a warning not to incinerate.

Practice Exercise

The pressure in a natural-gas tank is maintained at 222.9 kPa. On a day when the temperature is −15 °C, the volume of gas in the tank is $3.25 \times 10^3\text{ m}^3$. What is the volume of the same quantity of gas on a day when the temperature is 31 °C?

Sample Exercise 10.6

Using the Combined Gas Law

An inflated balloon has a volume of 6.0 L at sea level (101.3 kPa) and is allowed to ascend until the pressure is 45.6 kPa. During ascent, the temperature of the gas falls from 22 °C to −21 °C. Calculate the volume of the balloon at its final altitude.

SOLUTION

Analyze We need to determine a new volume for a gas sample when both pressure and temperature change.

Plan Let's again proceed by converting temperatures to kelvins and tabulating our information.

	P	*V*	*T*
Initial	101.3 kPa	6.0 L	295 K
Final	45.6 kPa	V_2	252 K

Because n is constant, we can use Equation 10.8.

Solve Rearranging Equation 10.8 to solve for V_2 gives

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$= (6.0\,\text{L})\left(\frac{101.3\,\text{kPa}}{45.6\,\text{kPa}}\right)\left(\frac{252\,\text{K}}{295\,\text{K}}\right) = 11\,\text{L}$$

Check The result appears reasonable. Notice that the calculation involves multiplying the initial volume by a ratio of pressures and a ratio of temperatures. Intuitively, we expect decreasing pressure to cause the volume to increase, while decreasing the temperature should have the opposite effect. Because the change in pressure is more dramatic than the change in temperature, we expect the effect of the pressure change to predominate in determining the final volume, as it does.

Practice Exercise

A 0.50-mol sample of oxygen gas is confined at 0 °C and 101.3 kPa in a cylinder with a movable piston. The piston compresses the gas so that the final volume is half the initial volume and the final pressure is 222.9 kPa. What is the final temperature of the gas in degrees Celsius?

If we represent the initial and final conditions by subscripts 1 and 2, respectively, we can write an equation that is often called the *combined gas law*:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad [10.8]$$

We now use the ideal gas equation first to define the relationship between the density of a gas and its molar mass and then to calculate the volumes of gases formed or consumed in chemical reactions.

Gas Densities and Molar Mass

Recall that density has units of mass per unit volume ($d = m/V$). We can arrange the ideal gas equation to obtain similar units of moles per unit volume:

$$\frac{n}{V} = \frac{P}{RT}$$

If we multiply both sides of this equation by the molar mass, $\mathcal{M}$, which is the number of grams in 1 mol of a substance, we obtain

$$\frac{n\mathcal{M}}{V} = \frac{P\mathcal{M}}{RT} \qquad [10.9]$$

The term on the left equals the density in grams per liter:

$$\frac{\text{moles}}{\text{liter}} \times \frac{\text{grams}}{\text{mole}} = \frac{\text{grams}}{\text{liter}}$$

Thus, the density of the gas is also given by the expression on the right in Equation 10.9:

$$d = \frac{n\mathcal{M}}{V} = \frac{P\mathcal{M}}{RT} \qquad [10.10]$$

Sample Exercise 10.7

Calculating Gas Density

What is the density of tetrachloromethane (CCl_4) vapor at 95.19 kPa and 125 °C?

SOLUTION

Analyze We are asked to calculate the density of a gas given its name, its pressure, and its temperature.

Plan We can use Equation 10.10 to calculate the density. Before we can do that, however, we must convert the given quantities to the appropriate units, degrees Celsius to kelvins. We must also calculate the molar mass of CCl_4.

Solve The absolute temperature is $125 + 273 = 398$ K. The pressure is 95.19 kPa. The molar mass of CCl_4 is $12.01 + (4)(35.45) = 153.8$ g/mol. Therefore,

$$d = \frac{P\mathcal{M}}{RT} = \frac{(95.19\times10^3\text{Pa})(153.8\ \text{g/mol})}{(8.314\ \text{m}^3\ \text{Pa>mol K})(398\ \text{K})} = 4424\ \text{g>m}^3 = 4.42\ \text{g>L}$$

Check If we divide molar mass (g/mol) by density (g/L), we end up with L/mol. The numerical value is roughly $154/4.4 = 35$, which is in the right ballpark for the molar volume of a gas heated to 125 °C at near atmospheric pressure. We may thus conclude our answer is reasonable.

Practice Exercise

The mean molar mass of the atmosphere at the surface of Titan, Saturn's largest moon, is 28.6 g/mol. The surface temperature is 95 K, and the pressure is 162 kPa. Assuming ideal behavior, calculate the density of Titan's atmosphere.



▲ **Figure 10.11** Carbon dioxide gas flows downward because it is denser than air.

This equation tells us that the density of a gas depends on its pressure, molar mass, and temperature. The higher the molar mass and pressure, the denser the gas. The higher the temperature, the less dense the gas. Although gases form homogeneous mixtures, a less dense gas will lie above a denser gas in the absence of mixing. For example, CO_2 has a higher molar mass than N_2 or O_2 and is therefore denser than air. For this reason, CO_2 released from a CO_2 fire extinguisher blankets a fire, preventing O_2 from reaching the combustible material. "Dry ice," which is solid CO_2, converts directly to CO_2 gas at room temperature, and the resulting "fog" (which is actually condensed water droplets cooled by the CO_2) is carried downward by the heavier, but colorless, CO_2 (**Figure 10.11**).

When we have equal molar masses of two gases at the same pressure but different temperatures, the hotter gas is less dense than the cooler one, so the hotter gas rises. The difference between the densities of hot and cold air is responsible for the lift of hot air balloons. It is also responsible for many phenomena in weather, such as the formation of large thunderheads during thunderstorms.

Equation 10.10 can be rearranged to solve for the molar mass of a gas:

$$\mathcal{M} = \frac{dRT}{P} \qquad [10.11]$$

Thus, we can use the experimentally measured density of a gas to determine the molar mass of the gas molecules, as shown in Sample Exercise 10.8.

Sample Exercise 10.8

Calculating the Molar Mass of a Gas

A large evacuated flask initially has a mass of 134.567 g. When the flask is filled with a gas of unknown molar mass to a pressure of 97.99 kPa at 31 °C, its mass is 137.456 g. When the flask is evacuated again and then filled with water at 31 °C, its mass is 1067.9 g. (The density of water at this temperature is 0.997 g/mL.) Assuming the ideal gas equation applies, calculate the molar mass of the gas.

SOLUTION

Analyze We are given the temperature (31 °C) and pressure (97.99 kPa) for a gas, together with information to determine its volume and mass, and we are asked to calculate its molar mass.

Plan The data obtained when the flask is filled with water can be used to calculate the volume of the container. The mass of the empty flask and of the flask when filled with gas can be used to calculate the mass of the gas. From these quantities we calculate the gas density and then apply Equation 10.11 to calculate the molar mass of the gas.

Solve The gas volume equals the volume of water the flask can hold, calculated from the mass and density of the water. The mass of the water is the difference between the masses of the full and evacuated flask:

$$1067.9\text{ g} - 134.567\text{ g} = 933.3\text{ g}$$

Rearranging the equation for density ($d = m/V$), we have

$$V = \frac{m}{d} = \frac{(933.3\text{ g})}{(0.997\text{ g/mL})} = 936\text{ mL} = 0.936\text{ L}$$

The gas mass is the difference between the mass of the flask filled with gas and the mass of the evacuated flask:

$$137.456\text{ g} - 134.567\text{ g} = 2.889\text{ g}$$

Knowing the mass of the gas (2.889 g) and its volume (0.936 L), we can calculate the density of the gas:

$$d = 2.889\text{ g}/0.936\text{ L} = 3.09\text{ g/L} = 3.09 \times 10^3\text{ g/m}^3$$

After converting temperature to kelvins, we can use Equation 10.11 to calculate the molar mass:

$$\mathcal{M} = \frac{dRT}{P} = \frac{(3.09 \times 10^3\text{ g/m}^3)(8.314\text{ m}^3\text{ Pa/mol K})(304\text{ K})}{(97.99 \times 10^3\text{ Pa})} = 79.7\text{ g/mol}$$

Check The units work out appropriately, and the value of molar mass obtained is reasonable for a substance that is gaseous near room temperature.

Practice Exercise

What is the molar mass of an unknown hydrocarbon whose density is measured to be 1.97 g/L at STP?
(**a**) 4.04 g/mol (**b**) 30.7 g/mol (**c**) 44.1 g/mol
(**d**) 48.2 g/mol

Volumes of Gases in Chemical Reactions

We are often concerned with knowing the identity and/or quantity of a gas involved in a chemical reaction. Thus, it is useful to be able to calculate the volumes of gases consumed or produced in reactions. Such calculations are based on the mole concept and balanced chemical equations. The coefficients in a balanced chemical equation tell us the relative amounts (in moles) of reactants and products in a reaction. The ideal gas equation relates the number of moles of a gas to P, V, and T.

Sample Exercise 10.9

Relating Gas Variables and Reaction Stoichiometry

Automobile air bags are inflated by nitrogen gas generated by the rapid decomposition of sodium azide, NaN_3:

$$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$$

If an air bag has a volume of 36 L and is to be filled with nitrogen gas at 116.5 kPa and 26 °C, how many grams of NaN_3 must be decomposed?

SOLUTION

Analyze This is a multistep problem. We are given the volume, pressure, and temperature of the N_2 gas and the chemical equation for the reaction by which the N_2 is generated. We must use this information to calculate the number of grams of NaN_3 needed to obtain the necessary N_2.

Plan We need to use the gas data (P, V, and T) and the ideal gas equation to calculate the number of moles of N_2 gas that should be formed for the air bag to operate correctly. We can then use the balanced equation to determine the number of moles of NaN_3 needed. Finally, we can convert moles of NaN_3 to grams.

Solve

The conversion sequence is:

Gas data → mol N_2 → mol NaN_3 → g NaN_3

Continued

The number of moles of N_2 is determined using the ideal gas equation:

$$n = \frac{PV}{RT} = \frac{(116.5 \times 10^3\ \text{Pa})(0.036\ \text{m}^3)}{(8.314\ \text{m}^3\ \text{Pa/mol K})(299\ \text{K})}$$

$$= 1.7\ \text{mol}\ N_2$$

We use the coefficients in the balanced equation to calculate the number of moles of NaN_3:

$$(1.7\ \text{mol}\ N_2)\left(\frac{2\ \text{mol}\ NaN_3}{3\ \text{mol}\ N_2}\right) = 1.1\ \text{mol}\ NaN_3$$

Finally, using the molar mass of NaN_3, we convert moles of NaN_3 to grams:

$$(1.1\ \text{mol}\ NaN_3)\left(\frac{65.0\ \text{g}\ NaN_3}{1\ \text{mol}\ NaN_3}\right) = 72\ \text{g}\ NaN_3$$

Check The units cancel properly at each step in the calculation, leaving us with the correct units in the answer, g NaN_3.

Practice Exercise

In the first step of the industrial process for making nitric acid, ammonia reacts with oxygen in the presence of a suitable catalyst to form nitric oxide and water vapor:

$$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 6\ H_2O(g)$$

How many liters of $NH_3(g)$ at 850 °C and 506.6 kPa are required to react with 1.00 mol of $O_2(g)$ in this reaction?

Self-Assessment Exercises

10.12 The Goodyear blimps frequently fly over sporting events. One such blimp holds approximately 4955 m^3 helium. If the gas is at 23 °C and 101.33 kPa, what mass of helium is in a blimp?

(a) 816 g

(b) 2.63 kg

(c) 816 kg

(d) 2630 kg

10.13 Calculate the density of dinitrogen tetroxide gas (N_2O_4) at 111.5 kPa and 0 °C.

(a) 0.0491 g/L

(b) 4.52 g/L

(c) 472 g/L

10.14 Calculate the molar mass of a gas if 2.70 g occupies 0.97 L at 134.7 kPa and 100 °C.

(a) 8.27 g/mol

(b) 17.2 g/mol

(c) 64.1 g/mol

Exercises

10.15 Suppose you are given two flasks at the same temperature, one of volume 2 L and the other of volume 3 L. The 2 L flask contains 4.8 g of gas, and the gas pressure is x kPa. The 3 L flask contains 0.36 g of gas, and the gas pressure is $0.1x$. Do the two gases have the same molar mass? If not, which contains the gas of higher molar mass?

10.16 Calculate each of the following quantities for an ideal gas: (**a**) the volume of the gas, in liters, if 1.50 mol has a pressure of 126.7 kPa at a temperature of −6 °C; (**b**) the absolute temperature of the gas at which 3.33×10^{-3} mol occupies 478 mL at 99.99 kPa; (**c**) the pressure, in pascals, if 0.00245 mol occupies 413 mL at 138 °C; (**d**) the quantity of gas, in moles, if 126.5 L at 54 °C has a pressure of 11.25 kPa.

10.17 A neon sign is made of glass tubing whose inside diameter is 3.0 cm and length is 10.0 m. If the sign contains neon at a pressure of 265 Pa at 30 °C, how many grams of neon are in the sign? (The volume of a cylinder is $\pi r^2 h$.)

10.18 Many gases are shipped in high-pressure containers. Consider a steel tank whose volume is 210.0 L that contains O_2 gas at a pressure of 16,500 kPa at 23 °C. (**a**) What mass of O_2 does the tank contain? (**b**) What volume would the gas occupy at STP? (**c**) At what temperature would the pressure in the tank equal 15.2 MPa? (**d**) What would be the pressure of the gas, in kPa, if it were transferred to a container at 24 °C whose volume is 55.0 L?

10.19 The physical fitness of athletes is measured by "V_{O_2} max," which is the maximum volume of oxygen consumed by an individual during incremental exercise (for example, on a treadmill). An average male has a V_{O_2} max of 45 mL O_2/kg body mass/min, but a world-class male athlete can have a V_{O_2} max reading of 88.0 mL O_2/kg body mass/min. (**a**) Calculate the volume of oxygen, in mL, consumed in 1 hr by an average man who weighs 85 kg and has a V_{O_2} max reading of 47.5 mL O_2/kg body mass/min. (**b**) If this man lost 10 kg, exercised,

and increased his V_{O_2} max to 65.0 mL O_2/kg body mass/min, how many mL of oxygen would he consume in 1 hr?

10.20 Rank the following gases and vapors from least dense to most dense at 101.33 kPa and 298 K: water vapor ($H_2O(g)$), nitrogen (N_2), hydrogen sulfide (H_2S).

10.21 (**a**) Calculate the density of sulfur hexafluoride gas at 94.26 kPa and 21 °C. (**b**) Calculate the molar mass of a vapor that has a density of 7.135 g/L at 12 °C and 99.06 kPa.

10.22 Calcium hydride, CaH_2, reacts with water to form hydrogen gas:

$$CaH_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2\,H_2(g)$$

This reaction is sometimes used to inflate life rafts, weather balloons, and the like, when a simple, compact means of generating H_2 is desired. How many grams of CaH_2 are needed to generate 145 L of H_2 gas if the pressure of H_2 is 110 kPa at 21 °C?

10.23 Both Jacques Charles and Joseph Louis Guy-Lussac were avid balloonists. In his original flight in 1783, Jacques Charles used a balloon that contained approximately 31,150 L of H_2. Charles generated the H_2 using the reaction between iron and hydrochloric acid:

$$Fe(s) + 2\,HCl(aq) \longrightarrow FeCl_2(aq) + H_2(g)$$

How many kilograms of iron were needed to produce this volume of H_2 if the temperature was 22 °C?

Answers to Self-Assessment Exercises

10.12 (c) **10.13** (b) **10.14** (c)

10.5 Gas Mixtures and Partial Pressures



Humphry Davy coined the term 'laughing gas' for nitrous oxide (N_2O) after observing that inhaling the gas provided a sense of euphoria. Laughing gas parties became popular among the British wealthy around 1800, but the gas also had a serious use as an anesthetic. It is still commonly used in density, where it is administered as a 2:1 ratio with oxygen. Controlling the proportion of the two gases breathed in by the patient is important to ensure pain relief while allowing sufficient oxygen to be present to allow normal respiration.

Other uses of nitrous oxide include its use as a rocket fuel, as a booster to fuel use in racing cars, and as the propellent in aerosol food stuffs such as cooking oil and whipped cream. N_2O dissolves well in fat and can provide a foam of twice the volume attainable by using air while not having the undesirable effect of making the fats go rancid.

By the end of this section, you should be able to

- Understand and use partial pressures and mole fractions

Thus far we have considered mainly pure gases—those that consist of only one substance in the gaseous state. How do we deal with mixtures of two or more different gases? While studying the properties of air, John Dalton made an important observation:

The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone.

The pressure exerted by a particular component of a mixture of gases is called the **partial pressure** of that component. Dalton's observation is known as **Dalton's law of partial pressures**.

If we let P_t be the total pressure of a mixture of gases and P_1, P_2, P_3, and so forth be the partial pressures of the individual gases, we can write Dalton's law of partial pressures as

$$P_t = P_1 + P_2 + P_3 + \ldots \qquad [10.12]$$

This equation implies that each gas behaves independently of the others, as we can see by the following analysis. Let n_1, n_2, n_3, and so forth be the number of moles of each of the gases in the mixture and n_t be the total number of moles of gas. If each gas obeys the ideal gas equation, we can write

$$P_1 = n_1\left(\frac{RT}{V}\right); \quad P_2 = n_2\left(\frac{RT}{V}\right); \quad P_3 = n_3\left(\frac{RT}{V}\right); \quad \text{and so forth}$$

All of the gases in a container must occupy the same volume and will come to the same temperature in a relatively short period of time. Using these facts to simplify Equation 10.12, we obtain

$$P_t = (n_1 + n_2 + n_3 + \ldots)\left(\frac{RT}{V}\right) = n_t\left(\frac{RT}{V}\right) \qquad [10.13]$$

That is, at constant temperature and constant volume the total pressure of a gas sample is determined by the total number of moles of gas present, whether that total represents just one gas or a mixture of gases.

Sample Exercise 10.10

Applying Dalton's Law of Partial Pressures

A mixture of 6.00 g of $O_2(g)$ and 9.00 g of $CH_4(g)$ is placed in a 15.0 L vessel at 0 °C. What is the partial pressure of each gas, and what is the total pressure in the vessel?

SOLUTION

Analyze We need to calculate the pressure for two gases in the same volume and at the same temperature.

Plan Because each gas behaves independently, we can use the ideal gas equation to calculate the pressure each would exert if the other were not present. From Dalton's law, the total pressure is the sum of these two partial pressures.

Solve We first convert the mass of each gas to moles:

$$n_{O_2} = (6.00\ \text{g}\ \cancel{O_2})\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ \cancel{O_2}}\right) = 0.188\ \text{mol}\ O_2$$

$$n_{CH_4} = (9.00\ \text{g}\ \cancel{CH_4})\left(\frac{1\ \text{mol}\ CH_4}{16.0\ \text{g}\ \cancel{CH_4}}\right) = 0.563\ \text{mol}\ CH_4$$

We use the ideal gas equation to calculate the partial pressure of each gas:

$$P_{O_2} = \frac{n_{O_2}RT}{V} = \frac{(0.188\ \cancel{\text{mol}})(8.314\ \text{m}^3\ \text{Pa/mol K})(273\ \cancel{\text{K}})}{0.015\ \text{m}^3}$$

$$= 28.45\ \text{kPa}$$

$$P_{CH_4} = \frac{n_{CH_4}RT}{V} = \frac{(0.563\ \cancel{\text{mol}})(8.314\ \text{m}^3\ \text{Pa/mol K})(273\ \cancel{\text{K}})}{0.015\ \text{m}^3}$$

$$= 85.19\ \text{kPa}$$

According to Dalton's law of partial pressures (Equation 10.12), the total pressure in the vessel is the sum of the partial pressures:

$$P_t = P_{O_2} + P_{CH_4}$$

$$= 28.45\ \text{kPa} + 85.19\ \text{kPa} = 113.64\ \text{kPa}$$

Check A pressure of around 101.3 kPa seems right for a mixture of about 0.2 mol O_2 and a bit more than 0.5 mol CH_4, together in a 15-L volume, because 1 mol of an ideal gas at 1 atm pressure and 0 °C occupies about 22 L.

Practice Exercise

What is the total pressure exerted by a mixture of 2.00 g of $H_2(g)$ and 8.00 g of $N_2(g)$ at 273 K in a 10.0-L vessel?

Partial Pressures and Mole Fractions

Because each gas in a mixture behaves independently, we can relate the amount of a given gas in a mixture to its partial pressure. For an ideal gas, we can write

$$\frac{P_1}{P_t} = \frac{n_1 RT/V}{n_t RT/V} = \frac{n_1}{n_t} \qquad [10.14]$$

The ratio n_1/n_t is called the *mole fraction of gas 1*, which we denote X_1. The **mole fraction**, X, is a dimensionless number that expresses the ratio of the number of moles of one component in a mixture to the total number of moles in the mixture. Thus, for gas 1 we have

$$X_1 = \frac{\text{Moles of compound 1}}{\text{Total moles}} = \frac{n_1}{n_t} \qquad [10.15]$$

We can combine Equations 10.14 and 10.15 to give

$$P_1 = \left(\frac{n_1}{n_t}\right)P_t = X_1 P_t \qquad [10.16]$$

The mole fraction of N_2 in air is 0.78—that is, 78% of the molecules in air are N_2. This means that if the barometric pressure is 101.3 kPa, the partial pressure of N_2 is

$$P_{N_2} = (0.78)(101.3 \text{ kPa}) = 79.04 \text{ kPa}$$

This result makes intuitive sense: Because N_2 makes up 78% of the mixture, it contributes 78% of the total pressure.

Sample Exercise 10.11

Relating Mole Fractions and Partial Pressures

A study of the effects of certain gases on plant growth requires a synthetic atmosphere composed of 1.5 mol % CO_2, 18.0 mol % O_2 and 80.5 mol % Ar. (**a**) Calculate the partial pressure of O_2 in the mixture if the total pressure of the atmosphere is to be 99.33 kPa. (**b**) If this atmosphere is to be held in a 121 L space at 295 K, how many moles of O_2 are needed?

SOLUTION

Analyze For (**a**) we need to calculate the partial pressure of O_2 given its mole percent and the total pressure of the mixture. For (**b**) we need to calculate the number of moles of O_2 in the mixture given its volume (121 L), temperature (295 K), and partial pressure from part (a).

Plan We calculate the partial pressures using Equation 10.16, and then use P_{O_2}, V, and T in the ideal gas equation to calculate the number of moles of O_2.

Solve

(**a**) The mole percent is the mole fraction times 100. Therefore, the mole fraction of O_2 is 0.180. Equation 10.16 gives:

$$P_{O_2} = (0.180)(99.33 \text{ kPa}) = 17.88 \text{ kPa}$$

(**b**) Tabulating the given variables and converting to appropriate units, we have:

$$P_{O_2} = 17.88 \text{ kPa}$$
$$V = 121 \text{ L} = 0.121 \text{ m}^3$$
$$n_{O_2} = ?$$
$$R = 8.314 \text{ m}^3 \text{ Pa/mol K}$$
$$T = 295 \text{ K}$$

Solving the ideal gas equation for n_{O_2}, we have:

$$n_{O_2} = P_{O_2}\left(\frac{V}{RT}\right)$$
$$= 17.88 \text{ kPa} \frac{0.121 \text{ m}^3}{(8.314 \text{ m}^3 \text{ Pa/mol K})(295 \text{ K})} = 0.882 \text{ mol}$$

Check The units check out, and the answer seems to be the right order of magnitude.

Practice Exercise

A 4.0-L vessel containing N_2 at STP and a 2.0-L vessel containing H_2 at STP are connected by a valve. If the valve is opened allowing the two gases to mix, what is the mole fraction of hydrogen in the mixture? (**a**) 0.034 (**b**) 0.33 (**c**) 0.50 (**d**) 0.67 (**e**) 0.96

Self-Assessment Exercise

10.24 At an underwater depth of 100 m, the pressure is 1.11 MPa. What should the partial pressure of oxygen be in the diving gas for the mole fraction of oxygen in the mixture to be 0.21, the same as in air?

(a) $P_{O_2} = 210$ kPa
(b) $P_{O_2} = 233$ kPa
(c) $P_{O_2} = 5.29$ MPa

Exercises

10.25 Consider a mixture of two gases, A and B, confined in a closed vessel. A quantity of a third gas, C, is added to the same vessel at the same temperature. How does the addition of gas C affect the following: (**a**) the partial pressure of gas A, (**b**) the total pressure in the vessel, (**c**) the mole fraction of gas B?

10.26 A deep-sea diver uses a gas cylinder with a volume of 10.0 L and a content of 51.2 g of O_2 and 32.6 g of He. Calculate the partial pressure of each gas and the total pressure if the temperature of the gas is 19 °C.

10.27 The atmospheric concentration of CO_2 gas is presently 407 ppm (parts per million, by volume; that is, 407 L of every 10^6 L of the atmosphere are CO_2). What is the mole fraction of CO_2 in the atmosphere?

10.28 A sample of 5.00 mL of diethylether ($C_2H_5OC_2H_5$, density = 0.7134 g/mL) is introduced into a 6.00-L vessel that already contains a mixture of N_2 and O_2, whose partial pressures are $P_{N_2} = 21.08$ kPa and $P_{O_2} = 76.1$ kPa. The temperature is held at 35.0 °C, and the diethylether totally evaporates. (**a**) Calculate the partial pressure of the diethylether. (**b**) Calculate the total pressure in the container.

10.29 A rigid vessel containing a 3:1 mol ratio of carbon dioxide and water vapor is held at 200 °C where it has a total pressure of 202.7 kPa. If the vessel is cooled to 10 °C so that all of the water vapor condenses, what is the pressure of carbon dioxide? Neglect the volume of the liquid water that forms on cooling.

10.30 (**a**) What are the mole fractions of each component in a mixture of 15.08 g of O_2, 8.17 g of N_2, and 2.64 g of H_2? (**b**) What is the partial pressure in atm of each component of this mixture if it is held in a 15.50 L vessel at 15 °C?

Answers to Self-Assessment Exercises

10.24 (b)

10.6 The Kinetic-Molecular Theory of Gases



The Roman philosopher Lucretius wrote:

Observe what happens when sunbeams are admitted into a building and shed light on its shadowy places. You will see a multitude of tiny particles...dancing.

In 1827, some 1900 years later, the Scottish botanist Robert Brown observed the movement of microscopic particles while studying pollen grains suspended in water. At first, he thought the movement was due to some living motion but showed it also occurred with inanimate particles such as those found in smoke. It became known as Brownian motion. Both Lucretius and Brown concluded the random motion was due to the particles being constantly bombarded by even smaller bodies—atoms and molecules. Einstein, in a 1905 publication, presented the mathematics behind the observed random movement and used it as indirect evidence of the existence of atoms and molecules.

By the end of this section, you should be able to

- Use the kinetic-molecular theory of gases to explain the gas laws and rates of effusion and diffusion

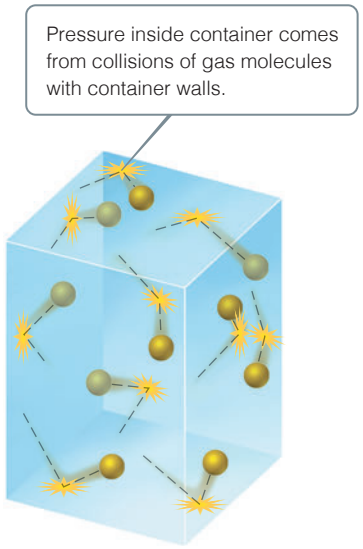
The ideal gas equation describes *how* gases behave but not *why* they behave as they do. Why does a gas expand when heated at constant pressure? Or why does its pressure increase when the gas is compressed at constant temperature? To understand the physical properties of gases, we need a model that helps us picture what happens to gas particles when conditions such as pressure or temperature change. Such a model, known as the **kinetic-molecular theory of gases**, was developed over a period of about 100 years, culminating in 1857 when Rudolf Clausius (1822–1888) published a complete and satisfactory form of the theory.

The kinetic-molecular theory (the theory of moving molecules) is summarized by the following statements:

1. **Random motion** Gases consist of large numbers of molecules that are in continuous, random motion. (The word *molecule* is used here to designate the smallest particle of any gas even though some gases, such as the noble gases, consist of individual atoms. All we learn about gas behavior from the kinetic-molecular theory applies equally to atomic gases.)
2. **Negligible molecular volume** The combined volume of all the molecules of the gas is negligible relative to the total volume in which the gas is contained.
3. **Negligible forces** Attractive and repulsive forces between gas molecules are negligible.
4. **Constant average kinetic energy** Energy can be transferred between molecules during collisions but, as long as temperature remains constant, the *average* kinetic energy of the molecules does not change with time.
5. **Average kinetic energy proportional to temperature** The average kinetic energy of the molecules is proportional to the absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy.

The kinetic-molecular theory explains both pressure and temperature at the molecular level. The pressure of a gas is caused by collisions of the molecules with the walls of the container (Figure 10.12). The magnitude of the pressure is determined by how often and how forcefully the molecules strike the walls.

The absolute temperature of a gas is a measure of the *average* kinetic energy of its molecules. If two gases are at the same temperature, their molecules have the same average kinetic energy (statement 5 of the kinetic-molecular theory). If the absolute temperature of a gas is doubled, the average kinetic energy of its molecules doubles. Thus, molecular motion increases with increasing temperature.

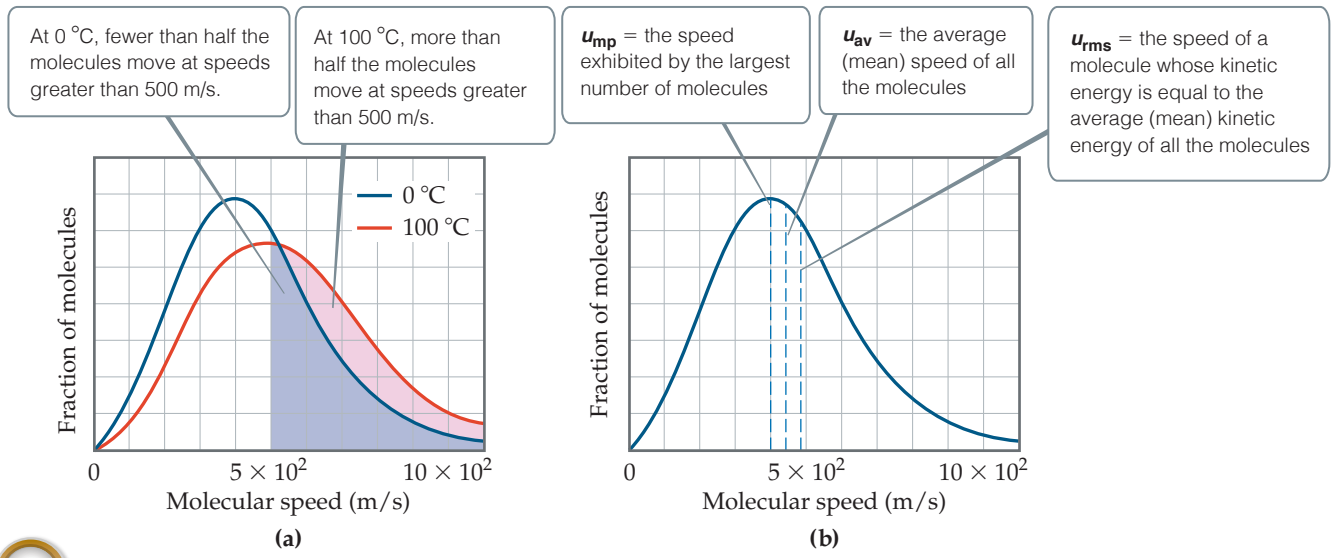


▲ **Figure 10.12 The molecular origin of gas pressure.**

Distributions of Molecular Speed

Although collectively the molecules in a sample of gas have an *average* kinetic energy and hence an average speed, the individual molecules are moving at different speeds. Each molecule collides frequently with other molecules. Momentum is conserved in each collision, but one of the colliding molecules might be deflected off at high speed while the other is nearly stopped. The result is that, at any instant, the molecules in the sample have a wide range of speeds. In Figure 10.13(a), which shows the distribution of

Go Figure Estimate the fraction of molecules at 100 °C with speeds less than 300 m/s.



▲ **Figure 10.13 Distribution of molecular speeds for nitrogen gas.** (**a**) The effect of temperature on molecular speed. The relative area under the curve for a range of speeds gives the relative fraction of molecules that have those speeds. (**b**) Position of most probable (u_{mp}), average (u_{av}), and root-mean-square (u_{rms}) speeds of gas molecules. The data shown here are for nitrogen gas at 0 °C.

molecular speeds for nitrogen gas at 0 °C and 100 °C, we see that a larger fraction of the 100 °C molecules moves at the higher speeds. This means that the 100 °C sample has the higher average kinetic energy.

In any graph of the distribution of molecular speeds in a gas sample, the peak of the curve represents the most probable speed, u_{mp} [Figure 10.13(b)]. The most probable speeds in Figure 10.13(a), for instance, are 4×10^2 m/s for the 0 °C sample and 5×10^2 m/s for the 100 °C sample. Figure 10.13(b) also shows the **root-mean-square (rms) speed**, u_{rms}, of the molecules. This is the speed of a molecule possessing a kinetic energy identical to the average kinetic energy of the sample. The rms speed is not quite the same as the average (mean) speed, u_{av}. The difference between the two is small, however. In Figure 10.13(b), for example, the root-mean-square speed is about 4.9×10^2 m/s and the average speed is about 4.5×10^2 m/s.

If you calculate the rms speeds (as we will in Section 10.7), you will find that the rms speed is almost 6×10^2 m/s for the 100 °C sample but slightly less than 5×10^2 m/s for the 0 °C sample. Notice that the distribution curve broadens as we go to a higher temperature, which tells us that the range of molecular speeds increases with temperature.

The rms speed is important because the average kinetic energy of the gas molecules in a sample is equal to $\frac{1}{2} m(u_{rms})^2$. Because mass does not change with temperature, the increase in the average kinetic energy $\frac{1}{2} m(u_{rms})^2$ as the temperature increases implies that the rms speed of the molecules (as well as u_{av} and u_{mp}) increases as temperature increases.

Application of Kinetic-Molecular Theory to the Gas Laws

The empirical observations of gas properties as expressed by the various gas laws are readily understood in terms of the kinetic-molecular theory. The following examples illustrate this point:

1. **An increase in volume at constant temperature causes pressure to decrease.** A constant temperature means that the average kinetic energy of the gas molecules remains unchanged. This means that the rms speed of the molecules remains unchanged. When the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time

with the container walls, which means the pressure decreases. Thus, kinetic-molecular theory explains Boyle's law.

2. **A temperature increase at constant volume causes pressure to increase.** An increase in temperature means an increase in the average kinetic energy of the molecules and in u_{rms}. Because there is no change in volume, the temperature increase causes more collisions with the walls per unit time because the molecules are all moving faster. Furthermore, the momentum in each collision increases (the molecules strike the walls more forcefully). A greater number of more forceful collisions means the pressure increases, and the theory explains this increase.

A CLOSER LOOK The Ideal Gas Equation

The ideal gas equation can be derived from the five statements given in the text for the kinetic-molecular theory. Rather than perform the derivation, however, let's consider in qualitative terms how the ideal gas equation might follow from these statements. The total force of the molecular collisions on the walls and hence the pressure (force per unit area, Section 10.2) produced by these collisions depend both on how strongly the molecules strike the walls (impulse imparted per collision) and on the rate at which the collisions occur:

$$P \propto \text{impulse imparted per collision} \times \text{collision rate}$$

For a molecule traveling at the rms speed, the impulse imparted by a collision with a wall depends on the momentum of the molecule; that is, it depends on the product of the molecule's mass and speed: mu_{rms}. The collision rate is proportional to the number of molecules per unit volume, n/V, and to their speed, which is u_{rms} because we are talking about only molecules traveling at this speed. Thus, we have

$$P \propto mu_{rms} \times \frac{n}{V} \times u_{rms} \propto \frac{nm(u_{rms})^2}{V} \qquad [10.17]$$

Because the average kinetic energy, $\frac{1}{2}m(u_{rms})^2$, is proportional to temperature, we have $m(u_{rms})^2 \propto T$. Making this substitution in Equation 10.17 gives

$$P \propto \frac{nm(u_{rms})^2}{V} \propto \frac{nT}{V} \qquad [10.18]$$

If we put in a proportionality constant, calling it R, the gas constant, you can see that we obtain the ideal gas equation:

$$P = \frac{nRT}{V} \qquad [10.19]$$

Related Exercises: 10.32, 10.91

Sample Exercise 10.12

Applying the Kinetic-Molecular Theory

A sample of O_2 gas initially at STP is compressed to a smaller volume at constant temperature. What effect does this change have on (**a**) the average kinetic energy of the molecules, (**b**) their average speed, (**c**) the number of collisions they make with the container walls per unit time, (**d**) the number of collisions they make with a unit area of container wall per unit time, (**e**) the pressure?

SOLUTION

Analyze We need to apply the concepts of the kinetic-molecular theory of gases to a gas compressed at constant temperature.

Plan We will determine how each of the quantities in (a)–(e) is affected by the change in volume at constant temperature.

Solve (**a**) Because the average kinetic energy of the O_2 molecules is determined only by temperature, this energy is unchanged by the compression. (**b**) Because the average kinetic energy of the molecules does not change, their average speed remains constant. (**c**) The number of collisions with the walls per unit time increases because the molecules are moving in a smaller volume but with the same average speed as before. Under these conditions they will strike the walls of the container more frequently. (**d**) The number of collisions with a unit area of wall per unit time increases because the total number of collisions with the walls per unit time increases and the area of the walls decreases. (**e**) Although the average force with which the molecules collide with the walls remains constant, the pressure increases because there are more collisions per unit area of wall per unit time.

Check In a conceptual exercise of this kind, there is no numerical answer to check. All we can check in such cases is our reasoning in the course of solving the problem. The increase in pressure seen in part (**e**) is consistent with Boyle's law.

Practice Exercise

Consider two gas cylinders of the same volume and temperature, one containing 1.0 mol of propane, C_3H_8, and the other 2.0 mol of methane, CH_4. Which of the following statements is true? (**a**) The C_3H_8 and CH_4 molecules have the same u_{rms} (**b**) The C_3H_8 and CH_4 molecules have the same average kinetic energy (**c**) The rate at which the molecules collide with the cylinder walls is the same for both cylinders (**d**) The gas pressure is the same in both cylinders

Self-Assessment Exercise

10.31 Consider three gases, all at 298 K: Kr, N_2, and NH_3. List the gases in order of increasing average speed of the molecules (or atoms).

(a) $Kr < N_2 < NH_3$
(b) $Kr < NH_3 < N_2$
(c) $NH_3 < N_2 < Kr$
(d) $N_2 < NH_3 < Kr$

Exercises

10.32 Indicate which of the following statements regarding the kinetic-molecular theory of gases are correct. (**a**) The average kinetic energy of a collection of gas molecules at a given temperature is proportional to $m^{1/2}$. (**b**) The gas molecules are assumed to exert no forces on each other. (**c**) All the molecules of a gas at a given temperature have the same kinetic energy. (**d**) The volume of the gas molecules is negligible in comparison to the total volume in which the gas is contained. (**e**) All gas molecules move with the same speed if they are at the same temperature.

10.33 Radon (Rn) is the heaviest (and only radioactive) member of the noble gases. How much slower is the root-mean-square speed of Rn than He at 300 K?

10.34 (**a**) Place the following gases in order of increasing average molecular speed at 300 K: CO, SF_6, H_2S, Cl_2, HBr. (**b**) Calculate the rms speeds of CO and Cl_2 molecules at 300 K. (**c**) Calculate the most probable speeds of CO and Cl_2 molecules at 300 K.

Answers to Self-Assessment Exercises

10.31 (a)

10.7 | Molecular Effusion and Diffusion



Natural gas is a convenient, efficient fuel source and is transported by pipes, pressurized tankers and in gas bottles. It is colorless and odorless, making the detection of leaks difficult. This is problematic as a buildup of gas in an enclosed space might go undetected and result in an explosion. To guard against this, an additive, usually ethanethiol (CH_3CH_2SH), which has an unpleasant smell that can alert people to the possibility of a leak, is used. This compound has the advantages that very small amounts are detected by the human nose (of the order of a few parts per billion), the compound has long term

stability when added to a gas supply and does not interfere with the combustion of the gas. It is sometimes referred to as 'stench gas' and in some countries is used to release into the ventilation system of underground mines to alert the miners in the case of an emergency.

By the end of this section, you should be able to

- Distinguish between effusion and diffusion and relate them to the molar mass of the gas.

According to the kinetic-molecular theory of gases, the average kinetic energy of *any* collection of gas molecules, $\frac{1}{2}m(u_{rms})^2$, has a specific value at a given temperature. Thus, for two gases at the same temperature a gas composed of low-mass particles, such as He, has the same average kinetic energy as one composed of more massive particles, such as Xe. The mass of the particles in the He sample is smaller than that in the Xe sample. Consequently, the He particles must have a higher rms speed than the Xe particles. The equation that expresses this fact quantitatively is

$$u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}} \qquad [10.20]$$

where $\mathcal{M}$ is the molar mass of the particles, which can be derived from the kinetic-molecular theory. Because $\mathcal{M}$ appears in the denominator, the less massive the gas particles, the higher their rms speed.

Figure 10.14 shows the distribution of molecular speeds for several gases at 25 °C. Notice how the distributions are shifted toward higher speeds for gases of lower molar masses.

The most probable speed of a gas molecule can also be derived:

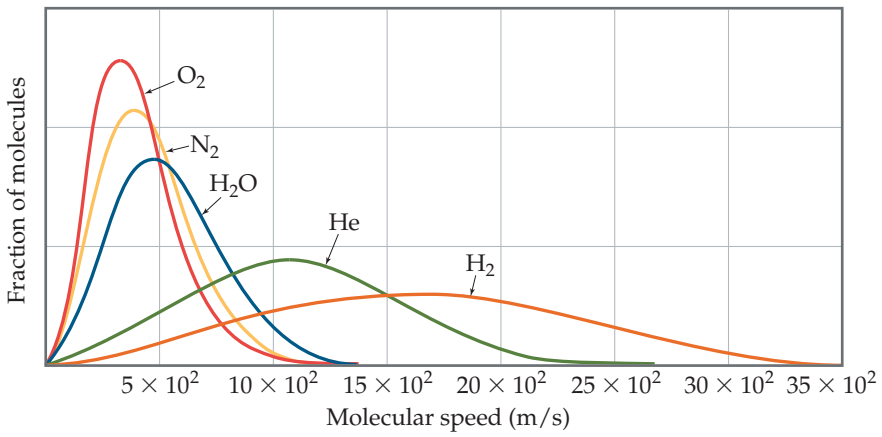
$$u_{mp} = \sqrt{\frac{2RT}{\mathcal{M}}} \qquad [10.21]$$

The dependence of molecular speed on mass has two interesting consequences. The first is **effusion**, which is the escape of gas molecules through a tiny hole (**Figure 10.15**). The second is **diffusion**, which is the spread of one substance throughout a space or throughout a second substance. For example, the molecules of a perfume diffuse throughout a room.

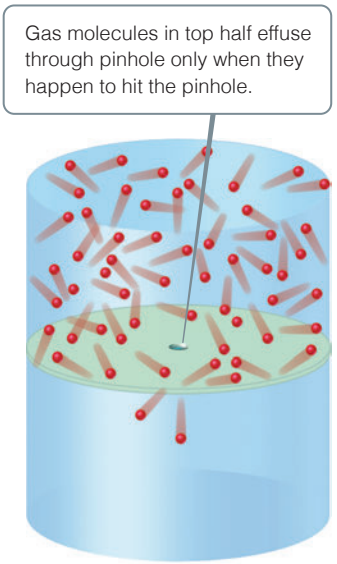
Graham's Law of Effusion

In 1846, Thomas Graham (1805–1869) discovered that the effusion rate of a gas is inversely proportional to the square root of its molar mass. Assume we have two gases at the same temperature and pressure in two containers with identical pinholes. If the rates

Go Figure Which of these gases has the largest molar mass? Which has the smallest?



▲ **Figure 10.14** The effect of molar mass on molecular speed at 25 °C.



▲ **Figure 10.15** Effusion.

Sample Exercise 10.13

Calculating a Root-Mean-Square Speed

Calculate the rms speed of the molecules in a sample of N_2 gas at 25 °C.

SOLUTION

Analyze We are given the identity of a gas and the temperature, the two quantities we need to calculate the rms speed.

Plan We calculate the rms speed using Equation 10.20.

Solve We must convert each quantity in our equation to SI units. We will also use R in units of J/mol K (Table 10.2) to make the units cancel correctly.

$$T = 25 + 273 = 298\ \text{K}$$

$$\mathcal{M} = 28.0\ \text{g/mol} = 28.0 \times 10^{-3}\ \text{kg/mol}$$

$$R = 8.314\ \text{J/mol K} = 8.314\ \text{kg m}^2/\text{s}^2\ \text{mol K}\ (\text{Since } 1\ \text{J} = 1\ \text{kg m}^2/\text{s}^2)$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

$$= \sqrt{\frac{3(8.314\ \text{kg m}^2/\text{s}^2\ \text{mol K})(298\ \text{K})}{28.0 \times 10^{-3}\ \text{kg/mol}}} = 5.15 \times 10^2\ \text{m/s}$$

Comment This corresponds to a speed of 1854 km/hr. Because the average molecular weight of air molecules is slightly greater than that of N_2, the rms speed of air molecules is a little smaller than that for N_2.

Practice Exercise

Fill in the blanks for the following statement: The rms speed of the molecules in a sample of H_2 gas at 300 K will be _____ times larger than the rms speed of O_2 molecules at the same temperature, and the ratio $u_{\text{rms}}(H_2)/u_{\text{rms}}(O_2)$ _____ with increasing temperature.
(**a**) four, will not change (**b**) four, will increase (**c**) sixteen, will not change (**d**) sixteen, will decrease (**e**) Not enough information is given to answer this question.

of effusion of the two gases are r_1 and r_2 and their molar masses are $\mathcal{M}_1$ and $\mathcal{M}_2$, **Graham's law** states that

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \qquad [10.22]$$

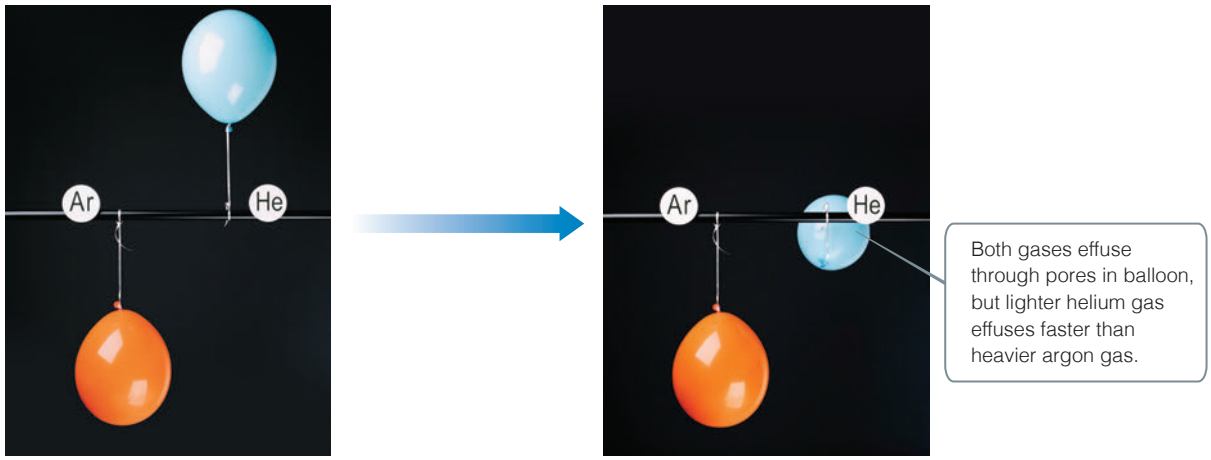
a relationship that indicates that the lighter gas has the higher effusion rate.

The only way for a molecule to escape from its container is for it to "hit" the hole in the partitioning wall of Figure 10.15. The faster the molecules are moving, the more often they hit the partition wall and the greater the likelihood that a molecule will hit the hole and effuse. This implies that the rate of effusion is directly proportional to the rms speed of the molecules. Because R and T are constant, we have, from Equation 10.22

$$\frac{r_1}{r_2} = \frac{u_{\text{rms1}}}{u_{\text{rms2}}} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}} \qquad [10.23]$$

As expected from Graham's law, helium escapes from containers through tiny pinhole leaks more rapidly than other gases of higher molecular weight (**Figure 10.16**).

Go Figure Because pressure and temperature are constant in this figure but volume changes, which other quantity in the ideal gas equation must also change?



▲ **Figure 10.16** An illustration of Graham's law of effusion.

Sample Exercise 10.14

Applying Graham's Law

An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is 0.355 times the rate at which O_2 gas effuses at the same temperature. Calculate the molar mass of the unknown and identify it.

SOLUTION

Analyze We are given the rate of effusion of an unknown gas relative to that of O_2 and asked to find the molar mass and identity of the unknown. Thus, we need to connect relative rates of effusion to relative molar masses.

Plan We use Equation 10.22 to determine the molar mass of the unknown gas. If we let r_x and $\mathcal{M}_x$ represent the rate of effusion and molar mass of the gas, we can write

$$\frac{r_x}{r_{O_2}} = \sqrt{\frac{\mathcal{M}_{O_2}}{\mathcal{M}_x}}$$

Solve From the information given,

$$r_x = 0.355 \times r_{O_2}$$

Thus,

$$\frac{r_x}{r_{O_2}} = 0.355 = \sqrt{\frac{32.0\ \text{g/mol}}{\mathcal{M}_x}}$$

$$\frac{32.0\ \text{g/mol}}{\mathcal{M}_x} = (0.355)^2 = 0.126$$

$$\mathcal{M}_x = \frac{32.0\ \text{g/mol}}{0.126} = 254\ \text{g/mol}$$

Because we are told that the unknown gas is composed of homonuclear diatomic molecules, it must be an element. The molar mass must represent twice the atomic weight of the atoms in the unknown gas. We conclude that the unknown gas must have an atomic weight of 127 g/mol and therefore is I_2.

▶ Calculate the ratio of the effusion rates of N_2 gas and O_2 gas.

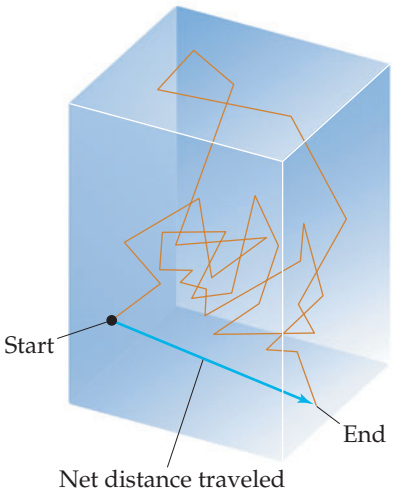
Diffusion and Mean Free Path

Although diffusion, like effusion, is faster for lower-mass molecules than for higher-mass ones, molecular collisions make diffusion more complicated than effusion.

Graham's law, Equation 10.22, approximates the ratio of the diffusion rates of two gases under identical conditions. We can see from the horizontal axis in Figure 10.15 that the speeds of molecules are quite high. For example, the rms speed of molecules of N_2 gas at room temperature is 515 m/s. In spite of this high speed, if someone opens a vial of perfume at one end of a room, some time elapses—perhaps a few minutes—before the scent is detected at the other end of the room. This tells us that the diffusion rate of gases throughout a volume of space is much slower than molecular speeds.* This difference is due to molecular collisions, which occur frequently for a gas at atmospheric pressure—about 10^{10} times per second for each molecule. Collisions occur because real gas molecules have finite volumes.

Because of molecular collisions, the direction of motion of a gas molecule is constantly changing. Therefore, the diffusion of a molecule from one point to another consists of many short, straight-line segments as collisions buffet it around in random directions (Figure 10.17).

The average distance traveled by a molecule between collisions, called the molecule's **mean free path**, varies with pressure as the following analogy illustrates. Imagine



▲ **Figure 10.17 Diffusion of a gas molecule.** For clarity, no other gas molecules in the container are shown.

*The rate at which the perfume moves across the room also depends on how well stirred the air is from temperature gradients and the movement of people. Nevertheless, even with the aid of these factors, it still takes much longer for the molecules to traverse the room than one would expect from their rms speed.

CHEMISTRY PUT TO WORK Gas Separations

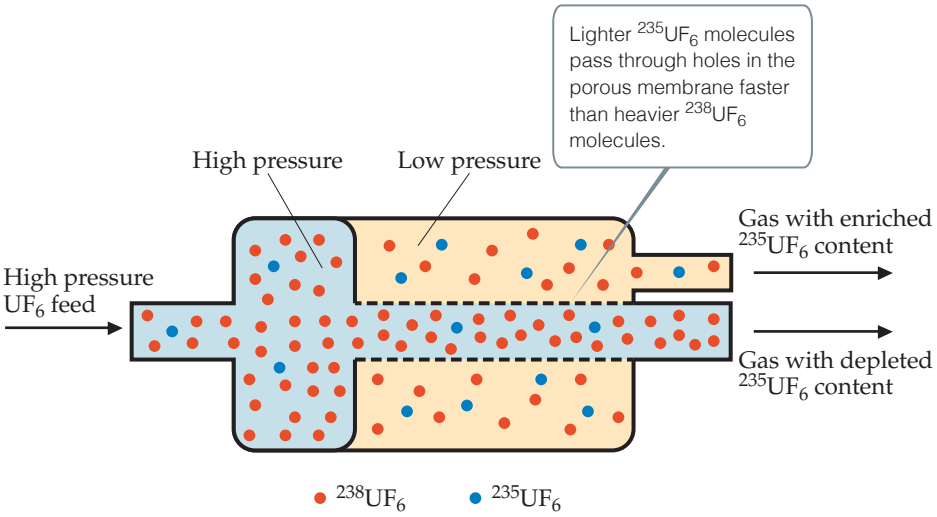
The fact that lighter molecules move at higher average speeds than more massive ones has many interesting applications. For example, developing the atomic bomb during World War II required scientists to separate the relatively low-abundance uranium isotope ^{235}U (0.7%) from the much more abundant ^{238}U (99.3%). This separation was accomplished by converting the uranium into a volatile compound, UF_6, that was then allowed to pass through a porous barrier (**Figure 10.18**). Because of the pore diameters, this process is not simple effusion. Nevertheless, the way in which rate of passing through the pores depends on molar mass is essentially the same as that in effusion. The slight difference in molar mass between $^{235}UF_6$ and $^{238}UF_6$ caused the molecules to move at slightly different rates:

$$\frac{r_{235}}{r_{238}} = \sqrt{\frac{352.04}{349.03}} = 1.0043$$

Thus, the gas initially appearing on the opposite side of the barrier is very slightly enriched in ^{235}U. The process is repeated thousands of times, leading to a nearly complete separation of the two isotopes. Because of the large number of steps needed to adequately separate the isotopes, gaseous diffusion facilities are large-scale structures.

An increasingly popular method of separating uranium isotopes is by a technique that uses centrifuges. In this procedure, cylindrical rotors containing UF_6 vapor spin at high speed inside an evacuated casing. Molecules of $^{238}UF_6$ move closer to the spinning walls, whereas molecules of $^{235}UF_6$ remain in the middle of the cylinders. A stream of gas moves the $^{235}UF_6$ from the center of one centrifuge into another. Plants that use centrifuges consume less energy than those that use effusion and can be constructed in a more compact, modular fashion.

Related Exercises: 10.37, 10.97



▲ **Figure 10.18 Uranium enrichment by gaseous diffusion.** The lighter $^{235}UF_6$ effuses through a porous barrier at a slightly faster rate than $^{238}UF_6$. The pressure difference across the membrane drives the effusion. The enrichment shown here for a single step is exaggerated for illustrative purposes.

walking through a shopping mall. When the mall is crowded (high pressure), the average distance you can walk before bumping into someone is short (short mean free path). When the mall is empty (low pressure), you can walk a long way (long mean free path) before bumping into someone. The mean free path for air molecules at sea level is about 60 nm. At about 100 km in altitude, where the air pressure is much lower, the mean free path is about 10 cm, over 1 million times longer than at the Earth's surface.

Self-Assessment Exercise

10.35 One of worst smelling compounds known is thioacetone (C_3H_6S). If a sample of thioacetone and ethanethiol (C_2H_6S) were released into a laboratory, which compound would travel farther in one minute?

(a) C_2H_6S
(b) C_3H_6S

Exercises

10.36 Which one or more of the following statements are true?

(**a**) O_2 will effuse faster than Cl_2.
(**b**) Effusion and diffusion are different names for the same process.
(**c**) Perfume molecules travel to your nose by the process of effusion.
(**d**) The higher the density of a gas, the shorter the mean free path.

10.37 As discussed in the "Chemistry Put to Work" box in Section 10.7, enriched uranium can be produced by effusion of gaseous UF_6 across a porous membrane. Suppose a process were developed to allow effusion of gaseous uranium atoms, U(*g*). Calculate the ratio of effusion rates for ^{235}U and ^{238}U, and compare it to the ratio for UF_6 given in the essay.

10.38 A gas of unknown molecular mass was allowed to effuse through a small opening under constant-pressure conditions. It required 105 s for 1.0 L of the gas to effuse. Under identical experimental conditions it required 31 s for 1.0 L of O_2 gas to effuse. Calculate the molar mass of the unknown gas. (Remember that the faster the rate of effusion, the shorter the time required for effusion of 1.0 L; in other words, rate is the amount that diffuses over the time it takes to diffuse.)

Answers to Self-Assessment Exercises

10.35 (a)

10.8 Real Gases: Deviations from Ideal Behavior



Many people are unaware of the vast network of underground pipelines that undergirds the developed world and that is used to move vast quantities of liquids and gases over considerable distances. The pipeline system consists of large diameter (120 cm) trunk lines at high pressure, with branch lines of small diameter (35 cm) at lower pressure for local transport to and from the trunk lines. Methane-rich natural gas is processed to remove particulates, water, and various gas impurities, such as hydrogen sulfide and carbon dioxide. The gas is then compressed to pressure of between 3.5 MPa and 10 MPa depending on the diameter of the pipe. The pressure is maintained by compressor stations along the pipeline at roughly 100 km intervals. The high pressures mean that chemical engineers can no longer rely on the ideal gas equation but employ more accurate equations to describe the behavior of the gas.

By the end of this section, you should be able to

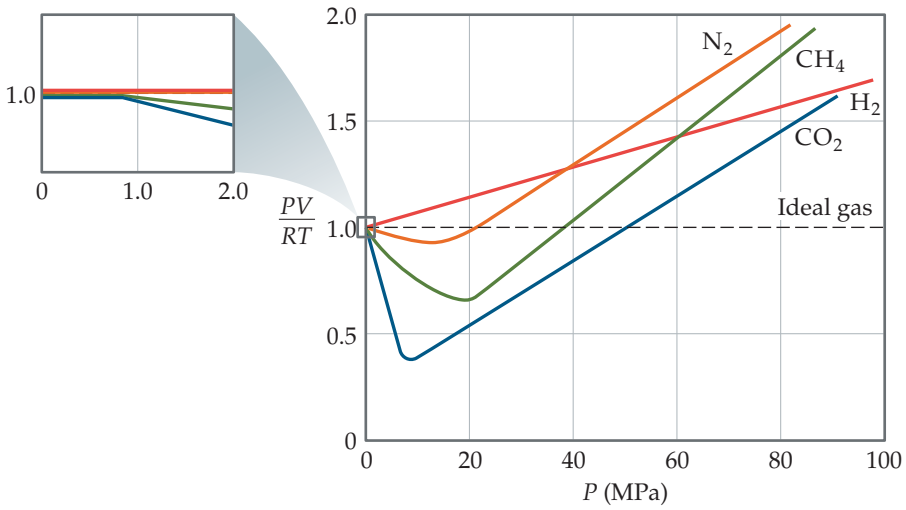
- Describe why a real gas does not conform to the ideal gas equation

The extent to which a real gas departs from ideal behavior can be seen by rearranging the ideal gas equation to solve for n:

$$\frac{PV}{RT} = n \qquad [10.24]$$

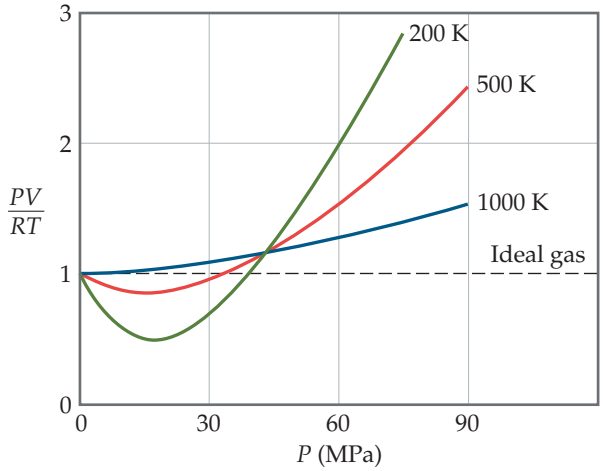
This form of the equation tells us that for 1 mol of ideal gas, the quantity PV/RT equals 1 at all pressures. In **Figure 10.19**, PV/RT is plotted as a function of P for 1 mol of several real gases. At high pressures (generally above 1.013 MPa), the deviation from ideal behavior ($PV/RT = 1$) is large and different for each gas. *Real gases, in other words, do not behave ideally at high pressure.* At lower pressures (usually below 1.013 MPa), however, the deviation from ideal behavior is small, and we can use the ideal gas equation without generating serious error.

Deviation from ideal behavior also depends on temperature. As temperature increases, the behavior of a real gas more nearly approaches that of the ideal gas (**Figure 10.20**). In general, *the deviation from ideal behavior increases as temperature decreases*, becoming significant near the temperature at which the gas liquefies.



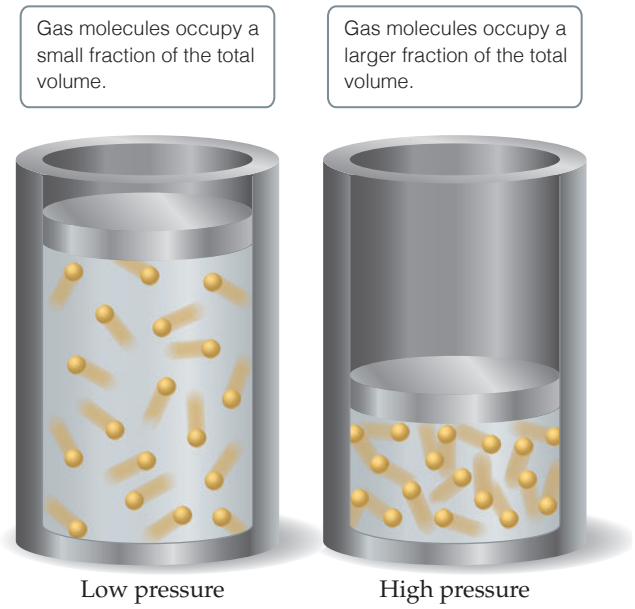
▶ **Figure 10.19 The effect of pressure on the behavior of several real gases.** Data for 1 mol of gas in all cases. Data for N_2, CH_4, and H_2 are at 300 K; for CO_2 data are at 313 K because under high pressure CO_2 liquefies at 300 K.

Go Figure True or false: Nitrogen gas behaves more like an ideal gas as the temperature increases.



▲ **Figure 10.20 The effect of temperature and pressure on the behavior of nitrogen gas.**

The basic assumptions of the kinetic-molecular theory of gases give us insight into why real gases deviate from ideal behavior. The molecules of an ideal gas are assumed to occupy no space and have no attraction for one another. *Real molecules, however, do have finite volumes and do attract one another.* As **Figure 10.21** shows, the unoccupied space in which real molecules can move is less than the container volume. At low pressures, the combined volume of the gas molecules is negligible relative to the container volume. Thus, the unoccupied volume available to the molecules is essentially the container volume. At high pressures, the combined volume of the gas molecules is *not* negligible relative to the container volume. Now the unoccupied volume available to the molecules is less than the container volume. At high pressures, therefore, gas volumes tend to be slightly greater than those predicted by the ideal gas equation.

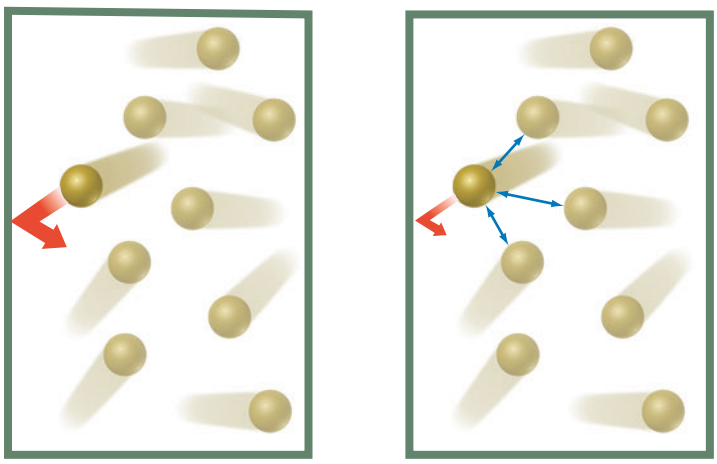


▲ **Figure 10.21** **Gases behave more ideally at low pressure than at high pressure.**

Another reason for nonideal behavior at high pressures is that the attractive forces between molecules come into play at the short intermolecular distances found when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the container wall is lessened. If we could stop the motion in a gas, as illustrated in **Figure 10.22**, we would see that a molecule about to collide with the wall experiences the attractive forces of nearby molecules. These attractions lessen the force with which the molecule hits the wall. As a result, the gas pressure is less than that of an ideal gas. This effect decreases PV/RT to below its ideal value, as seen at the lower pressures in Figures 10.20 and 10.21. When the pressure is sufficiently high, however, the volume effects dominate and PV/RT increases to above the ideal value.

Temperature determines how effective attractive forces between gas molecules are in causing deviations from ideal behavior at lower pressures. Figure 10.21 shows that, at pressures below about 40 MPa, cooling increases the extent to which a gas deviates from ideal behavior. As the gas cools, the average kinetic energy of the molecules decreases. This drop in kinetic energy means the molecules do not have the energy needed to overcome intermolecular attraction, and the molecules will be more likely to stick to each other than bounce off each other.

Go Figure How would you expect the pressure of a gas to change if suddenly the intermolecular forces were repulsive rather than attractive?



▲ **Figure 10.22** **In any real gas, attractive intermolecular forces reduce pressure to values lower than in an ideal gas.**

As the temperature of a gas increases—as, say, from 200 to 1000 K in Figure 10.21—the negative deviation of PV/RT from the ideal value of 1 disappears. As noted earlier, the deviations seen at high temperatures stem mainly from the effect of the finite volumes of the molecules.

The van der Waals Equation

Engineers and scientists who work with gases at high pressures often cannot use the ideal gas equation because departures from ideal behavior are too large. One useful equation developed to predict the behavior of real gases was proposed by the Dutch scientist Johannes van der Waals (1837–1923).

As we have seen, a real gas has a lower pressure due to intermolecular forces, and a larger volume due to the finite volume of the molecules, relative to an ideal gas. Van der Waals recognized that it would be possible to retain the form of the ideal gas equation, $PV = nRT$, if corrections were made to the pressure and the volume. He introduced two constants for these corrections: a, a measure of how strongly the gas molecules attract one another, and b, a measure of the finite volume occupied by the molecules. His description of gas behavior is known as the **van der Waals equation**:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \qquad [10.25]$$

The term n^2a/V^2 accounts for the attractive forces. The equation adjusts the pressure upward by adding n^2a/V^2 because attractive forces between molecules tend to reduce the pressure (Figure 10.22). The added term has the form n^2a/V^2 because the attractive force between pairs of molecules increases as the square of the number of molecules per unit volume, $(n/V)^2$.

The term nb accounts for the small but finite volume occupied by the gas molecules (Figure 10.22). The van der Waals equation subtracts nb to adjust the volume downward to give the volume that would be available to the molecules in the ideal case. The constants a and b, called *van der Waals constants*, are experimentally determined positive quantities that differ from one gas to another. Notice in **Table 10.3** that a and b generally increase with increasing molecular mass. Larger, more massive molecules have larger volumes and tend to have greater intermolecular attractive forces.

TABLE 10.3 Van der Waals Constants for Gas Molecules

Substance	a (L^2 kPa/mol^2)	b (L/mol)
He	3.46	0.02370
Ne	21.4	0.0171
Ar	135	0.0322
Kr	235	0.0398
Xe	425	0.0510
H_2	24.7	0.0266
N_2	141	0.0391
O_2	138	0.0318
F_2	107	0.0290
Cl_2	658	0.0562
H_2O	553	0.0305
NH_3	423	0.0371
CH_4	228	0.0428
CO_2	364	0.0427
CCl_4	2067	0.1383

Sample Exercise 10.15

Using the van der Waals Equation

If 10.00 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.013 MPa. Use the van der Waals equation and Table 10.3 to estimate the pressure exerted by 10.00 mol of $Cl_2(g)$ in 22.41 L at 0.0 °C.

SOLUTION

Analyze We need to determine a pressure. Because we will use the van der Waals equation, we must identify the appropriate values for the constants in the equation.

Plan Rearrange Equation 10.25 to isolate P.

Solve Substituting $n = 10.00$ mol, $R = 8.314\ m^3\,Pa/mol\,K$ $T = 273.2$ K, $V = 22.41\ L = 2.241 \times 10^{-2}\ m^3$, $a = 658\ L^2\,kPa/mol^2$, and $b = 0.0562$ L/mol:

$$P = \frac{(10.00\ \text{mol})(8.314\ m^3\,Pa/mol\,K)(273.2\ K)}{2.241 \times 10^{-2}\ m^3 - (10.00\ \text{mol})(5.62 \times 10^{-5}\ m^3/mol)} - \frac{(10.00\ \text{mol})^2(658\ L^2\,kPa/mol^2)}{(22.41\ L)^2}$$

$$= 1039.6\ kPa - 130.7\ kPa = 908.9\ kPa$$

Comment Notice that the term 1039.6 kPa is the pressure corrected for molecular volume. This value is higher than the ideal value, 1.013 MPa, because the volume in which the molecules are free to move is smaller than the container volume, 22.41 L. Thus, the molecules collide more frequently with the container walls and the pressure is higher than that of a real gas. The term 130.7 kPa makes a correction in the opposite direction for intermolecular forces. The correction for intermolecular forces is the larger of the two, and thus the pressure 908.9 kPa is smaller than would be observed for an ideal gas.

Practice Exercise

A sample of 1.000 mol of $CO_2\,(g)$ is confined to a 3.000-L container at 0.000 °C. Calculate the pressure of the gas using (**a**) the ideal gas equation and (**b**) the van der Waals equation.

Sample Integrative Exercise

Putting Concepts Together

Cyanogen, a highly toxic gas, is 46.2% C and 53.8% N by mass. At 25 °C and 100.1 kPa, 1.05 g of cyanogen occupies 0.500 L. (**a**) What is the molecular formula of cyanogen? Predict (**b**) its molecular structure and (**c**) its polarity.

SOLUTION

Analyze We need to determine the molecular formula of a gas from elemental analysis data and data on its properties. Then we need to predict the structure of the molecule and from that, its polarity.

(**a**) **Plan** We can use the percentage composition of the compound to calculate its empirical formula. Then we can determine the molecular formula by comparing the mass of the empirical formula with the molar mass.

Solve To determine the empirical formula, we assume we have a 100-g sample and calculate the number of moles of each element in the sample:

$$\text{Moles C} = (46.2\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 3.85\ \text{mol C}$$

$$\text{Moles N} = (53.8\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 3.84\ \text{mol N}$$

Because the ratio of the moles of the two elements is essentially 1:1, the empirical formula is CN. To determine the molar mass, we use Equation 10.11.

$$\mathcal{M} = \frac{dRT}{P} = \frac{(1.05\ \text{g}/0.500\ L)(10^3\ m^3/L)(8.314\ m^3\,Pa/mol\,K)\,(298\ K)}{100.1 \times 10^3\ Pa} = 52.0\ \text{g/mol}$$

The molar mass associated with the empirical formula CN is $12.0 + 14.0 = 26.0$ g/mol. Dividing the molar mass by that of its empirical formula gives $(52.0\ \text{g/mol})/(26.0\ \text{g/mol}) = 2.00$. Thus, the molecule has twice as many atoms of each element as the empirical formula, giving the molecular formula C_2N_2.

(**b**) **Plan** To determine the molecular structure, we must determine the Lewis structure. We can then use the VSEPR model to predict the structure.

Solve The molecule has $2(4) + 2(5) = 18$ valence-shell electrons. By trial and error, we seek a Lewis structure with 18 valence electrons in which each atom has an octet and the formal charges are as low as possible. The structure

$$:N{\equiv}C{-}C{\equiv}N:$$

meets these criteria. (This structure has zero formal charge on each atom.)

The Lewis structure shows that each atom has two electron domains. (Each nitrogen has a nonbonding pair of electrons and a triple bond, whereas each carbon has a triple bond and a single bond.) Thus, the electron-domain geometry around each atom is linear, causing the overall molecule to be linear.

(**c**) **Plan** To determine the polarity of the molecule, we must examine the polarity of the individual bonds and the overall geometry of the molecule.

Solve Because the molecule is linear, we expect the two dipoles created by the polarity in the carbon–nitrogen bond to cancel each other, leaving the molecule with no dipole moment.

Self-Assessment Exercise

10.39 Under which conditions do you expect H_2 gas to deviate most from ideal behavior?

(a) 70 K and 101.3 kPa
(b) 70 K and 506.6 kPa
(c) 350 K and 202.7 kPa

Exercises

10.40 (**a**) List two experimental conditions under which gases deviate from ideal behavior. (**b**) List two reasons why the gases deviate from ideal behavior.

10.41 Based on their respective van der Waals constants (Table 10.3), is Ar or CO_2 expected to behave more nearly like an ideal gas at high pressures?

10.42 Calculate the pressure that CCl_4 will exert at 80 °C if 1.00 mol occupies 33.3 L, assuming that (**a**) CCl_4 obeys the ideal gas equation; (**b**) CCl_4 obeys the van der Waals equation. (Values for the van der Waals constants are given in Table 10.3.) (**c**) Which would you expect to deviate more from ideal behavior under these conditions, Cl_2 or CCl_4? Explain.

10.43 Table 10.3 shows that the van der Waals b parameter has units of L/mol. This means that we can calculate the sizes of atoms or molecules from the b parameter. Refer back to the discussion in Section 7.3. Is the van der Waals radius we calculate from the b parameter of Table 10.3 more closely associated with the bonding or nonbonding atomic radius discussed there? Explain.

Answers to Self-Assessment Exercises

10.39 (b)

Chapter Summary and Key Terms

CHARACTERISTICS OF GASES (SECTION 10.1) Substances that are gases at room temperature tend to be molecular substances with low molar masses. Air, a mixture composed mainly of N_2 and O_2, is the most common gas we encounter. Some liquids and solids can also exist in the gaseous state, where they are known as **vapors**. Gases are compressible; they mix in all proportions because their component molecules are far apart from each other.

PRESSURE (SECTION 10.2) To describe the state or condition of a gas, we must specify four variables: pressure (P), volume (V), temperature (T), and quantity (n). Volume is usually measured in liters, temperature in kelvins, and quantity of gas in moles. **Pressure** is the force per unit area and is expressed in SI units as **pascals**, Pa ($1\ Pa = 1\ N/m^2$). A related unit, the **bar**, equals 10^5 Pa. In chemistry, **standard atmospheric pressure** is used to define the **atmosphere** (atm) and the **torr** (also called the millimeter of mercury). One atmosphere of pressure equals 101.325 kPa, or 760 torr. A barometer is often used to measure the atmospheric pressure. A manometer can be used to measure the pressure of enclosed gases.

THE GAS LAWS (SECTION 10.3) Studies have revealed several simple gas laws: For a constant quantity of gas at constant temperature, the volume of the gas is inversely proportional to the pressure (**Boyle's law**). For a fixed quantity of gas at constant pressure, the volume is directly proportional to its absolute temperature (**Charles's law**). Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules (**Avogadro's hypothesis**). For a gas at constant temperature and pressure, the volume of the gas is directly proportional to the number of moles of gas (**Avogadro's law**). Each of these gas laws is a special case of the ideal gas equation.

THE IDEAL GAS EQUATION (SECTIONS 10.4) The **ideal gas equation**, $PV = nRT$, is the equation of state for an **ideal gas**. The term R in this equation is the **gas constant**. We can use the ideal gas equation to calculate variations in one variable when one or more of the others are changed. Most gases at pressures less than 10 atm and temperatures near 273 K and above obey the ideal gas equation reasonably well. The conditions of 273 K (0 °C) and 1 atm are known as the **standard temperature and pressure (STP)**. In all applications of the ideal gas equation, we must remember to convert temperatures to the absolute-temperature scale (the kelvin scale).

Using the ideal gas equation, we can relate the density of a gas to its molar mass: $\mathcal{M} = dRT/P$. We can also use the ideal gas equation to solve problems involving gases as reactants or products in chemical reactions.

GAS MIXTURES AND PARTIAL PRESSURES (SECTION 10.5) In gas mixtures, the total pressure is the sum of the **partial pressures** that each gas would exert if it were present alone under the same conditions (**Dalton's law of partial pressures**). The partial pressure of a component of a mixture is equal to its mole fraction times the total pressure: $P_1 = X_1P_t$. The **mole fraction** X is the ratio of the moles of one component of a mixture to the total moles of all components.

THE KINETIC-MOLECULAR THEORY OF GASES (SECTION 10.6) The **kinetic-molecular theory of gases** accounts for the properties of an ideal gas in terms of a set of statements about the nature of gases. Briefly, these statements are as follows: Molecules are in continuous chaotic motion. The volume of gas molecules is negligible compared to the volume of their container. The gas molecules neither attract nor repel each other. The average kinetic energy of the gas molecules is proportional to the absolute temperature and does not change if the temperature remains constant.

The individual molecules of a gas do not all have the same kinetic energy at a given instant. Their speeds are distributed over a

wide range; the distribution varies with the molar mass of the gas and with temperature. The **root-mean-square (rms) speed**, u_{rms}, varies in proportion to the square root of the absolute temperature and inversely with the square root of the molar mass: $u_{rms} = \sqrt{3RT/\mathcal{M}}$. The most probable speed of a gas molecule is given by $u_{mp} = \sqrt{2RT/\mathcal{M}}$.

MOLECULAR EFFUSION AND DIFFUSION (SECTION 10.7) It follows from kinetic-molecular theory that the rate at which a gas undergoes **effusion** (escapes through a tiny hole) is inversely proportional to the square root of its molar mass (**Graham's law**). The **diffusion** of one gas through the space occupied by a second gas is another phenomenon related to the speeds at which molecules move. Because moving molecules undergo frequent collisions with one another, the **mean free path**—the mean distance traveled between collisions—is short. Collisions between molecules limit the rate at which a gas molecule can diffuse.

REAL GASES: DEVIATIONS FROM IDEAL BEHAVIOR (SECTION 10.8) Departures from ideal behavior increase in magnitude as pressure increases and as temperature decreases. Real gases depart from ideal behavior because (1) the molecules possess finite volume and (2) the molecules experience attractive forces for one another. These two effects make the volumes of real gases larger and their pressures smaller than those of an ideal gas. The **van der Waals equation** is an equation of state for gases, which modifies the ideal gas equation to account for intrinsic molecular volume and intermolecular forces.

Learning Outcomes

After studying this chapter, you should be able to:

- Calculate pressure and convert between pressure units with an emphasis on torr and atmospheres. (Section 10.2) *Related Exercises*: *10.57, 10.58, 10.59*
- Calculate P, V, n, or T using the ideal gas equation. (Section 10.4) *Related Exercises*: *10.66, 10.69, 10.73*
- Explain how the gas laws relate to the ideal gas equation and apply the gas laws in calculations. (Sections 10.3 and 10.4) *Related Exercises*: *10.10, 10.69, 10.71*
- Calculate the density or molecular weight of a gas. (Section 10.4) *Related Exercises*: *10.13, 10.75, 10.78*
- Calculate the volume of gas consumed or formed in a chemical reaction. (Section 10.4) *Related Exercises*: *10.80, 10.83*
- Calculate the total pressure of a gas mixture given its partial pressures or given information for calculating partial pressures. (Section 10.5) *Related Exercises*: *10.50, 10.84, 10.85*
- Describe the kinetic-molecular theory of gases and how it explains the pressure and temperature of a gas, the gas laws, and the rates of effusion and diffusion. (Sections 10.6 and 10.7) *Related Exercises*: *10.52, 10.91, 10.93, 10.97*
- Explain why intermolecular attractions and molecular volumes cause real gases to deviate from ideal behavior at high pressure or low temperature. (Section 10.8) *Related Exercises*: *10.40, 10.100, 10.120*

Key Equations

• $PV = nRT$	[10.5]	Ideal gas equation
• $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	[10.8]	The combined gas law, showing how P, V, and T are related for a constant n
• $d = \frac{P\mathcal{M}}{RT}$	[10.10]	Density or molar mass of a gas
• $P_t = P_1 + P_2 + P_3 + \ldots$	[10.12]	Relating the total pressure of a gas mixture to the partial pressures of its components (Dalton's law of partial pressures)
• $P_1 = \left(\frac{n_1}{n_t}\right)P_t = X_1P_t$	[10.16]	Relating partial pressure to mole fraction
• $u_{rms} = \sqrt{\frac{3RT}{\mathcal{M}}}$	[10.20]	Definition of the root-mean-square (rms) speed of gas molecules
• $\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$	[10.22]	Relating the relative rates of effusion of two gases to their molar masses
• $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$	[10.25]	The van der Waals equation

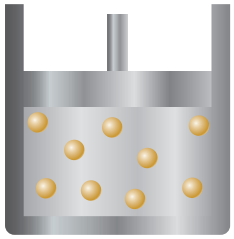
Exercises

Visualizing Concepts

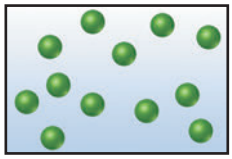
10.44 Mars has an average atmospheric pressure of 709 Pa. Would it be easier or harder to drink from a straw on Mars than on Earth? Explain. [Section 10.2]

10.45 You have a sample of gas in a container with a movable piston, such as the one in the drawing. (**a**) Redraw the container to show what it might look like if the temperature of the gas is increased from 300 to 500 K while the pressure is kept constant. (**b**) Redraw the container to show what it might look

like if the external pressure on the piston is increased from 101.3 kPa to 202.7 kPa while the temperature is kept constant. (**c**) Redraw the container to show what it might look like if the temperature of the gas decreases from 300 to 200 K while the pressure is kept constant (assume the gas does not liquefy). [Section 10.3]



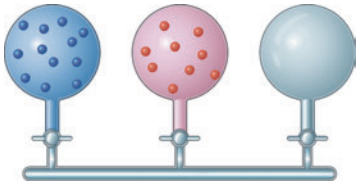
10.46 Consider the sample of gas depicted here. What would the drawing look like if the volume and temperature remained constant while you removed enough of the gas to decrease the pressure by a factor of 2? [Section 10.3]
(**a**) It would contain the same number of molecules.
(**b**) It would contain half as many molecules.
(**c**) It would contain twice as many molecules.
(**d**) There is insufficient data to say.



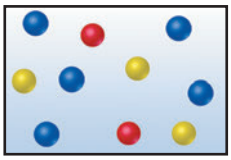
10.47 Imagine that the reaction $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$ occurs in a container that has a piston that moves to maintain a constant pressure when the reaction occurs at constant temperature. Which of the following statements describes how the volume of the container changes due to the reaction: (**a**) the volume increases by 50%, (**b**) the volume increases by 33%, (**c**) the volume remains constant, (**d**) the volume decreases by 33%, (**e**) the volume decreases by 50%. [Sections 10.3 and 10.4]

10.48 Suppose you have a fixed amount of an ideal gas at a constant volume. If the pressure of the gas is doubled while the volume is held constant, what happens to its temperature? [Section 10.4]

10.49 The apparatus shown here has two gas-filled containers and one empty container, all attached to a hollow horizontal tube. When the valves are opened and the gases are allowed to mix at constant temperature, what is the distribution of atoms in each container? Assume that the containers are of equal volume and ignore the volume of the connecting tube. Which gas has the greater partial pressure after the valves are opened? [Section 10.6]

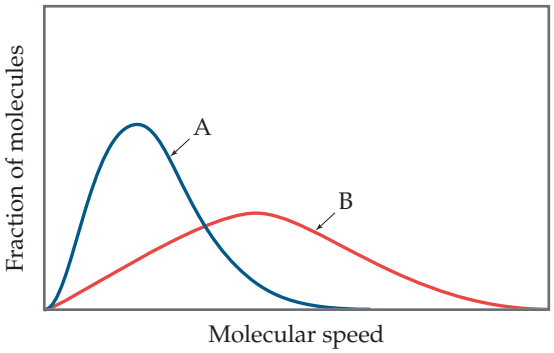


10.50 The accompanying drawing represents a mixture of three different gases. (**a**) Rank the three components in order of increasing partial pressure. (**b**) If the total pressure of the mixture is 141.9 kPa, calculate the partial pressure of each gas. [Section 10.6]

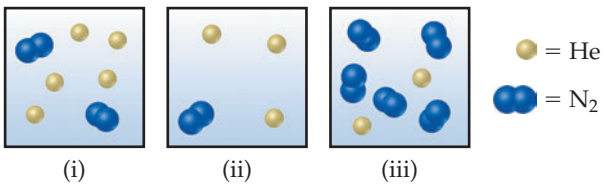


10.51 On a single plot, qualitatively sketch the distribution of molecular speeds for (**a**) Kr(g) at −50 °C, (**b**) Kr(g) at 0 °C, (**c**) Ar(g) at 0 °C. [Section 10.6]

10.52 Consider the following graph. (**a**) If curves A and B refer to two different gases, He and O_2, at the same temperature, which curve corresponds to He? (**b**) If A and B refer to the same gas at two different temperatures, which represents the higher temperature? (**c**) For each curve, which speed is highest: the most probable speed, the root-mean-square speed, or the average speed? [Section 10.6]

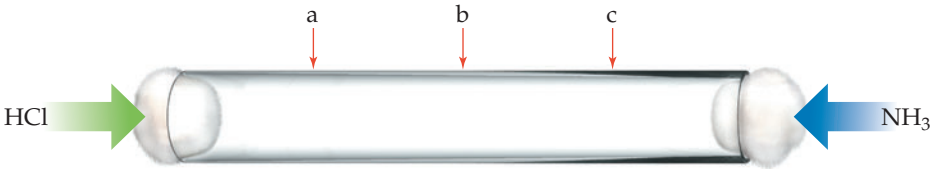


10.53 Consider the following samples of gases:

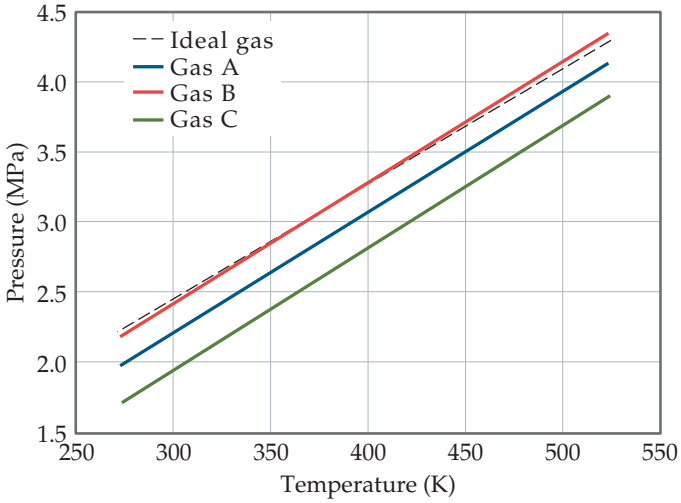


If the three samples are all at the same temperature, rank them with respect to (**a**) total pressure, (**b**) partial pressure of helium, (**c**) density, (**d**) average kinetic energy of particles. [Sections 10.5 and 10.6]

10.54 A thin glass tube 1 m long is filled with Ar gas at 101.3 kPa, and the ends are stoppered with cotton plugs as shown. HCl gas is introduced at one end of the tube, and simultaneously NH_3 gas is introduced at the other end. When the two gases diffuse through the cotton plugs down the tube and meet, a white ring appears due to the formation of $NH_4Cl(s)$. At which location—a, b, or c—do you expect the ring to form? [Section 10.7]



10.55 This shows the change in pressure as the temperature increases for a 1-mol sample of a gas confined to a 1-L container. The four plots correspond to an ideal gas and three real gases: CO_2, N_2, and Cl_2. (**a**) At room temperature, all three real gases have a pressure less than the ideal gas. Which van der Waals constant, *a* or *b*, accounts for the influence intermolecular forces have in lowering the pressure of a real gas? (**b**) Use the van der Waals constants in Table 10.3 to match the labels in the plot (A, B, and C) with the respective gases (CO_2, N_2, and Cl_2). [Section 10.8]



Gas Characteristics; Pressure (Sections 10.1 and 10.2)

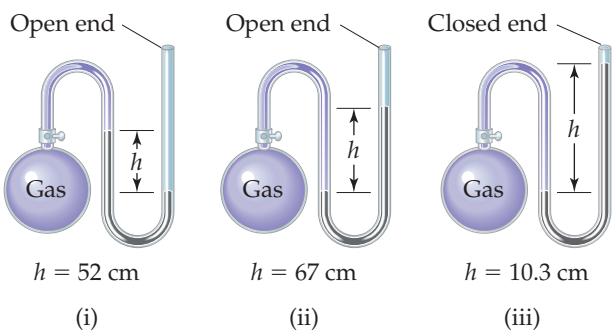
10.56 (**a**) Are you more likely to see the density of a gas reported in g/mL, g/L, or kg/cm^3? (**b**) Which units are appropriate for expressing atmospheric pressures, N, Pa, atm, kg/m^2? (**c**) Which is most likely to be a gas at room temperature and ordinary atmospheric pressure, F_2, Br_2, K_2O.

10.57 A person weighing 75 kg is standing on a three-legged stool. The stool momentarily tilts so that the entire weight is on one foot. If the contact area of each foot is 5.0 cm^2, calculate the pressure exerted on the underlying surface in (**a**) bars, (**b**) atmospheres, and (**c**) pounds per square inch.

10.58 (**a**) How high in meters must a column of ethanol be to exert a pressure equal to that of a 100-mm column of mercury? The density of ethanol is 0.79 g/mL, whereas that of mercury is 13.6 g/mL. (**b**) What pressure, in atmospheres, is exerted on the body of a diver if she is 10 m below the surface of the water when the atmospheric pressure is 100 kPa? Assume that the density of the water is 1.00 = 1.00 × 10^3 kg/m^3. The gravitational constant is 9.81 m/s^2, and 1 Pa = 1 kg/ms^2.

10.59 The highest barometric pressure ever recorded was 823.7 torr at Agata in Siberia, Russia on December 31, 1968. Convert this pressure to (**a**) atm, (**b**) mm Hg, (**c**) pascals, (**d**) bars, (**e**) psi.

10.60 If the atmospheric pressure is 0.995 atm, what is the pressure of the enclosed gas in each of the three cases depicted in the drawing? Assume that the gray liquid is mercury.



The Gas Laws (Section 10.3)

10.61 A fixed quantity of gas at 25 °C exhibits a pressure of 99 kPa and occupies a volume of 4.00 L. (**a**) Calculate the volume the gas will occupy if the pressure is increased to 202.6 kPa while the temperature is held constant. (**b**) Calculate the volume the gas will occupy if the temperature is increased to100 °C while the pressure is held constant.

10.62 (**a**) Amonton's law expresses the relationship between pressure and temperature. Use Charles's law and Boyle's law to derive the proportionality relationship between *P* and *T*. (**b**) If a car tire is filled to a pressure of 220.6 kPa measured at 24 °C, what will be the tire pressure if the tires heat up to 49 °C during driving?

The Ideal Gas Equation (Section 10.4)

10.63 (**a**) What conditions are represented by the abbreviation STP? (**b**) What is the molar volume of an ideal gas at STP? (**c**) Room temperature is often assumed to be 25 °C. Calculate the molar volume of an ideal gas at 25 °C and 101.3 kPa pressure. (**d**) If you measure pressure in bars instead of atmospheres, calculate the corresponding value of *R* in L bar/mol K.

10.64 To derive the ideal-gas equation, we assume that the volume of a gas's atoms/molecules can be neglected. Given that the atomic radius of argon 0.097 nm, and knowing that a sphere has a volume of $4\pi r^3/3$, calculate the fraction of space that Ar atoms occupy in a sample of argon at STP.

10.65 Suppose you are given two 2-L flasks and told that one contains a gas of molar mass 28, the other a gas of molar mass 56, both at the same temperature and pressure. The mass of gas in the flask A is 1.0 g and the mass of gas in the flask B is 2.0 g. Which flask contains the gas of molar mass 28, and which contains the gas of molar mass 56?

10.66 Complete the following table for an ideal gas:

P	*V*	*n*	*T*
303.98 kPa	3.00 L	1.500 mol	? K
50.663 kPa	0.750 L	? mol	300 K
101.33 kPa	? L	3.333 mol	300 K
? kPa	.750 L	0.750 mol	298 K

10.67 (**a**) Calculate the number of molecules in a deep breath of air whose volume is 2.25 L at body temperature, 37 °C, and a pressure of 97.99 kPa. (**b**) The adult blue whale has a lung capacity of 5.0 × 10^3 L. Calculate the mass of air (assume an average molar mass of 28.98 g/mol) contained in an adult blue whale's lungs at 0.0 °C and 101.33 kPa, assuming the air behaves ideally.

10.68 (**a**) If the pressure exerted by ozone, O_3, in the stratosphere is 304 Pa and the temperature is 250 K, how many ozone molecules are in a liter? (**b**) Carbon dioxide makes up approximately 0.04% of Earth's atmosphere. If you collect a 2.0-L sample from the atmosphere at sea level (101.33 kPa) on a warm day (27 °C), how many CO_2 molecules are in your sample?

10.69 A scuba diver's tank contains 2.50 kg of O_2 compressed into a volume of 11.0 L. (**a**) Calculate the gas pressure inside the tank at 10 °C. (**b**) What volume would this oxygen occupy at 25 °C and 101.33 kPa?

10.70 An aerosol spray can with a volume of 125 mL contains 1.30 g of propane gas (C_3H_8) as a propellant. (**a**) If the can is at 25 °C, what is the pressure in the can? (**b**) What volume would the butane occupy at STP? (**c**) The can's label says that exposure to temperatures above 50 °C may cause the can to burst. What is the pressure in the can at this temperature?

10.71 A 50.0 g sample of solid CO_2 (dry ice) is added at −100 °C to an evacuated (all of the gas removed) container with a volume of 5.0 L. If the container is sealed and then allowed to warm to room temperature (25 °C) so that the entire solid CO_2 is converted to a gas, what is the pressure inside the container?

10.72 A 334-mL cylinder for use in chemistry lectures contains 5.225 g of helium at 23 °C. How many grams of helium must be released to reduce the pressure to 7.60 MPa assuming ideal gas behavior?

10.73 Chlorine is widely used to purify municipal water supplies and to treat swimming pool waters. Suppose that the volume of a particular sample of Cl_2 gas is 8.70 L at 119.3 kPa and 24 °C. (**a**) How many grams of Cl_2 are in the sample? (**b**) What volume will the Cl_2 occupy at STP? (**c**) At what temperature will the volume be 15.00 L if the pressure is 116.8 kPa? (**d**) At what pressure will the volume equal 5.00 L if the temperature is 58 °C?

10.74 In an experiment reported in the scientific literature, male cockroaches were made to run at different speeds on a miniature treadmill while their oxygen consumption was measured. In 30 minutes, the average cockroach (running at 0.08 km/h) consumed 1.0 mL of O_2 at 101.33 kPa pressure and 20 °C per gram of insect mass. (**a**) How many moles of O_2 would be consumed in 1 day by a 6.3-g cockroach moving at this speed? (**b**) This same cockroach is caught by a child and placed in a 2.0 L fruit jar with a tight lid. Assuming the same level of continuous activity as in the research, how much of the available O_2 will the cockroach consume in 1 day? (Air is 21 mol% O_2.)

10.75 Rank the following gases from least dense to most dense at 101.33 kPa and 298 K: O_2, Ar, NH_3, HCl.

10.76 Which of the following statements best explains why a closed balloon filled with helium gas rises in air?

(**a**) Helium is a monatomic gas, whereas nearly all the molecules that make up air, such as nitrogen and oxygen, are diatomic.

(**b**) The average speed of helium atoms is greater than the average speed of air molecules, and the greater speed of collisions with the balloon walls propels the balloon upward.

(**c**) Because the helium atoms are of lower mass than the average air molecule, the helium gas is less dense than air. The mass of the balloon is thus less than the mass of the air displaced by its volume.

(**d**) Because helium has a lower molar mass than the average air molecule, the helium atoms are in faster motion. This means that the temperature of the helium is greater than the air temperature. Hot gases tend to rise.

10.77 Which of the following statements best explains why nitrogen gas at STP is less dense than Xe gas at STP?

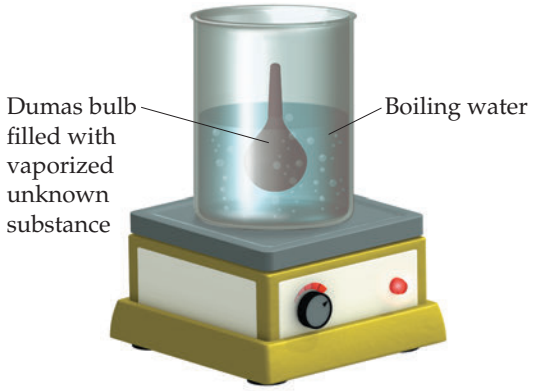
(**a**) Because Xe is a noble gas, there is less tendency for the Xe atoms to repel one another, so they pack more densely in the gaseous state.

(**b**) Xe atoms have a higher mass than N_2 molecules. Because both gases at STP have the same number of molecules per unit volume, the Xe gas must be denser.

(**c**) The Xe atoms are larger than N_2 molecules and thus take up a larger fraction of the space occupied by the gas.

(**d**) Because the Xe atoms are much more massive than the N_2 molecules, they move more slowly and thus exert less upward force on the gas container and make the gas appear denser.

10.78 In the Dumas-bulb technique for determining the molar mass of an unknown liquid, you vaporize the sample of a liquid that boils below 100 °C in a boiling-water bath and determine the mass of vapor required to fill the bulb. From the following data, calculate the molar mass of the unknown liquid: mass of unknown vapor, 1.012 g; volume of bulb, 354 cm^3; pressure, 98.93 kPa; temperature, 99 °C.



10.79 The molar mass of a volatile substance was determined by the Dumas-bulb method described in Exercise 10.78. The unknown vapor had a mass of 2.55 g; the volume of the bulb was 500 mL, pressure 101.33 kPa, and temperature 37 °C.Calculate the molar mass of the unknown vapor.

10.80 The metabolic oxidation of glucose, $C_6H_{12}O_6$, in our bodies produces CO_2, which is expelled from our lungs as a gas:

$$C_6H_{12}O_6(aq) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

(**a**) Calculate the volume of dry CO_2 produced at normal body temperature, 37 °C, and 101.33 kPa when 10.0 g of glucose is consumed in this reaction. (**b**) Calculate the volume of oxygen you would need, at 100 kPa and 298 K, to completely oxidize 15.0 g of glucose.

10.81 In a "Kipp generator", hydrogen gas is produced when zinc flakes react with hydrochloric acid:

$$2\,HCl(aq) + Zn(s) \longrightarrow ZnCl_2(aq) + H_2(g)$$

If 30.0 mL of wet H_2 is collected over water at 20 °C and a barometric pressure of 101.33 kPa, how many grams of Zn have been consumed? (The vapor pressure of water is tabulated in Appendix B.)

10.82 Acetylene gas, $C_2H_2(g)$, can be prepared by the reaction of calcium carbide with water:

$$CaC_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g)$$

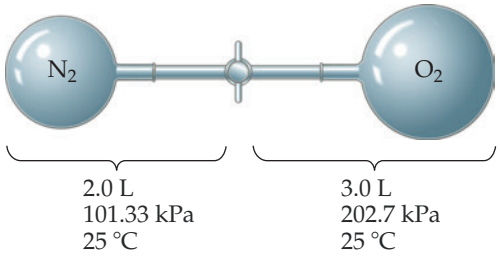
Calculate the volume of C_2H_2 that is collected over water at 23 °C by reaction of 1.524 g of CaC_2 if the total pressure of the gas is 100.4 kPa. (The vapor pressure of water is tabulated in Appendix B.)

Partial Pressures (Section 10.5)

10.83 Magnesium can be used as a "getter" in evacuated enclosures to react with the last traces of oxygen. (The magnesium is usually heated by passing an electric current through a wire or ribbon of the metal.) If an enclosure of 5.67 L has a partial pressure of O_2 of 7.066 mPa at 30 °C, what mass of magnesium will react according to the following equation?

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$$

10.84 Consider the apparatus shown in the following drawing. (**a**) When the valve between the two containers is opened and the gases are allowed to mix, how does the volume occupied by the N_2 gas change? What is the partial pressure of N_2 after mixing? (**b**) How does the volume of the O_2 gas change when the gases mix? What is the partial pressure of O_2 in the mixture? (**c**) What is the total pressure in the container after the gases mix?



10.85 A mixture containing 0.50 mol $H_2(g)$, 1.00 mol $O_2(g)$, and 3.50 mol $N_2(g)$ is confined in a 25.0-L vessel at 25 °C. (**a**) Calculate the total pressure of the mixture. (**b**) Calculate the partial pressure of each of the gases in the mixture.

10.86 A plasma-screen TV contains thousands of tiny cells filled with a mixture of Xe, Ne, and He gases that emits light of specific wavelengths when a voltage is applied. A particular plasma cell, 0.900 mm × 0.300 mm × 10.0 mm, contains 4% Xe in a 1:1 Ne:He mixture at a total pressure of 66.66 kPa. Calculate the number of Xe, Ne, and He atoms in the cell and state the assumptions you need to make in your calculation.

10.87 A piece of dry ice (solid carbon dioxide) with a mass of 20.0 g is placed in a 25.0-L vessel that already contains air at 50.66 kPa and 25 °C. After the carbon dioxide has totally sublimed, what is the partial pressure of the resultant CO_2 gas, and the total pressure in the container at 25 °C?

10.88 If 5.15 g of Ag_2O is sealed in a 75.0-mL tube filled with 101.3 kPa of N_2 gas at 32 °C, and the tube is heated to 320 °C, the Ag_2O decomposes to form oxygen and silver. What is the total pressure inside the tube assuming the volume of the tube remains constant?

10.89 A quantity of N_2 gas originally held at 531.96 kPa pressure in a 1.00-L container at 26 °C is transferred to a 12.5-L container at 20 °C. A quantity of O_2 gas originally at 531.96 kPa and 26 °C in a 5.00 L container is transferred to this same container. What is the total pressure in the new container?

10.90 A sample of 3.00 g of $SO_2(g)$ originally in a 5.00 L vessel at 21 °C is transferred to a 10.0 L vessel at 26 °C. A sample of 2.35 g of $N_2(g)$ originally in a 2.50 L vessel at 20 °C is transferred to this same 10.0 L vessel. (**a**) What is the partial pressure of $SO_2(g)$ in the larger container? (**b**) What is the partial pressure of $N_2(g)$ in this vessel? (**c**) What is the total pressure in the vessel?

Kinetic-Molecular Theory of Gases; Effusion and Diffusion (Sections 10.6 and 10.7)

10.91 Determine whether each of the following changes will increase, decrease, or not affect the rate with which gas molecules collide with the walls of their container: (**a**) increasing the volume of the container, (**b**) increasing the temperature, **(c)** increasing the molar mass of the gas.

10.92 You have an evacuated container of fixed volume and known mass and introduce a known mass of a gas sample. Measuring the pressure at constant temperature over time, you are surprised to see it slowly dropping. You measure the mass of the gas-filled container and find that the mass is what it should be—gas plus container—and the mass does not change over time, so you do not have a leak. Suggest an explanation for your observations.

10.93 The temperature of a 5.00-L container of N_2 gas is increased from 20 °C to 250 °C. If the volume is held constant, predict qualitatively how this change affects the following: (**a**) the average kinetic energy of the molecules; (**b**) the root-mean-square speed of the molecules; (**c**) the strength of the impact of an average molecule with the container walls; (**d**) the total number of collisions of molecules with walls per second.

10.94 Suppose you have two 1 L flasks, one containing N_2 at STP, the other containing CH_4 at STP. How do these systems compare with respect to (**a**) number of molecules, (**b**) density, (**c**) average kinetic energy of the molecules, (**d**) rate of effusion through a pinhole leak?

10.95 (**a**) Place the following gases in order of increasing average molecular speed at 25 °C: O_2, Ar, CO, HCl, CH_4. (**b**) Calculate the rms speed of CO molecules at 25 °C. (**c**) Calculate the most probable speed of an argon atom in the stratosphere, where the temperature is 0 °C.

10.96 At constant pressure, the mean free path (λ) of a gas molecule is directly proportional to temperature. At constant temperature, λ is inversely proportional to pressure. If you compare two different gas molecules at the same temperature and pressure, λ is inversely proportional to the square of the diameter of the gas molecules. Put these facts together to create a formula for the mean free path of a gas molecule with a proportionality constant (call it R_{mfp}, like the ideal gas constant) and define units for R_{mfp}.

10.97 Hydrogen has two naturally occurring isotopes, ^1H and ^2H. Chlorine also has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl. Thus, hydrogen chloride gas consists of four distinct types of molecules: $^1H^{35}Cl$, $^1H^{37}Cl$, $^2H^{35}Cl$, and $^2H^{37}Cl$. Place these four molecules in order of increasing rate of effusion.

10.98 Arsenic(III) sulfide sublimes readily, even below its melting point of 320 °C. The molecules of the vapor phase are found to effuse through a tiny hole at 0.52 times the rate of effusion of Xe atoms under the same conditions of temperature and pressure. What is the molecular formula of arsenic(III) sulfide in the gas phase?

Nonideal Gas Behavior (Section 10.8)

10.99 The planet Jupiter has a surface temperature of 140 K and a mass 318 times that of Earth. Mercury (the planet) has a surface temperature between 600 K and 700 K and a mass 0.05 times that of Earth. On which planet is the atmosphere more likely to obey the ideal gas law? Explain.

10.100 Which statement concerning the van der Waals constants a and b is true?

(**a**) The magnitude of a relates to molecular volume, whereas b relates to attractions between molecules.
(**b**) The magnitude of a relates to attractions between molecules, whereas b relates to molecular volume.
(**c**) The magnitudes of a and b depend on pressure.
(**d**) The magnitudes of a and b depend on temperature.

10.101 In Sample Exercise 10.15, we found that ten mole of Cl_2 confined to 22.41 L at 0 °C deviated slightly from ideal behavior. Calculate the pressure exerted by 1.00 mol Cl_2 confined to a smaller volume, 5.00 L, at 25 °C. (**a**) First use the ideal gas equation and (**b**) then use the van der Waals equation for your calculation. (Values for the van der Waals constants are given in Table 10.3.) (**c**) Why is the difference between the result for an ideal gas and that calculated using the van der Waals equation greater when the gas is confined to 5.00 L compared to 22.4 L?

10.102 Table 10.3 shows that the van der Waals b parameter has units of L/mol. This implies that we can calculate the size of atoms or molecules from b. Using the value of b for Xe, calculate the radius of a Xe atom and compare it to the value found in Figure 7.7, that is, 140 pm. Recall that the volume of a sphere is $(4/3)\pi r^3$.

Additional Exercises

10.103 Torricelli, who invented the barometer, used mercury in its construction because mercury has a very high density, which makes it possible to make a more compact barometer than one based on a less dense fluid. Calculate the density of mercury using the observation that the column of mercury is 760 mm high when the atmospheric pressure is 1.01×10^5 Pa. Assume the tube containing the mercury is a cylinder with a constant cross-sectional area.

10.104 Consider a lake that is about 40 m deep. A gas bubble with a diameter of 1.0 mm originates at the bottom of a lake where the pressure is 405.3 kPa. Calculate its volume when the bubble reaches the surface of the lake where the pressure is 98 kPa, assuming that the temperature does not change.

10.105 A 6.0 L tank is filled with helium gas at a pressure of 2 MPa. How many balloons (each 2.00 L) can be inflated to a pressure of 101.3 kPa, assuming that the temperature remains constant and that the tank cannot be emptied below 101.3 kPa?

10.106 A 500 mL incandescent light bulb is filled with 1.5×10^{-5} mol of xenon to minimize the rate of evaporation of the tungsten filament. What is the pressure of xenon in the light bulb at 25 °C?

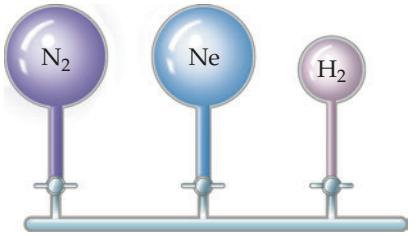
10.107 Carbon dioxide, which is recognized as the major contributor to global warming as a "greenhouse gas," is formed when fossil fuels are combusted, as in electrical power plants fueled by coal, oil, or natural gas. One potential way to reduce the amount of CO_2 added to the atmosphere is to store it as a compressed gas in underground formations. Consider a 1000 megawatt coal-fired power plant that produces about 6×10^6 tons of CO_2 per year. (**a**) Assuming ideal gas behavior, 101.3 kPa, and 27 °C, calculate the volume of CO_2 produced by this power plant. (**b**) If the CO_2 is stored underground as a liquid at 10 °C and 12.16 MPa and a density of 1.2 g/cm^3, what volume does it possess? (**c**) If it is stored underground as a gas at 30 °C and 7.09 MPa, what volume does it occupy?

10.108 Propane, C_3H_8, liquefies under modest pressure, allowing a large amount to be stored in a container. (**a**) Calculate the number of moles of propane gas in a 20 L container at 709.3 kPa and 25 °C. (**b**) Calculate the number of moles of liquid propane that can be stored in the same volume if the density of the liquid is 0.590 g/mL. (**c**) Calculate the ratio of the number of moles of liquid to moles of gas. Discuss this ratio in light of the kinetic-molecular theory of gases.

10.109 Nickel carbonyl, $Ni(CO)_4$, is one of the most toxic substances known. The present maximum allowable concentration in laboratory air during an 8 hr workday is 1 ppb (parts per billion) by volume, which means that there is one mole of $Ni(CO)_4$ for every 10^9 moles of gas. Assume 24 °C and 101.3 kPa pressure. What mass of $Ni(CO)_4$ is allowable in a laboratory room that is 3.5 m × 6.0 m × 2.5 m?

10.110 When a large evacuated flask is filled with argon gas, its mass increases by 3.224 g. When the same flask is again evacuated and then filled with a gas of unknown molar mass, the mass increase is 8.102 g. (**a**) Based on the molar mass of argon, estimate the molar mass of the unknown gas. (**b**) What assumptions did you make in arriving at your answer?

10.111 Consider the arrangement of bulbs shown in the drawing. Each of the bulbs contains a gas at the pressure shown. What is the pressure of the system when all the stopcocks are opened, assuming that the temperature remains constant? (We can neglect the volume of the capillary tubing connecting the bulbs.)

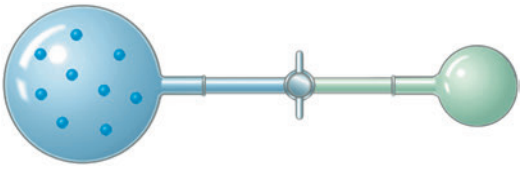


10.112 Assume that a single cylinder of an automobile engine has a volume of 524 cm^3. (**a**) If the cylinder is full of air at 74 °C and 99.3 kPa, how many moles of O_2 are present? (The mole fraction of O_2 in dry air is 0.2095.) (**b**) How many grams of C_8H_{18} could be combusted by this quantity of O_2, assuming complete combustion with formation of CO_2 and H_2O?

10.113 Assume that an exhaled breath of air consists of 74.8% N_2, 15.3% O_2, 3.7% CO_2, and 6.2% water vapor. (**a**) If the total pressure of the gases is 99.8 kPa, calculate the partial pressure of each component of the mixture. (**b**) If the volume of the exhaled gas is 455 mL and its temperature is 37 °C, calculate the number of moles of CO_2 exhaled. (**c**) How many grams of glucose ($C_6H_{12}O_6$) would need to be metabolized to produce this quantity of CO_2? (The chemical reaction is the same as that for combustion of $C_6H_{12}O_6$. See Section 3.2 and Exercise 10.80.)

10.114 An 8.40 g sample of argon and an unknown mass of H_2 are mixed in a flask at room temperature. The partial pressure of the argon is 44.0 kPa, and that of the hydrogen is 57.33 kPa. What is the mass of the hydrogen?

10.115 An ideal gas at a pressure of 152 kPa is contained in a bulb of unknown volume. A stopcock is used to connect this bulb with a previously evacuated bulb that has a volume of 0.800 L as shown here. When the stopcock is opened, the gas expands into the empty bulb. If the temperature is held constant during this process and the final pressure is 92.66 kPa, what is the volume of the bulb that was originally filled with gas?



10.116 The density of a gas of unknown molar mass was measured as a function of pressure at 0 °C, as in the table that follows. (**a**) Determine a precise molar mass for the gas. [*Hint:* Graph d/P versus P.] (**b**) Why is d/P not a constant as a function of pressure?

Pressure (kPa)	101.3	67.48	50.66	33.74	25.33
Density (g/L)	2.3074	1.5263	1.1401	0.7571	0.5660

10.117 A glass vessel fitted with a stopcock valve has a mass of 337.428 g when evacuated. When filled with Ar, it has a mass of 339.854 g. When evacuated and refilled with a mixture of Ne and Ar, under the same conditions of temperature and pressure, it has a mass of 339.076 g. What is the mole percent of Ne in the gas mixture?

10.118 You have a sample of gas at 0 °C. You wish to increase the rms speed by a factor of 3. To what temperature should the gas be heated?

10.119 Consider the following gases, all at STP: Ne, SF_6, N_2, CH_4. (**a**) Which gas is most likely to depart from the assumption of the kinetic-molecular theory that says there are no attractive or repulsive forces between molecules? (**b**) Which one is closest to an ideal gas in its behavior? (**c**) Which one has the highest root-mean-square molecular speed at a given temperature? (**d**) Which one has the highest total molecular volume relative to the space occupied by the gas? (**e**) Which has the highest average kinetic-molecular energy? (**f**) Which one would effuse more rapidly than N_2? **(g)** Which one would have the largest van der Waals *b* parameter?

10.120 Does the effect of intermolecular attraction on the properties of a gas become more significant or less significant if (**a**) the gas is compressed to a smaller volume at constant temperature; (**b**) the temperature of the gas is increased at constant volume?

10.121 Which of the noble gases other than radon would you expect to depart most readily from ideal behavior? Use the density data in Table 7.8 to show evidence in support of your answer.

10.122 It turns out that the van der Waals constant *b* equals four times the total volume actually occupied by the molecules of a mole of gas. Using this figure, calculate the fraction of the volume in a container actually occupied by Ar atoms (**a**) at STP, (**b**) at 20.27 MPa pressure and 0 °C. (Assume for simplicity that the ideal gas equation still holds.)

10.123 Large amounts of nitrogen gas are used in the manufacture of ammonia, principally for use in fertilizers. Suppose 120.00 kg of $N_2(g)$ is stored in a 1100.0-L metal cylinder at 280 °C. (**a**) Calculate the pressure of the gas, assuming ideal gas behavior. (**b**) By using the data in Table 10.3, calculate the pressure of the gas according to the van der Waals equation. (**c**) Under the conditions of this problem, which correction dominates, the one for finite volume of gas molecules or the one for attractive interactions?

Integrative Exercises

10.124 Cyclopropane, a gas used with oxygen as a general anesthetic, is composed of 85.7% C and 14.3% H by mass. (**a**) If 1.56 g of cyclopropane has a volume of 1.00 L at 99.7 kPa and 50.0 °C, what is the molecular formula of cyclopropane? (**b**) Judging from its molecular formula, would you expect cyclopropane to deviate more or less than Ar from ideal gas behavior at moderately high pressures and room temperature? Explain. (**c**) Would cyclopropane effuse through a pinhole faster or more slowly than methane, CH_4?

10.125 Consider the combustion reaction between 1.00 L of liquid methanol (density = 0.850 g/mL) and 500 L of oxygen gas measured at STP. The products of the reaction are $CO_2(g)$ and $H_2O(g)$. Calculate the volume of liquid H_2O formed if the reaction goes to completion and you condense the water vapor.

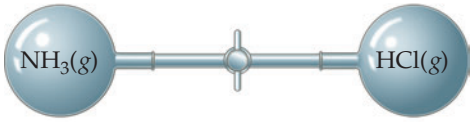
10.126 An herbicide is found to contain only C, H, N, and Cl. The complete combustion of a 100.0-mg sample of the herbicide in excess oxygen produces 83.16 mL of CO_2 and 73.30 mL of H_2O vapor expressed at STP. A separate analysis shows that the sample also contains 16.44 mg of Cl. (**a**) Determine the percentage of the composition of the substance. (**b**) Calculate its empirical formula. (**c**) What other information would you need to know about this compound to calculate its true molecular formula?

10.127 A 4.00 g sample of a mixture of CaO and BaO is placed in a 1.00-L vessel containing CO_2 gas at a pressure of 97.33 kPa and a temperature of 25 °C. The CO_2 reacts with the CaO and BaO, forming $CaCO_3$ and $BaCO_3$. When the reaction is complete, the pressure of the remaining CO_2 is 20.0 kPa. (**a**) Calculate the number of moles of CO_2 that have reacted. (**b**) Calculate the mass percentage of CaO in the mixture.

10.128 Ammonia and hydrogen chloride react to form solid ammonium chloride:

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

Two 2.00 L flasks at 25 °C are connected by a valve, as shown in the drawing. One flask contains 5.00 g of $NH_3(g)$, and the other contains 5.00 g of HCl(*g*). When the valve is opened, the gases react until one is completely consumed. (**a**) Which gas will remain in the system after the reaction is complete? (**b**) What will be the final pressure of the system after the reaction is complete? (Neglect the volume of the ammonium chloride formed.) (**c**) What mass of ammonium chloride will be formed?



10.129 Gas pipelines are used to deliver natural gas (methane, CH_4) to the various regions of the United States. The total volume of natural gas that is delivered is on the order of 2.7×10^{12} L per day, measured at STP. Calculate the total enthalpy change for combustion of this quantity of methane. (*Note*: Less than this amount of methane is actually combusted daily. Some of the delivered gas is passed through to other regions.)

10.130 Chlorine dioxide gas (ClO_2) is used as a commercial bleaching agent. It bleaches materials by oxidizing them. In the course of these reactions, the ClO_2 is itself reduced. (**a**) What is the Lewis structure for ClO_2? (**b**) Why do you think that ClO_2 is reduced so readily? (**c**) When a ClO_2 molecule gains an electron, the chlorite ion, ClO_2^-, forms. Draw the Lewis structure for ClO_2^-. (**d**) Predict the O—Cl—O bond angle in the ClO_2^- ion. (**e**) One method of preparing ClO_2 is by the reaction of chlorine and sodium chlorite:

$$Cl_2(g) + 2\,NaClO_2(s) \longrightarrow 2\,ClO_2(g) + 2\,NaCl(s)$$

If you allow 15.0 g of $NaClO_2$ to react with 2.00 L of chlorine gas at a pressure of 152.0 kPa at 21 °C, how many grams of ClO_2 can be prepared?

10.131 Natural gas is very abundant in many Middle Eastern oil fields. However, the costs of shipping the gas to markets in other parts of the world are high because it is necessary to liquefy the gas, which is mainly methane and has a boiling point at atmospheric pressure of −164 °C. One possible strategy is to oxidize the methane to methanol, CH_3OH, which has a boiling point of 65 °C and can therefore be shipped more readily. Suppose that 3.03×10^8 m^3 of methane at atmospheric pressure and 25 °C is oxidized to

methanol. (**a**) What volume of methanol is formed if the density of CH_3OH is 0.791 g/mL? (**b**) Write balanced chemical equations for the oxidations of methane and methanol to $CO_2(g)$ and $H_2O(l)$. Calculate the total enthalpy change for complete combustion of the 3.03×10^8 m^3 of methane just described and for complete combustion of the equivalent amount of methanol, as calculated in part (a). (**c**) Methane, when liquefied, has a density of 0.466 g/mL; the density of methanol at 25 °C is 0.791 g/mL. Compare the enthalpy change upon combustion of a unit volume of liquid methane and liquid methanol. From the standpoint of energy production, which substance has the higher enthalpy of combustion per unit volume?

10.132 Gaseous iodine pentafluoride, IF_5, can be prepared by the reaction of solid iodine and gaseous fluorine:

$$I_2(s) + 5\,F_2(g) \longrightarrow 2\,IF_5(g)$$

A 5.00-L flask containing 10.0 g of I_2 is charged with 10.0 g of F_2, and the reaction proceeds until one of the reagents is completely consumed. After the reaction is complete, the temperature in the flask is 125 °C. (**a**) What is the partial pressure of IF_5 in the flask? (**b**) What is the mole fraction of IF_5 in the flask (**c**) Draw the Lewis structure of IF_5. (**d**) What is the total mass of reactants and products in the flask?

10.133 A 6.53-g sample of a mixture of magnesium carbonate and calcium carbonate is treated with excess hydrochloric acid. The resulting reaction produces 1.72 L of carbon dioxide gas at 28 °C and 99.06 kPa pressure. (**a**) Write balanced chemical equations for the reactions that occur between hydrochloric acid and each component of the mixture. (**b**) Calculate the total number of moles of carbon dioxide that forms from these reactions. (**c**) Assuming that the reactions are complete, calculate the percentage by mass of magnesium carbonate in the mixture.

Design an Experiment

You are given a cylinder of an unknown, nonradioactive, noble gas and tasked to determine its molar mass and use that value to identify the gas. The tools available to you are several empty mylar balloons that are about the size of a grapefruit when inflated (gases diffuse through mylar much more slowly than conventional latex balloons), an analytical balance, and three graduated glass beakers of different sizes (100 mL, 500 mL, and 2 L). (**a**) To how many significant figures would you need to determine the molar mass to identify the gas? (**b**) Propose an experiment or series of experiments that would allow you to determine the molar mass of the unknown gas. Describe the tools, calculations, and assumptions you would need to use. (**c**) If you had access to a broader range of analytical instruments, describe an alternative way you could identify the gas using any experimental methods that you have learned about in the earlier chapters.

11

LIQUIDS AND INTERMOLECULAR FORCES

WHAT'S AHEAD

11.1 A Molecular Comparison of Gases, Liquids, and Solids
11.2 Intermolecular Forces
11.3 Select Properties of Liquids
11.4 Phase Changes
11.5 Vapor Pressure
11.6 Phase Diagrams
11.7 Liquid Crystals

11.1 A Molecular Comparison of Gases, Liquids, and Solids



Empedocles lived around 2400 years ago, a citizen of the Greek city of Akragas, situated on what is now the island of Sicily. He was a philosopher and is best remembered for proposing four elements from which all matter was made: air, water, earth, and fire. We can understand his choice as it represents the three states of matter and energy, which is inseparable from all chemical reactions.

In this brief section, we remind ourselves of the differences between the states. At the end of this section, you should be able to

- Recognize the characteristic properties of the states

As we learned in Chapter 10, the molecules in a gas are widely separated and in a state of constant, chaotic motion. One of the key tenets of kinetic-molecular theory of gases is the assumption that we can neglect the interactions between molecules. The properties of liquids and solids are quite different from those of gases largely because the intermolecular forces in liquids and solids are much stronger. A comparison of the properties of gases, liquids, and solids is given in **Table 11.1**.

In liquids the intermolecular attractive forces are strong enough to hold particles close together. Thus, liquids are much denser and far less compressible than gases. Unlike gases, liquids have a definite volume, independent of the size and shape of their container. The attractive forces in liquids are not strong enough, however, to keep the particles from moving past one another. Thus, any liquid can be poured and assumes the shape of the container it occupies.

In solids the intermolecular attractive forces are strong enough to hold particles close together and to lock them virtually in place. Solids, like liquids, are not very compressible because the particles have little free space between them. Because the particles in a solid or liquid are fairly close together compared with those of a gas, we often refer to solids and liquids as *condensed phases*. We will study solids in Chapter 12. For now it is sufficient to know that the particles of a solid are not free to undergo long-range movement, which makes solids rigid.*

Figure 11.1 compares the three states of matter. *The state of a substance depends largely on the balance between the kinetic energies of the particles (atoms, molecules, or ions) and the interparticle energies of attraction*. The kinetic energies, which depend on temperature, tend to keep the particles apart and moving. The interparticle attractions tend to draw the particles together. Substances that are gases at room temperature have much weaker interparticle attractions than those that are liquids; substances that are liquids have weaker interparticle attractions than those that are solids. The different states of matter adopted by the halogens at room temperature—iodine is a solid, bromine is a liquid, and chlorine is a gas—are a direct consequence of a decrease in the strength of the intermolecular forces as we move from I_2 to Br_2 to Cl_2.

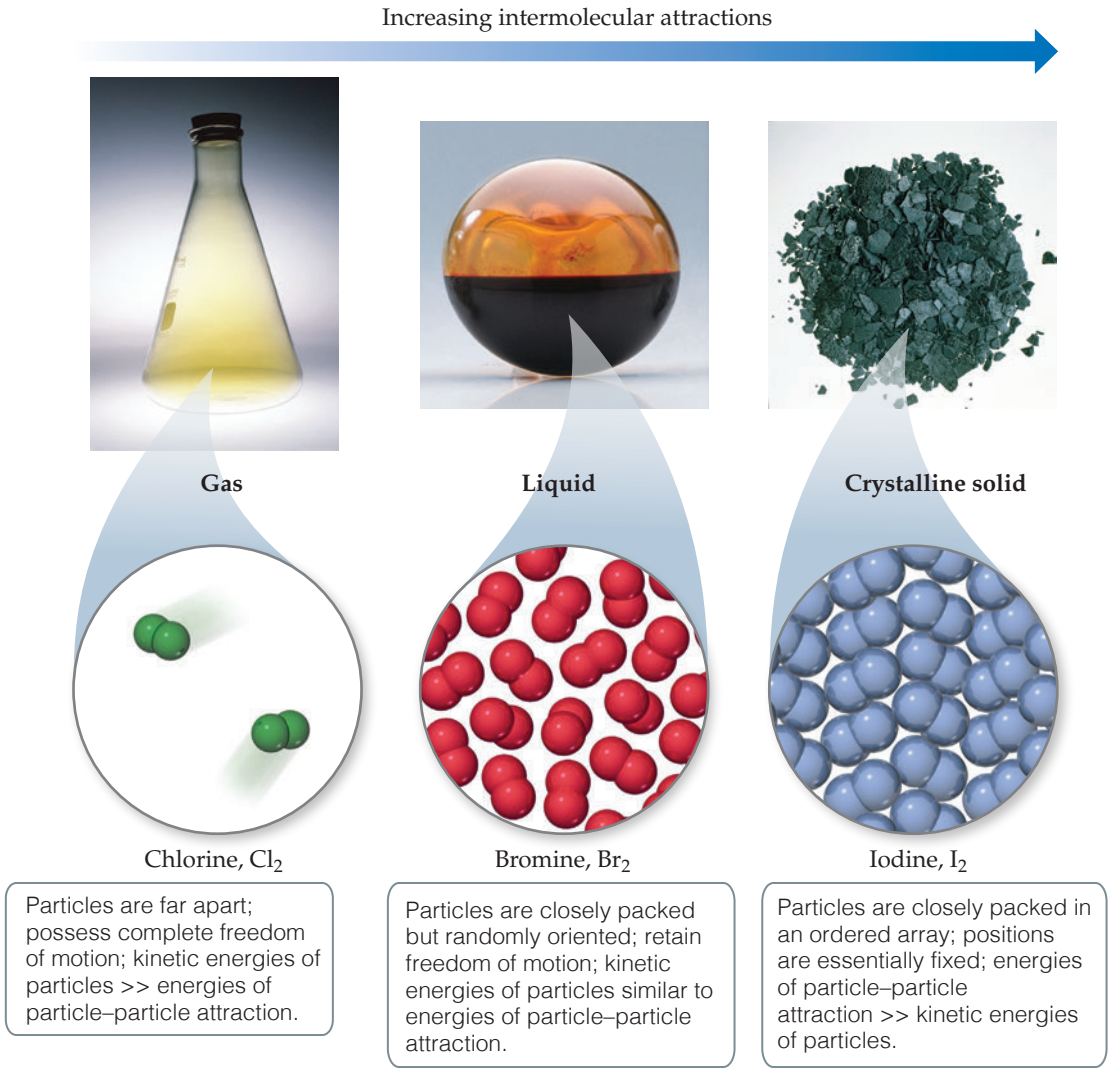
We can change a substance from one state to another by heating or cooling, which changes the average kinetic energy of the particles. NaCl, for example, a solid at room temperature, melts at 1074 K and boils at 1686 K under a pressure of 101.3 kPa, and Cl_2, a gas at room temperature, liquefies at 239 K and solidifies at 172 K under a pressure of 101.3 kPa. As the temperature of a gas decreases, the average kinetic energy of its particles decreases, allowing the attractions between the particles to draw the particles close together, forming a liquid, and then to virtually lock them in place, forming a solid. Increasing the pressure on a gas can also drive transformations from gas to liquid to solid because the increased pressure brings the molecules closer together, thus making intermolecular forces more effective. For example, propane (C_3H_8) is a gas at room temperature and 101.3 kPa, whereas liquefied propane (LP) is a liquid at room temperature because it is stored under much higher pressure.

TABLE 11.1 Characteristic Properties of the States of Matter

Gas	Liquid	Solid
Assumes both volume and shape of its container	Assumes shape of portion of container it occupies	Retains own shape and volume
Expands to fill its container	Does not expand to fill its container	Does not expand to fill its container
Is compressible	Is virtually incompressible	Is virtually incompressible
Flows readily	Flows readily	Does not flow
Diffusion within a gas occurs rapidly	Diffusion within a liquid occurs slowly	Diffusion within a solid occurs extremely slowly

*The atoms in a solid are able to vibrate in place. As the temperature of the solid increases, the vibrational motion increases.

Go Figure For a given substance, do you expect the density of the substance in its liquid state to be closer to the density in the gaseous state or in the solid state?



▲ **Figure 11.1 Gases, liquids, and solids.** Chlorine, bromine, and iodine are all diatomic molecules as a result of covalent bonding. However, due to differences in the strength of the intermolecular forces, they exist in three different states at room temperature and standard pressure: Cl_2 is a gas, Br_2 is a liquid, and I_2 is a solid.

Self-Assessment Exercise

11.1 A substance has a density of around 1 g/L. Is it likely to be a solid, liquid, or gas? Hint: think of the density of water for comparison.

(a) Solid

(b) Liquid

(c) Gas

Exercises

11.2 (**a**) How does the average kinetic energy of molecules compare with the average energy of attraction between molecules in solids, liquids, and gases? (**b**) Why does increasing the temperature cause a solid substance to change in succession from a solid to a liquid to a gas? (**c**) What happens to a gas if you put it under extremely high pressure?

11.3 At room temperature, CO_2 is a gas, CCl_4 is a liquid, and C_{60} (fullerene) is a solid. List these substances in order of (**a**) increasing intermolecular energy of attraction and (**b**) increasing boiling point.

11.4 At standard temperature and pressure, the molar volumes of Cl_2 and NH_3 gases are 22.06 and 22.40 L, respectively. (**a**) Given the different molecular weights, dipole moments, and molecular shapes, why are their molar volumes nearly the same? (**b**) On cooling to 160 K, both substances form crystalline solids. Do you expect the molar volumes to decrease or increase on cooling the gases to 160 K? (**c**) The densities of crystalline Cl_2 and NH_3 at 160 K are 2.02 and 0.84 g/cm^3, respectively. Calculate their molar volumes. (**d**) Are the molar volumes in the solid state as similar as they are in the gaseous state? Explain. (**e**) Would you expect the molar volumes in the liquid state to be closer to those in the solid or gaseous state?

Answers to Self-Assessment Exercises

11.1 (c)

11.2 | Intermolecular Forces



The lotus plant grows in aquatic environments. To thrive in such an environment, the surface of a lotus leaf is highly water repellent. Scientists call surfaces with this property "superhydrophobic." The superhydrophobic character of the lotus leaf not only allows it to float on water but also causes any water that falls on the leaf to bead up and roll off. The water drops collect dirt as they roll off, keeping the leaf clean, even in the muddy ponds and lakes where lotus plants tend to grow. Because of its self-cleaning properties, the lotus plant is considered a symbol of purity in many Eastern cultures.

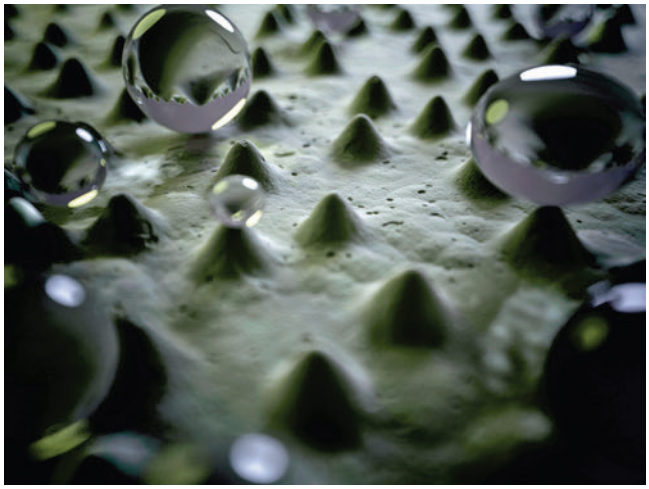
By the end of this section, you should be able to

- Identify the intermolecular forces that exist within a substance.

What forces cause the lotus leaf to repel water so efficiently? Although this plant's self-cleaning nature has been known for millennia, the effect was not fully understood until the 1970s, when scanning electron microscopy images revealed a rough leaf surface

(**Figure 11.2**). The rough surface helps minimize contact between water and leaf, and also minimizes contact between dirt and leaf so that the dirt does not stick.

The lotus effect has inspired scientists to design superhydrophobic surfaces for applications such as self-cleaning windows and water-repellent clothing. To understand the lotus effect and other phenomena involving liquids and solids, we must understand intermolecular forces, the forces that exist between molecules. Only by understanding the nature and strength of these forces can we understand how the composition and structure of a substance are related to its physical properties in the liquid or solid state.



▲ **Figure 11.2** **A microscopic view of a water droplets on the surface of a lotus leaf.**

The strengths of *intermolecular* forces, those forces acting between molecules, vary over a wide range but are generally much weaker than *intramolecular* forces—ionic, metallic, or covalent bonds (**Figure 11.3**). Less energy, therefore, is required to vaporize a liquid or melt a solid than to break covalent bonds. For example, only 16 kJ/mol is required to overcome the intermolecular attractions in liquid HCl to vaporize it. In contrast, the energy required to break the covalent bond in HCl is 431 kJ/mol. Thus, when a molecular substance such as HCl changes from solid to liquid to gas, the molecules remain intact.

Many properties of liquids, including boiling points, reflect the strength of the intermolecular forces. A liquid boils when bubbles of its vapor form within the liquid. The molecules of the liquid must overcome their attractive forces to separate and form a vapor. The stronger the attractive forces, the higher the temperature at which the liquid boils. Similarly, the melting points of solids increase as the strengths of the intermolecular forces increase. As shown in **Table 11.2**, the melting and boiling points of substances in which the particles are held together by chemical bonds tend to be much higher than those of substances in which the particles are held together by intermolecular forces.

There are three types of intermolecular attractions that exist between electrically neutral molecules:

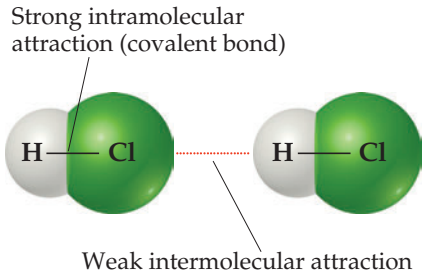
- dispersion forces
- dipole–dipole attractions
- hydrogen bonding.

The first two are collectively called *van der Waals forces* after Johannes van der Waals (1837–1923), who developed the equation for predicting the deviation of gases from ideal behavior. Another kind of attractive force, the ion–dipole force, is important in solutions.

All intermolecular interactions are electrostatic, involving attractions between positive and negative species, much like ionic bonds. Why then are intermolecular forces so much weaker than ionic bonds? Recall from Equation 8.4 that electrostatic interactions

Go Figure

How would you expect the H—Cl distance represented by the red dotted line to compare with the H—Cl distance within the HCl molecule?



▲ **Figure 11.3** **Intermolecular and intramolecular interactions.**

TABLE 11.2 Melting and Boiling Points of Representative Substances

Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
Chemical bonds			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
Intermolecular forces			
Dispersion forces	Nitrogen (N_2)	63	77
Dipole–dipole interactions	Hydrogen chloride (HCl)	158	188
Hydrogen bonding	Hydrogen fluoride (HF)	190	293

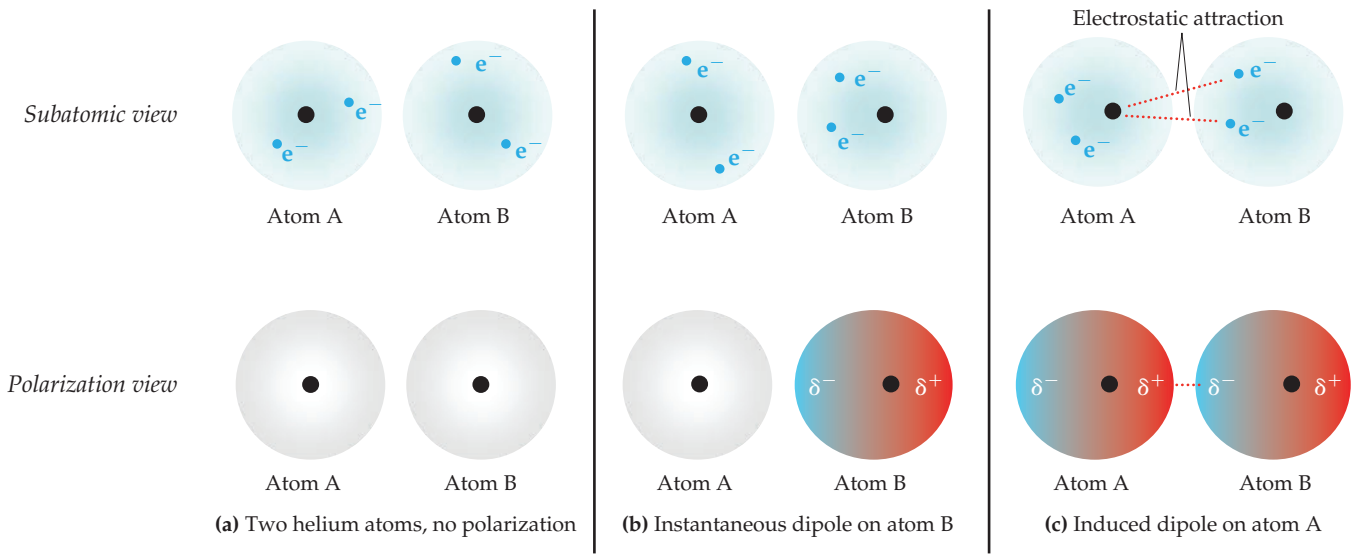
get stronger as the magnitude of the charges increases and weaker as the distance between charges increases. The charges responsible for intermolecular forces are generally much smaller than the charges in ionic compounds. For example, from its dipole moment it is possible to estimate charges of +0.178 and −0.178 for the hydrogen and chlorine ends of the HCl molecule, respectively (see Sample Exercise 8.5). Furthermore, the distances between molecules are often larger than the distances between atoms held together by chemical bonds.

Dispersion Forces

You might think there would be no electrostatic interactions between electrically neutral, nonpolar atoms and/or molecules. Yet some kind of attractive interactions must exist because nonpolar gases like helium, argon, and nitrogen can be liquefied. Fritz London, a German-American physicist, first proposed the origin of this attraction in 1930. London recognized that the motion of electrons in an atom or molecule can create an *instantaneous,* or momentary, dipole moment.

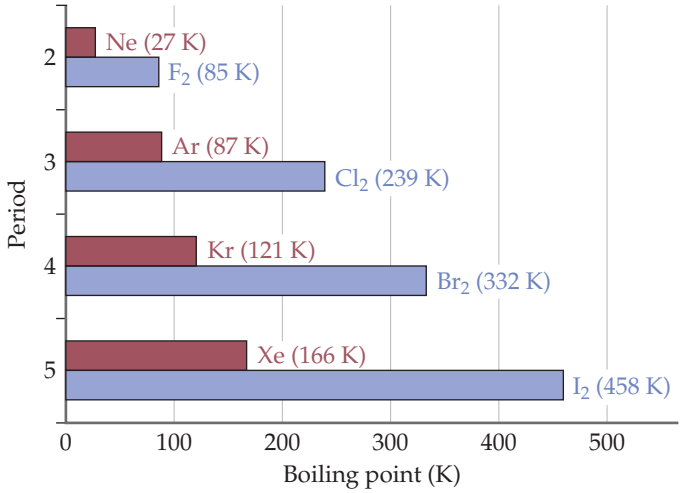
In a collection of helium atoms, for example, the *average* distribution of the electrons about each nucleus is spherically symmetrical, as shown in Figure 11.4(**a**). The atoms are nonpolar and so possess no permanent dipole moment. The *instantaneous* distribution of the electrons, however, can be different from the average distribution. If we could freeze the motion of the electrons at any given instant, both electrons could be on one side of the nucleus. At just that instant, the atom has an instantaneous dipole moment as shown in Figure 11.4(**b**). The motions of electrons in one atom influence the motions of electrons in its neighbors. The instantaneous dipole on one atom can induce an instantaneous dipole on an adjacent atom, causing the atoms to be attracted to each other as shown in Figure 11.4(**c**). This attractive interaction is called the **dispersion force** (also called *London dispersion forces* or *induced dipole–induced dipole interactions*). It is significant only when molecules are very close together.

The strength of the dispersion force depends on the ease with which the charge distribution in a molecule can be distorted to induce an instantaneous dipole. The ease with which the charge distribution is distorted is called the molecule's **polarizability**. We can think of the polarizability of a molecule as a measure of the "squashiness" of its electron cloud: The greater the polarizability, the more easily the electron cloud can be distorted to give an instantaneous dipole. Therefore, more polarizable molecules have larger dispersion forces.



▲ **Figure 11.4 Dispersion forces.** "Snapshots" of the charge distribution for a pair of helium atoms at three instants.

Go Figure Why is the boiling point of the halogen in each period greater than the noble gas?



▲ **Figure 11.5 Boiling points of the halogens and noble gases.** This plot shows how the boiling points increase due to stronger dispersion forces as the atomic/molecular weight increases.

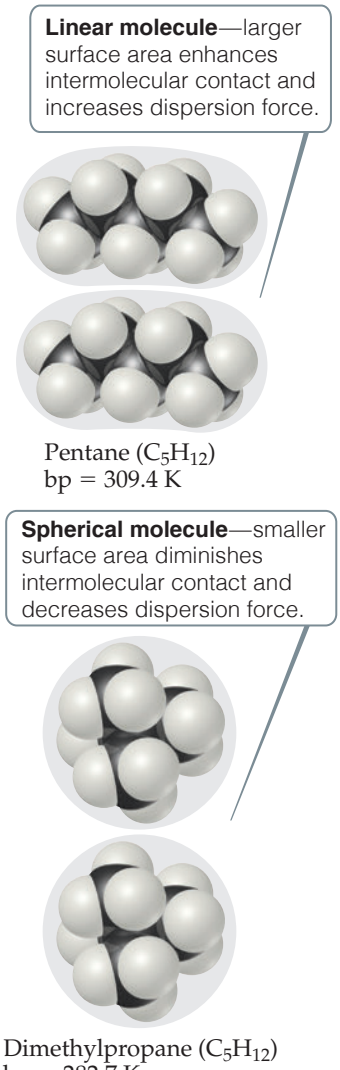
In general, polarizability increases as the number of electrons in an atom or molecule increases. The strength of dispersion forces therefore tends to increase with increasing atomic or molecular size. Because molecular size and mass generally parallel each other, *dispersion forces tend to increase in strength with increasing molecular weight*. We can see this in the boiling points of the halogens and noble gases (**Figure 11.5**), where dispersion forces are the only intermolecular forces at work. In both families the atomic/molecular weight increases on moving down the periodic table. The higher atomic/molecular weights translate into stronger dispersion forces, which in turn lead to higher boiling points.

Molecular shape also influences the magnitude of dispersion forces. For example, pentane and dimethylpropane (**Figure 11.6**) have the same molecular formula (C_5H_{12}), yet the boiling point of pentane is about 27 K higher than that of dimethylpropane. The difference can be traced to the different shapes of the two molecules. Intermolecular attraction is greater for pentane because the molecules can come in contact over the entire length of the long, somewhat cylindrical molecules. Less contact is possible between the more compact and nearly spherical dimethylpropane molecules.

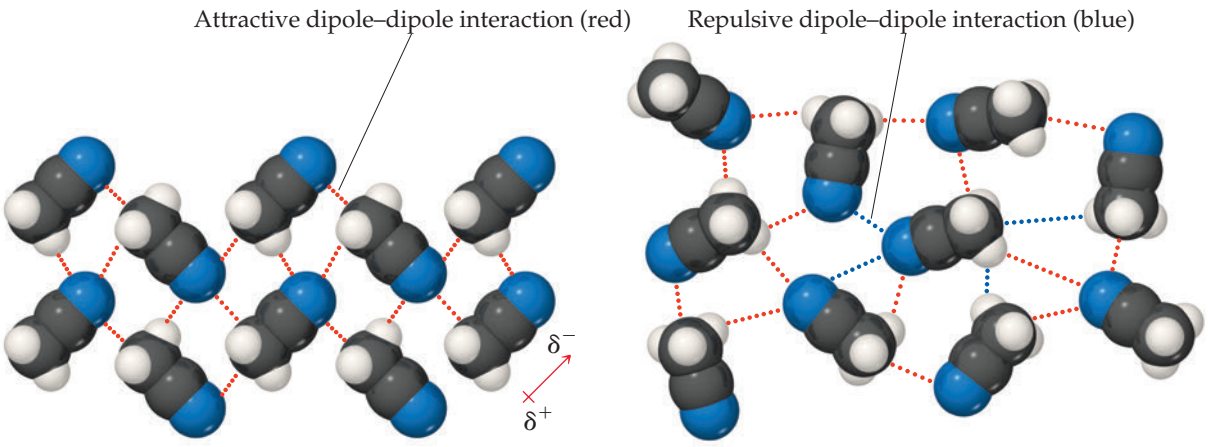
Dipole–Dipole Interactions

The presence of a permanent dipole moment in polar molecules gives rise to **dipole–dipole interactions**. These interactions originate from electrostatic attractions between the partially positive end of one molecule and the partially negative end of a neighboring molecule. Repulsions can also occur when the positive (or negative) ends of two molecules are in close proximity. Dipole–dipole interactions are effective only when molecules are very close together.

To see the effect of dipole–dipole interactions, we compare the boiling points of two compounds of similar molecular weight: acetonitrile (CH_3CN, MW 41 u, bp 355 K) and propane ($CH_3CH_2CH_3$, MW 44 u, bp 231 K). Acetonitrile is a polar molecule, with a dipole moment of 3.9 D, so dipole–dipole interactions are present. However, propane is essentially nonpolar, which means that dipole–dipole interactions are absent. Because acetonitrile and propane have similar molecular weights, dispersion forces are similar for these two molecules. Therefore, the higher boiling point of acetonitrile can be attributed to dipole–dipole interactions.



▲ **Figure 11.6 Molecular shape affects intermolecular attraction.** Molecules of *n*-pentane make more contact with each other than do neopentane molecules. Thus, *n*-pentane has stronger intermolecular attractive forces and therefore a higher boiling point.



▲ **Figure 11.7 Dipole–dipole interactions.** The dipole–dipole interactions in (**a**) crystalline CH_3CN and (**b**) liquid CH_3CN.

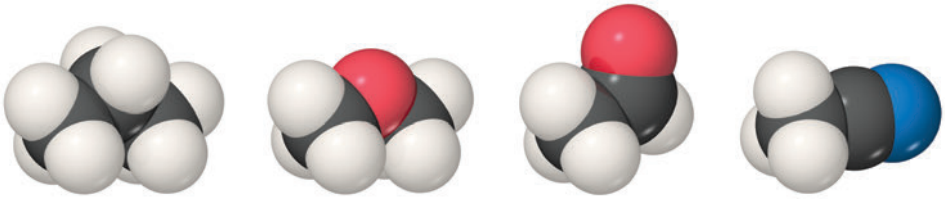
To better understand these forces, consider how CH_3CN molecules pack together in the solid and liquid states. In the solid [**Figure 11.7**(**a**)], the molecules are arranged with the negatively charged nitrogen end of each molecule close to the positively charged $—CH_3$ ends of its neighbors. In the liquid [Figure 11.7(**b**)], the molecules are free to move with respect to one another, and their arrangement becomes more disordered. This means that, at any given instant, both attractive and repulsive dipole–dipole interactions are present. However, not only are there more attractive interactions than repulsive ones, but also molecules that are attracting each other spend more time near each other than do molecules that are repelling each other. The overall effect is a net attraction strong enough to keep the molecules in liquid CH_3CN from moving apart to form a gas.

For molecules of approximately equal mass and size, the strength of intermolecular attractions increases with increasing polarity, a trend we see in **Figure 11.8**. Notice how the boiling point increases as the dipole moment increases.

Hydrogen Bonding

Figure 11.9 shows the boiling points of the binary compounds that form between hydrogen and the elements in Groups 14 through 17. The boiling points of the compounds containing

Go Figure Moving from left to right, do the dispersion forces get stronger, get weaker, or stay roughly the same in the molecules shown here?

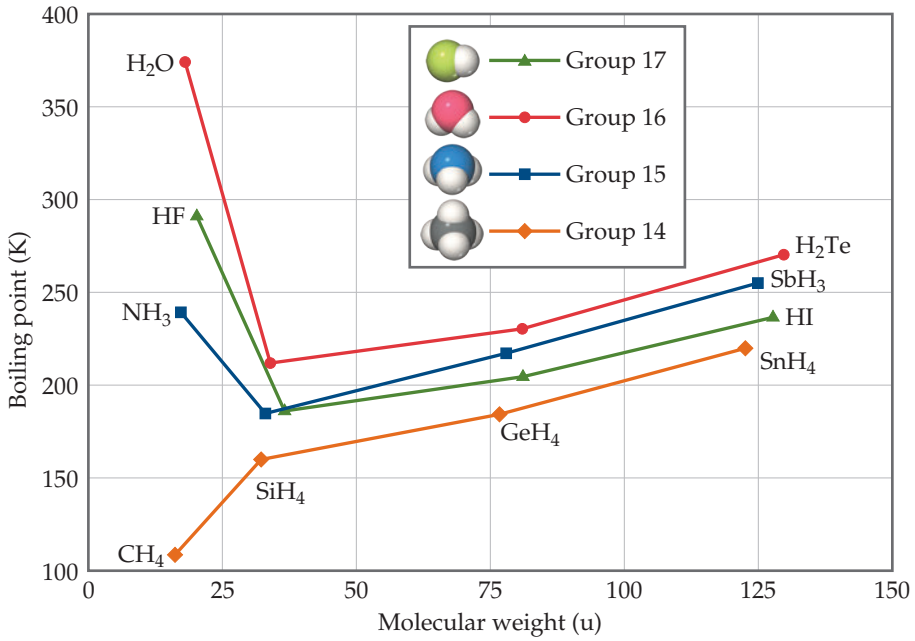


Propane	Dimethyl ether	Acetaldehyde	Acetonitrile
$CH_3CH_2CH_3$	CH_3OCH_3	CH_3CHO	CH_3CN
MW = 44 u	MW = 46 u	MW = 44 u	MW = 41 u
μ = 0.1 D	μ = 1.3 D	μ = 2.7 D	μ = 3.9 D
bp = 231 K	bp = 248 K	bp = 294 K	bp = 355 K

Increasing polarity
Increasing dipole–dipole interactions

▲ **Figure 11.8 Molecular weights, dipole moments, and boiling points of several simple organic substances.**

Go Figure Explain the difference in boiling points between PH_3 and AsH_3.

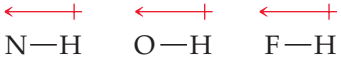


▲ **Figure 11.9 Boiling points of the covalent hydrides of the elements in Groups 14–17 as a function of molecular weight.**

Group 14 elements (CH_4 through SnH_4, all nonpolar) increase systematically moving down the group. This is the expected trend because polarizability and, hence, dispersion forces generally increase as molecular weight increases. The heavier members of Groups 15, 16, and 17 follow the same trend, but NH_3, H_2O, and HF have boiling points that are much higher than expected. In fact, these three compounds also have many other characteristics that distinguish them from other substances of similar molecular weight and polarity. For example, water has a high melting point, a high specific heat, and a high heat of vaporization. Each of these properties indicates that the intermolecular forces are abnormally strong.

The strong intermolecular attractions in HF, H_2O, and NH_3 result from *hydrogen bonding*. *A* ***hydrogen bond*** *is an attraction between a hydrogen atom attached to a highly electronegative atom (usually F, O, or N) and a nearby small electronegative atom in another molecule or chemical group.* Thus, H—F, H—O, or H—N bonds in one molecule can form hydrogen bonds with an F, O, or N atom in another molecule. Several examples of hydrogen bonds are shown in **Figure 11.10**, including the hydrogen bond that exists between the H atom in an H_2O molecule and the O atom of an adjacent H_2O molecule. Notice in each case that the H atom in the hydrogen bond interacts with a nonbonding electron pair.

Hydrogen bonds can be considered a special type of dipole–dipole attraction. Because N, O, and F are so electronegative, a bond between hydrogen and any of these elements is quite polar, with hydrogen at the positive end (remember the + on the right-hand side of the dipole symbol represents the positive end of the dipole):

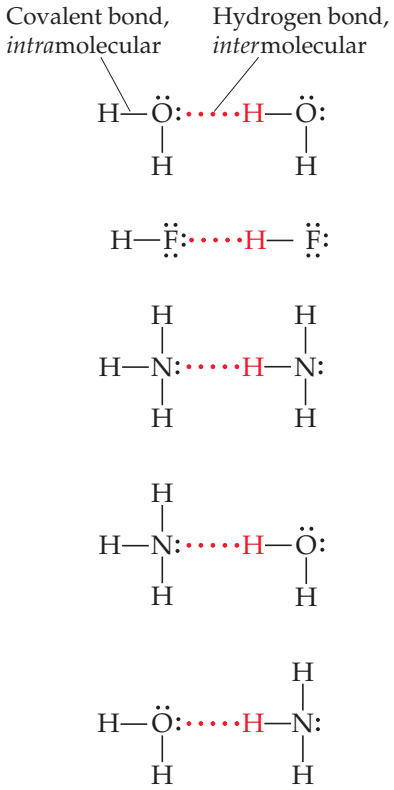


The hydrogen atom has no inner electrons. Thus, the positive side of the dipole has the concentrated charge of the nearly bare hydrogen nucleus. This positive charge is attracted to the negative charge of an electronegative atom in a nearby molecule. Because the electron-poor hydrogen is so small, it can approach an electronegative atom very closely and, thus, interact strongly with it.

Hydrogen bonding plays important roles in many chemical systems, especially those of biological significance. For example, hydrogen bonding helps stabilize the three-dimensional structure of proteins, which is critical to their function. Hydrogen bonding is also responsible for the double-helical structure of DNA, which is key to its genetic function.

Go Figure

To form a hydrogen bond, what must the nonhydrogen atom (N, O, or F) involved in the bond possess?



▲ **Figure 11.10 Hydrogen bonding.** Hydrogen bonding occurs between an H atom that is bonded to N, O, or F in one molecule and an N, O, or F atom in another molecule.

Sample Exercise 11.1

Identifying Substances That Can Form Hydrogen Bonds

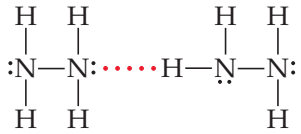
In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), fluoromethane (CH_3F), hydrogen sulfide (H_2S)?

SOLUTION

Analyze We are given the chemical formulas of four compounds and asked to predict whether they can participate in hydrogen bonding. All the compounds contain H, but hydrogen bonding usually occurs only when the hydrogen is covalently bonded to N, O, or F.

Plan We analyze each formula to see if it contains N, O, or F directly bonded to H. There also needs to be a nonbonding pair of electrons on an electronegative atom (usually N, O, or F) in a nearby molecule, which can be revealed by drawing the Lewis structure for the molecule.

Solve The foregoing criteria eliminate CH_4 and H_2S, which do not contain H bonded to N, O, or F. They also eliminate CH_3F, whose Lewis structure shows a central C atom surrounded by three H atoms and an F atom. (Carbon always forms four bonds, whereas hydrogen and fluorine form one each.) Because the molecule contains a C—F bond and not an H—F bond, it does not form hydrogen bonds. In H_2NNH_2, however, we find N—H bonds, and the Lewis structure shows a nonbonding pair of electrons on each N atom, telling us hydrogen bonds can exist between the molecules:



Check Although we can generally identify substances that participate in hydrogen bonding based on their containing N, O, or F covalently bonded to H, drawing the Lewis structure for the interaction provides a way to check the prediction.

Practice Exercise

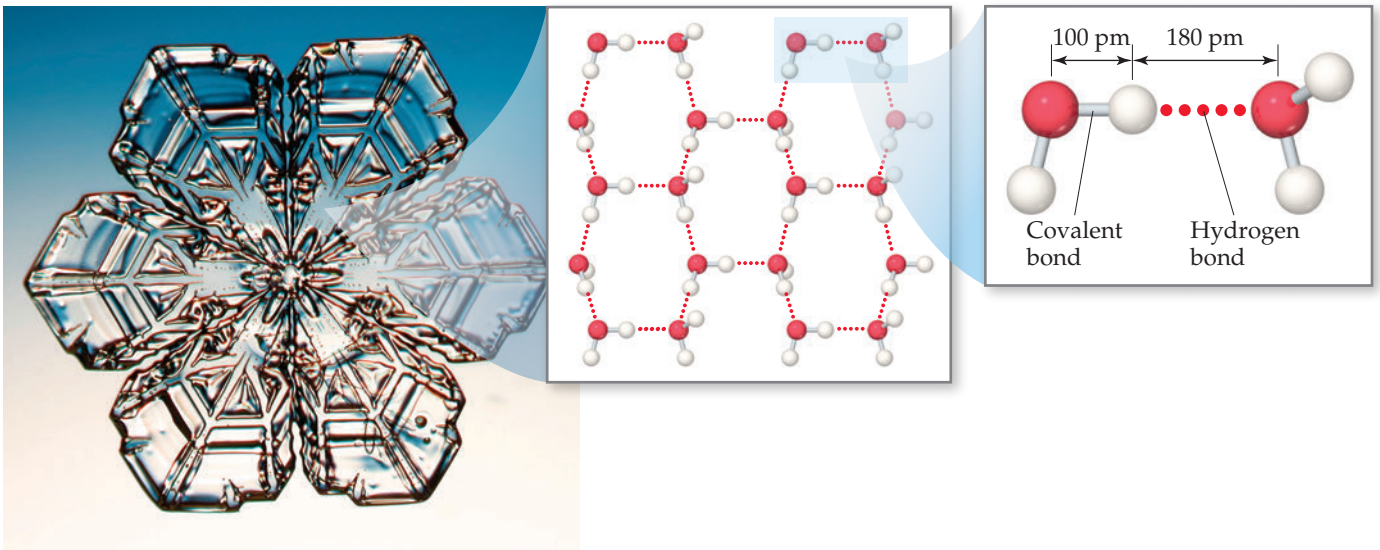
Which of the following substances is most likely to be a liquid at room temperature?

(**a**) formaldehyde, H_2CO (**b**) fluoromethane, CH_3F
(**c**) hydrogen cyanide, HCN (**d**) hydrogen peroxide, H_2O_2
(**e**) hydrogen sulfide, H_2S

One remarkable consequence of hydrogen bonding is seen in the densities of ice and liquid water. In most substances the molecules in the solid are more densely packed than those in the liquid, making the solid phase denser than the liquid phase. By contrast, the density of ice at 0 °C (0.917 g/mL) is less than that of liquid water at 0 °C (1.00 g/mL), so ice floats on liquid water.

The lower density of ice can be understood in terms of hydrogen bonding. In ice, the H_2O molecules assume the ordered, open arrangement shown in **Figure 11.11**. This

Go Figure What is the approximate H—O · · · H bond angle in ice, where H—O is the covalent bond and O · · · H is the hydrogen bond?



▲ **Figure 11.11 Hydrogen bonding in ice.** The empty channels in the structure of ice make water less dense as a solid than as a liquid.

arrangement optimizes hydrogen bonding between molecules, with each H_2O molecule forming hydrogen bonds to four neighboring H_2O molecules. These hydrogen bonds, however, create the cavities seen in the middle image of Figure 11.11. When ice melts, the motions of the molecules cause the structure to collapse. The hydrogen bonding in the liquid is more random than that in the solid but is strong enough to hold the molecules close together. Consequently, liquid water has a denser structure than ice, meaning that a given mass of water occupies a smaller volume than the same mass of ice.

The expansion of water upon freezing (**Figure 11.12**) is responsible for many phenomena we take for granted. It causes icebergs to float and water pipes to burst in cold weather. The lower density of ice compared to liquid water also profoundly affects life on Earth. Because ice floats, it covers the top of the water when a lake freezes, thereby insulating the water. If ice were denser than water, ice forming at the top of a lake would sink to the bottom, and the lake could freeze solid. Most aquatic life could not survive under these conditions.



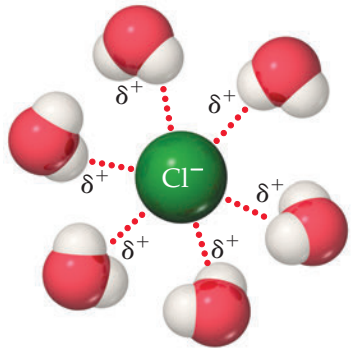
▲ **Figure 11.12** **Expansion of water upon freezing.**

Ion–Dipole Forces

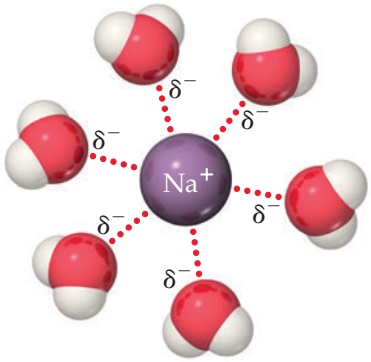
An **ion–dipole force** exists between an ion and a polar molecule (**Figure 11.13**). Cations are attracted to the negative end of a dipole, and anions are attracted to the positive end. The magnitude of the attraction increases as either the ionic charge or the magnitude of the dipole moment increases. Ion–dipole forces are especially important for solutions of ionic substances in polar liquids, such as a solution of NaCl in water.

Go Figure

Why does the O side of H_2O point toward the Na^+ ion?



Positive ends of polar molecules are oriented toward negatively charged anion.



Negative ends of polar molecules are oriented toward positively charged cation.

▲ **Figure 11.13** **Ion–dipole forces.**

Comparing Intermolecular Forces

We can identify the intermolecular forces operative in a substance by considering its composition and structure. *Dispersion forces are found in all substances.* The strength of these attractive forces increases with increasing molecular weight and depends on molecular shapes. With polar molecules dipole–dipole interactions are also operative, but these interactions often make a smaller contribution to the total intermolecular attraction than do dispersion forces. For example, in liquid HCl, dispersion forces are estimated to account for more than 80% of the total attraction between molecules, while dipole–dipole attractions account for the rest. Hydrogen bonds, when present, make an important contribution to the total intermolecular interaction.

In general, the energies associated with dispersion forces are 0.1–30 kJ/mol. The wide range reflects the wide range in polarizabilities of molecules. By comparison, the energies associated with dipole–dipole interactions and hydrogen bonds are approximately 2–15 kJ/mol and 10–40 kJ/mol, respectively. Ion–dipole forces tend to be stronger than the aforementioned intermolecular forces, with energies typically exceeding 50 kJ/mol. All these interactions are considerably weaker than covalent and ionic bonds, which have energies that are hundreds of kilojoules per mole.

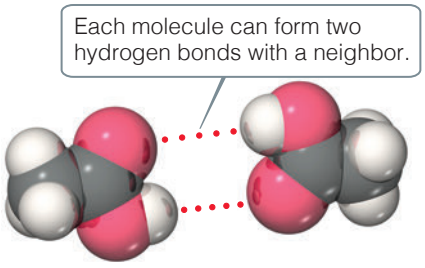
Figure 11.14 presents a systematic way of identifying the intermolecular forces in a particular system.

It is important to realize that the effects of all these attractions are additive. For example, acetic acid, CH_3COOH, and 1-propanol, $CH_3CH_2CH_2OH$, have the same molecular weight, 60 u, and both are capable of forming hydrogen bonds. However, a pair of acetic acid molecules can form two hydrogen bonds, whereas a pair of 1-propanol molecules can form only one (**Figure 11.15**). Hence, the boiling point of acetic acid is higher. These effects can be important, especially for very large polar molecules such as proteins, which have multiple dipoles and hydrogen-bonding groups over their surfaces. These molecules can be held together in solution to a surprisingly high degree due to the presence of multiple attractive interactions.

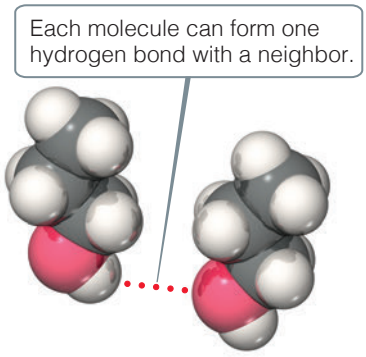
Go Figure Can the energies of multiple dispersion forces between two molecules be larger than the energy of hydrogen bonding between the two molecules?

Type of intermolecular interaction	Atoms Examples: Ne, Ar	Nonpolar molecules Examples: BF_3, CH_4	Polar molecules without OH, NH, or HF groups Examples: HCl, CH_3CN	Polar molecules containing OH, NH, or HF groups Examples: H_2O, NH_3	Ionic solids dissolved in polar liquids Examples: NaCl in H_2O
Dispersion forces (0.1–30 kJ/mol)	√	√	√	√	√
Dipole–dipole interactions (2–15 kJ/mol)			√	√	
Hydrogen bonding (10–40 kJ/mol)				√	
Ion–dipole interactions (>50 kJ/mol)					√

▲ **Figure 11.14 Checklist for determining intermolecular forces.** Multiple types of intermolecular forces can be operating in a given substance or mixture. Note that dispersion forces occur in all substances.



Acetic acid, CH_3COOH
MW = 60 u
bp = 391 K



1-Propanol, $CH_3CH_2CH_2OH$
MW = 60 u
bp = 370 K

▲ **Figure 11.15 Hydrogen bonding in acetic acid and 1-propanol.** The greater the number of hydrogen bonds possible, the more tightly the molecules are held together and, therefore, the higher the boiling point.

When comparing the relative strengths of intermolecular attractions, consider these generalizations:

1. **When the molecules of two substances have comparable molecular weights and shapes, dispersion forces are approximately equal in the two substances.** Differences in the magnitudes of the intermolecular forces are due to differences in the strengths of dipole–dipole attractions. The intermolecular forces get stronger as molecule polarity increases, with those molecules capable of hydrogen bonding having the strongest interactions.
2. **When the molecules of two substances differ widely in molecular weights, and there is no hydrogen bonding, dispersion forces tend to determine which substance has the stronger intermolecular attractions.** Intermolecular attractive forces are generally higher in the substance with higher molecular weight.

Self-Assessment Exercise

11.5 Rank the following molecules from lowest to highest boiling point: $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2OCH_3$

(a) $CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_3 < CH_3CH_2OCH_3$

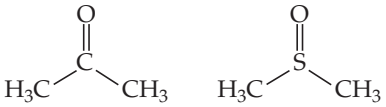
(b) $CH_3CH_2CH_2CH_3 < CH_3CH_2OCH_3 < CH_3CH_2CH_2OH$

(c) $CH_3CH_2OCH_3 < CH_3CH_2CH_2CH_3 < CH_3CH_2CH_2OH$

Exercises

11.6 (**a**) Which is generally stronger, intermolecular interactions or intramolecular interactions? (**b**) Which of these kinds of interactions are broken when a liquid is converted to a gas?

11.7 Which type of intermolecular force accounts for each of these differences? (**a**) Acetone, $(CH_3)_2CO$, boils at 56 °C; dimethyl sulfoxide or DMSO, $(CH_3)_2SO$, boils at 189 °C. (**b**) CCl_4 is a liquid at atmospheric pressure and room temperature, whereas CH_4 is a gas under the same conditions. (**c**) H_2O boils at 100 °C but H_2S boils at −60 °C. (**d**) 1-propanol $(CH_3CH_2CH_2OH)$ boils at 97 °C, whereas 2-propanol $(CH_3CH(OH)CH_3)$ boils at 82.6 °C.



Acetone DMSO

11.8 True or false: (**a**) Molecules containing polar bonds must be polar molecules and have dipole–dipole forces. (**b**) For the halogen gases, the dispersion forces decrease while the boiling points increase as you go down the column in the periodic table. (**c**) In terms of the total attractive forces for a given substance, the more polar bonds there are in a molecule, the stronger the dipole–dipole interaction. (**d**) All other factors being the same, total attractive forces between linear molecules are greater than those between molecules whose shapes are nearly spherical. (**e**) The more electronegative the atom, the more polarizable it is.

11.9 Which member in each pair has the stronger intermolecular dispersion forces? (**a**) H_2O or CH_3OH, (**b**) CBr_3CBr_3 or CCl_3CCl_3, (**c**) $C(CH_3)_4$ or $CH_3CH_2CH_2CH_2CH_3$.

11.10 (**a**) What atoms must a molecule contain to participate in hydrogen bonding with other molecules of the same kind? (**b**) Which of the following molecules can form hydrogen bonds with other molecules of the same kind: CH_3F, CH_3NH_2, CH_3OH, CH_3Br?

11.11 Based on the type or types of intermolecular forces, predict the substance in each pair that has the higher boiling point: (**a**) propane (C_3H_8) or *n*-butane (C_4H_{10}), (**b**) diethyl ether $(CH_3CH_2OCH_2CH_3)$ or 1-butanol $(CH_3CH_2CH_2CH_2OH)$, (**c**) sulfur dioxide (SO_2) or sulfur trioxide (SO_3), (**d**) phosgene (Cl_2CO) or formaldehyde (H_2CO).

11.12 Freon, CCl_2F_2, and dichloromethane, CH_2Cl_2, are common organic substances. Freon is a gas with a normal boiling point of −29.8 °C; dichloromethane's normal boiling point is 39.6 °C. Which statement is the best explanation of these data? (**a**) Dichloromethane can form hydrogen bonds, but freon cannot. (**b**) Dichloromethane has a larger dipole moment than freon. (**c**) Freon is more polarizable than dichloromethane.

Answers to Self-Assessment Exercises

11.5 (b)

11.3 Select Properties of Liquids



Honey is an example of a non-Newtonian fluid; that is, one in which viscosity changes with the applied stress. Another that you may be familiar with is a suspension of corn starch in water. In the case of honey, its viscosity increases as a sheer force is applied. Dip a spoon into a honey jar and try and stir it rapidly and you find the honey acts as a very viscous material. Remove the spoon and the honey flows smoothly off the spoon.

The intermolecular attractions we have just discussed can help us understand many familiar properties of liquids. In this section, we examine three: viscosity, surface tension, and capillary action.

By the end of this section, you should be able to

- Explain the concepts of viscosity, surface tension, and capillary action.

Sample Exercise 11.2

Predicting Types and Relative Strengths of Intermolecular Attractions

List the substances $BaCl_2$, H_2, CO, HF, and Ne in order of increasing boiling point.

SOLUTION

Analyze We need to assess the intermolecular forces in these substances and use that information to determine the relative boiling points.

Plan The boiling point depends in part on the attractive forces in each substance. We need to order these substances according to the relative strengths of the different kinds of intermolecular attractions.

Solve The attractive forces are stronger for ionic substances than for molecular ones, so $BaCl_2$ should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2, 2 u; CO, 28 u; HF, 20 u; and Ne, 20 u. The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO, HF, and Ne are similar. Because HF can hydrogen-bond, it should have the highest boiling point of the three. Next is CO, which is slightly polar and has the highest molecular weight. Finally, Ne, which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is, therefore,

$$H_2 < Ne < CO < HF < BaCl_2$$

Check The boiling points reported in the literature are H_2, 20 K; Ne, 27 K; CO, 83 K; HF, 293 K; and $BaCl_2$, 1813 K—in agreement with our predictions.

Practice Exercise

List the substances Ar, Cl_2, CH_4, and CH_3COOH in order of increasing strength of intermolecular attractions.

(**a**) $CH_4 < Ar < CH_3COOH < Cl_2$
(**b**) $Cl_2 < CH_3COOH < Ar < CH_4$
(**c**) $CH_4 < Ar < Cl_2 < CH_3COOH$
(**d**) $CH_3COOH < Cl_2 < Ar < CH_4$
(**e**) $Ar < Cl_2 < CH_4 < CH_3COOH$



SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

▲ **Figure 11.16 Comparing viscosities.** The Society of Automotive Engineers (SAE) has established a numeric scale to indicate motor-oil viscosity.

Viscosity

Some liquids, such as molasses and motor oil, flow very slowly; others, such as water and gasoline, flow easily. The resistance of a liquid to flow is called **viscosity**. The greater a liquid's viscosity, the more slowly it flows. Viscosity can be measured by timing how long it takes a certain amount of the liquid to flow through a thin vertical tube (Figure 11.16). Viscosity can also be determined by measuring the rate at which steel balls fall through the liquid. The balls fall more slowly as the viscosity increases. The SI unit for viscosity is kg/m s.

The viscosity of a liquid is related to how easily its molecules flow past one another. It depends on the attractive forces between molecules and on whether the shapes and flexibility of the molecules are such that they tend to become entangled (for example, long molecules can become tangled like spaghetti). For a series of related compounds, viscosity increases with molecular weight, as illustrated in Table 11.3.

TABLE 11.3 Viscosities of a Series of Hydrocarbons at 20 °C

Substance	Formula	Viscosity (kg/m-s)
Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	3.26×10^{-4}
Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	4.09×10^{-4}
Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	5.42×10^{-4}
Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	7.11×10^{-4}
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42×10^{-3}

CHEMISTRY PUT TO WORK Ionic Liquids

The strong electrostatic attractions between cations and anions explain why most ionic compounds are solids at room temperature, with high melting and boiling points. However, the melting point of an ionic compound can be low if the ionic charges are not too high and the cation–anion distance is sufficiently large. For example, the melting point of NH_4NO_3, where both cation and anion are larger polyatomic ions, is 170 °C. If the ammonium cation is replaced by the even larger ethylammonium cation, $CH_3CH_2NH_3^+$, the melting point drops to 12 °C, making ethylammonium nitrate a liquid at room temperature. Ethylammonium nitrate is an example of an *ionic liquid*: a salt that is a liquid at room temperature.

Not only is $CH_3CH_2NH_3^+$ larger than NH_4^+ but also it is less symmetric. In general, the larger and more irregularly shaped the ions in an ionic substance, the better the chances of forming an ionic liquid. Among the cations that form ionic liquids, one of the most widely used is the 1-butyl-3-methylimidazolium cation (abbreviated $bmim^+$, Figure 11.17 and Table 11.4), which has two arms of different lengths coming off a five-atom central ring. This feature gives $bmim^+$ an irregular shape, which makes it difficult for the molecules to pack together in a solid.

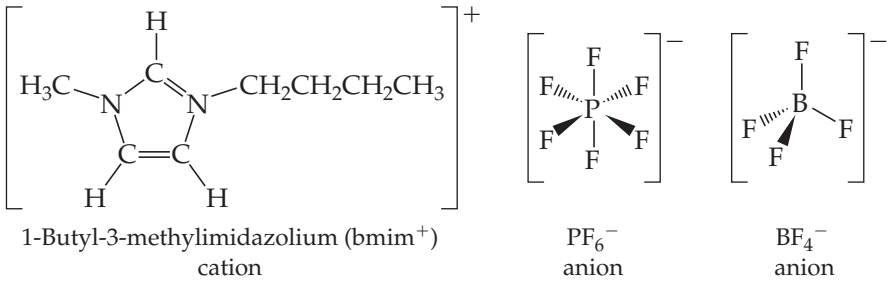
TABLE 11.4 Melting Point and Decomposition Temperature of Four 1-Butyl-3-Methylimidazolium ($bmim^+$) Salts

Cation	Anion	Melting Point (°C)	Decomposition Temperature (°C)
$bmim^+$	Cl^-	41	254
$bmim^+$	I^-	−72	265
$bmim^+$	PF_6^-	10	349
$bmim^+$	BF_4^-	−81	403

Common anions found in ionic liquids include the PF_6^-, BF_4^-, and halide ions.

Ionic liquids have many useful properties. Unlike most molecular liquids, they are nonvolatile (that is, they don't evaporate readily) and nonflammable. They tend to remain in the liquid state at temperatures up to about 400 °C. Most molecular substances are liquids only at much lower temperatures, 100 °C or less in most cases. Because ionic liquids are good solvents for a wide range of substances, ionic liquids can be used for a variety of reactions and separations. These properties make them attractive replacements for volatile organic solvents in many industrial processes. Relative to traditional organic solvents, ionic liquids offer the promise of reduced volumes, safer handling, and easier reuse, thereby reducing the environmental impact of industrial chemical processes.

Related Exercises: 11.59, 11.17, 11.89



1-Butyl-3-methylimidazolium ($bmim^+$) cation | PF_6^- anion | BF_4^- anion

▲ Figure 11.17 Representative ions found in ionic liquids.

The viscosity of a substance decreases with increasing temperature. This can be seen in the viscosity of octane:

$$7.06 \times 10^{-4}\ \text{kg/m s at } 0\ ^\circ\text{C}$$

$$4.33 \times 10^{-4}\ \text{kg/m s at } 40\ ^\circ\text{C}$$

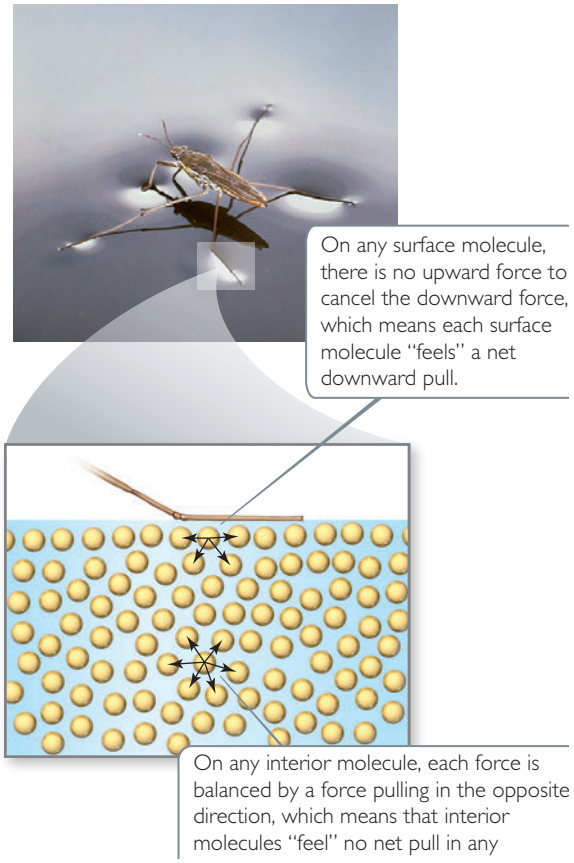
At higher temperatures, the greater average kinetic energy of the molecules overcomes the attractive forces between molecules.

Surface Tension

The surface of water behaves almost as if it had an elastic skin, as evidenced by the ability of certain insects to "walk" on water. This behavior is due to an imbalance of intermolecular forces at the surface of the liquid. As shown in Figure 11.18, molecules in the interior are attracted equally in all directions, but those at the surface experience a net inward force. This net force tends to pull surface molecules toward the interior, thereby reducing the surface area and making the molecules at the surface pack closely together.

Because spheres have the smallest surface area for their volume, water droplets assume an almost spherical shape. This explains the tendency of water to "bead up" when it contacts a surface made of nonpolar molecules, like a lotus leaf or a newly waxed car.

A measure of the net inward force that must be overcome to expand the surface area of a liquid is given by its surface tension. **Surface tension** is the energy required to increase the surface area of a liquid by a unit amount. For example, the surface tension of water at 20 °C is $7.29 \times 10^{-2}\ \text{J/m}^2$, which means that an energy of 7.29×10^{-2} J must be supplied to increase the surface area of a given amount of water by 1 m^2. Water has a



▲ **Figure 11.18 Molecular-level view of surface tension.** The high surface tension of water keeps the water strider from sinking.

high surface tension because of its strong hydrogen bonds. The surface tension of mercury is even higher ($4.6 \times 10^{-1}\,J/m^2$) because of even stronger metallic bonds between the atoms of mercury.

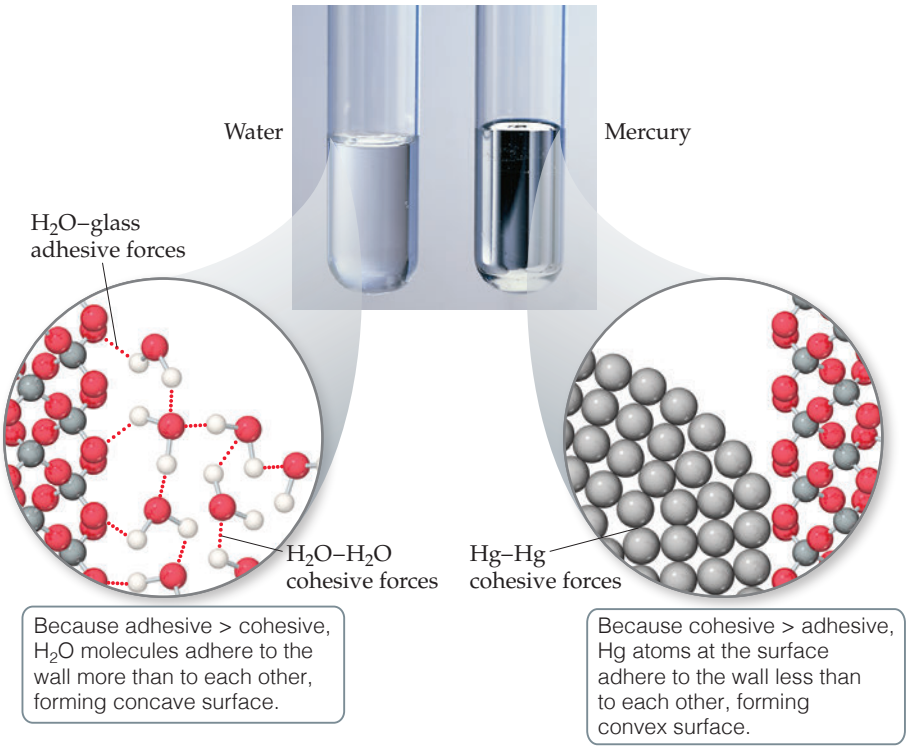
Capillary Action

Intermolecular forces that bind similar molecules to one another, such as the hydrogen bonding in water, are called *cohesive forces*. Intermolecular forces that bind a substance to a surface are called *adhesive forces*. Water placed in a glass tube adheres to the glass because the adhesive forces between the water and the glass are greater than the cohesive forces between water molecules; glass is principally SiO_2, which has a very polar surface. The curved surface, or *meniscus,* of the water is therefore U-shaped (**Figure 11.19**). For mercury, however, the situation is different. Mercury atoms can form bonds with one another but not with the glass. As a result, the cohesive forces are much greater than the adhesive forces and the meniscus is shaped like an inverted U.

When a small-diameter glass tube, or capillary, is placed in water, water rises in the tube. The rise of liquids up very narrow tubes is called **capillary action**. The adhesive forces between the liquid and the walls of the tube tend to increase the surface area of the liquid. The surface tension of the liquid tends to reduce the area, thereby pulling the liquid up the tube. The liquid climbs until the force of gravity on the liquid balances the adhesive and cohesive forces.

Capillary action is widespread. For example, towels absorb liquid, and "stay-dry" synthetic fabrics move sweat away from the skin by capillary action. Capillary action also plays a role in moving water and dissolved nutrients upward through plants.

Go Figure If the inside surface of each tube were coated with wax, would the general shape of the water meniscus change? Would the general shape of the mercury meniscus change?



▲ **Figure 11.19 Meniscus shapes for water and mercury in glass tubes.**

Self-Assessment Exercise

11.13 As the temperature increases, how do you expect the surface tension of a liquid to change?

(a) It would increase

(b) It would decrease

(c) It would stay the same

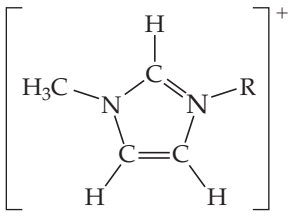
Exercises

11.14 Based on their composition and structure, list CH_3COOH, CH_3COOCH_3, and CH_3CH_2OH in order of (**a**) increasing intermolecular forces, (**b**) increasing viscosity, (**c**) increasing surface tension.

11.15 Hydrazine (H_2NNH_2), hydrogen peroxide (HOOH), and water (H_2O) all have exceptionally high surface tensions compared with other substances of comparable molecular weights. (**a**) Draw the Lewis structures for these three compounds. (**b**) What structural property do these substances have in common, and how might that account for the high surface tensions?

11.16 (**a**) Would you expect the viscosity of 2-propanol, $(CH_3)_2CHOH$, to be larger or smaller than the viscosity of ethanol, CH_3CH_2OH? (**b**) Would you expect the viscosity of 2-propanol to be smaller or larger than the viscosity of 1-propanol, $CH_3CH_2CH_2OH$?

11.17 The generic structural formula for a 1-alkyl-3-methylimidazolium cation is



where R is a $-CH_2(CH_2)_nCH_3$ alkyl group. The melting points of the salts that form between the 1-alkyl-3-methylimidazolium cation and the PF_6^- anion are as follows: R = CH_2CH_3 (m.p. = 60 °C), R = $CH_2CH_2CH_3$ (m.p. = 40 °C), R = $CH_2CH_2CH_2CH_3$ (m.p. = 10 °C), and R = $CH_2CH_2CH_2CH_2CH_2CH_3$ (m.p. = −61 °C). Why does the melting point decrease as the length of alkyl group increases?

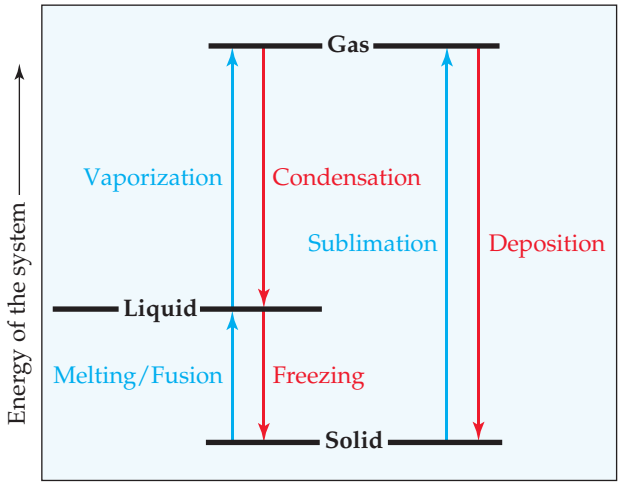
Answers to Self-Assessment Exercises

11.13 (b)

11.4 | Phase Changes



Go Figure How is energy evolved in deposition related to those for condensation and freezing?



▲ **Figure 11.20** **Phase changes and the names associated with them.**

Heat packs are often used for the on-site treatment of sports injuries. They consist of a flexible thick plastic bag divided into two compartments, one containing water and the other a salt. Breaking the seal between the compartments allows the salt to dissolve, and this is accompanied by a temperature change. Hot packs typically have magnesium sulfate or calcium chloride as the salt, which dissolves exothermically, while cold packs use ammonium nitrate or urea. These packs are for a single use. A variation is a reusable hot pack that contains a supercooled solution of sodium acetate and a small strip of metal. When the metal is bent, small changes on its surface initiate the crystallization of the sodium acetate from solution, releasing heat. The pack may be reused by heating it in boiling water to redissolve the sodium acetate, putting it aside and, without disturbing it, allowing it to cool to room temperature.

By the end of this section, you should be able to

- List the names of the various changes of state for a pure substance and indicate which are endothermic and which are exothermic.

Liquid water left uncovered in a glass eventually evaporates. An ice cube left in a warm room quickly melts. Solid CO_2 (sold as a product called dry ice) *sublimes* at room temperature; that is, it changes directly from solid to gas. In general, each state of matter—solid, liquid, gas—can transform into either of the other two states. **Figure 11.20** shows the names associated with these transformations, which are called either **phase changes** or *changes of state*.

Energy Changes Accompany Phase Changes

Every phase change is accompanied by a change in the energy of the system. In a solid, for example, the particles (molecules, ions, or atoms) are in more or less fixed positions with respect to one another and closely arranged to minimize the energy of the system. As the temperature of the solid increases, the particles vibrate about their equilibrium positions with increasing energetic motion. When the solid melts, the particles begin moving freely relative to one another, which means their average kinetic energy increases.

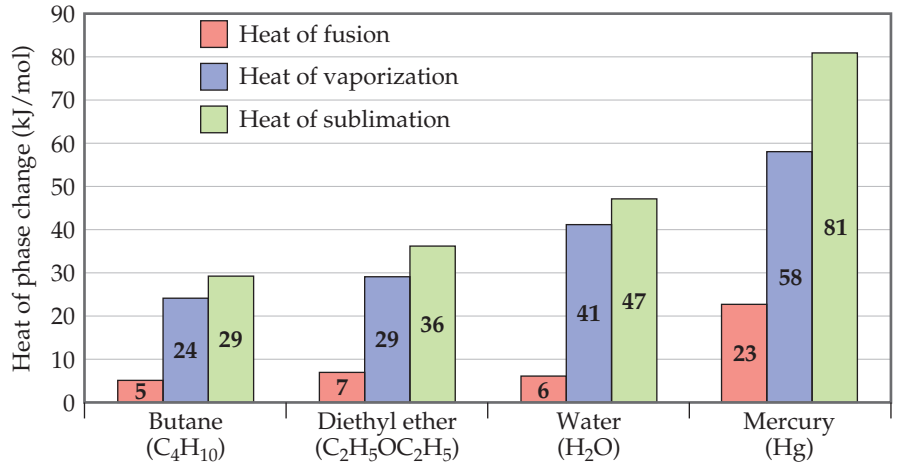
Melting is called (somewhat confusingly) *fusion*. The increased freedom of motion of the particles requires energy, measured by the **heat of fusion** or *enthalpy of fusion,* ΔH_{fus}. The heat of fusion of ice, for example, is 6.01 kJ/mol:

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H_{fus} = 6.01 \text{ kJ}$$

As the temperature of the liquid increases, the particles move about more vigorously. The increased motion allows some particles to escape into the gas phase. As a result, the concentration of gas-phase particles above the liquid surface increases with temperature. These gas-phase particles exert a pressure called *vapor pressure*. We explore vapor pressure in Section 11.5. For now we just need to understand that vapor pressure increases with increasing temperature until it equals the external pressure above the liquid, typically atmospheric pressure. At this point the liquid boils—bubbles of the vapor form within the liquid. The energy required to cause the transition of a given quantity of the liquid to the vapor is called either the **heat of vaporization** or the *enthalpy of vaporization,* ΔH_{vap}. For water, the heat of vaporization is 40.7 kJ/mol.

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H_{vap} = 40.7 \text{ kJ}$$

Go Figure Why does water have a higher heat of vaporization than diethyl ether?



▲ **Figure 11.21** **Heats of fusion, vaporization, and sublimation.**

Figure 11.21 shows ΔH_{fus} and ΔH_{vap} values for four substances. The values of ΔH_{vap} tend to be larger than the values of ΔH_{fus} because in the transition from liquid to gas, particles must essentially sever all their interparticle attractions, whereas in the transition from solid to liquid, many of these attractive interactions remain operative.

The particles of a solid can move directly into the gaseous state. The enthalpy change required for this transition is called the **heat of sublimation**, denoted ΔH_{sub}. As illustrated in Figure 11.20, ΔH_{sub} is the sum of ΔH_{fus} and ΔH_{vap}. Thus, ΔH_{sub} for water is approximately 47 kJ/mol.

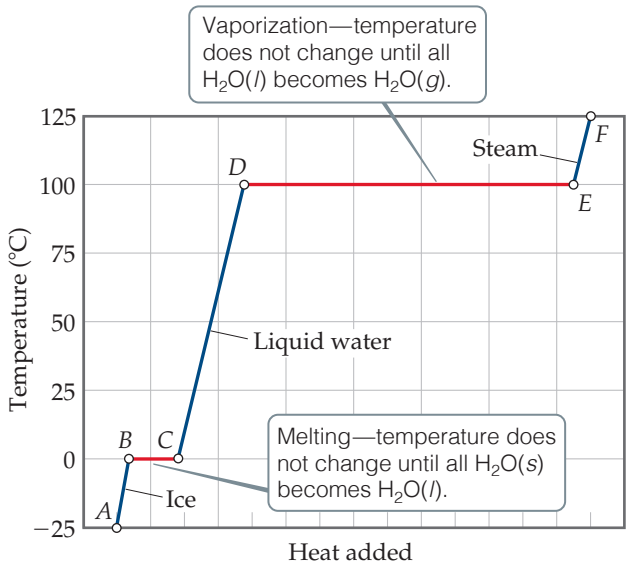
Phase changes show up in important ways in our everyday experiences. When we use ice cubes to cool a drink, for instance, the heat of fusion of the ice cools the liquid. We feel cool when we step out of a swimming pool or a warm shower because the liquid water's heat of vaporization is drawn from our bodies as the water evaporates from our skin. Our bodies use this mechanism to regulate body temperature, especially when we exercise vigorously in warm weather. A refrigerator also relies on the cooling effects of vaporization. Its mechanism contains an enclosed gas that can be liquefied under pressure. The liquid absorbs heat as it subsequently evaporates, thereby cooling the interior of the refrigerator.

What happens to the heat absorbed when the liquid refrigerant vaporizes? According to the first law of thermodynamics, this absorbed heat must be released when the gas condenses to liquid. As this phase change occurs, the heat released is dissipated through cooling coils in the back of the refrigerator. Just as for a given substance the heat of condensation is equal in magnitude to the heat of vaporization and has the opposite sign, so too the *heat of deposition* for a given substance is exothermic to the same degree that the heat of sublimation is endothermic; the *heat of freezing* is exothermic to the same degree that the heat of fusion is endothermic (see Figure 11.20).

Heating Curves

When we heat an ice cube initially at −25 °C and 101.3 kPa, the temperature of the ice increases. As long as the temperature is below 0 °C, the ice cube remains in the solid state. When the temperature reaches 0 °C, the ice begins to melt. Because melting is an endothermic process, the heat we add at 0 °C is used to convert ice to liquid water, and *the temperature remains constant until all the ice has melted*. Once all the ice has melted, adding more heat causes the temperature of the liquid water to increase.

Go Figure What process is occurring between points C and D?



▲ **Figure 11.22 Heating curve for water.** Changes that occur when 1.00 mol of H_2O is heated from $H_2O(s)$ at −25 °C to $H_2O(g)$ at 125 °C at a constant pressure of 101.3 kPa. Even though heat is being added continuously, the system temperature does not change during the two phase changes (red lines).

A graph of temperature versus amount of heat added is called a *heating curve*. **Figure 11.22** shows the heating curve for transforming ice, $H_2O(s)$, initially at −25 °C to steam, $H_2O(g)$, at 125 °C. As heat is added at a constant rate, the heating curve forms distinct regions:

- Line *AB:* Heating increases the temperature of $H_2O(s)$ from –25 to 0 °C.
- Line *BC*: Heating converts $H_2O(s)$ to $H_2O(l)$ as the ice melts at a constant temperature of 0 °C.
- Line *CD*: Heating increases the temperature of the $H_2O(l)$ from 0 °C to 100 °C.
- Line *DE*: Heating converts $H_2O(l)$ to $H_2O(g)$ as the water boils at a constant temperature of 100 °C.
- Line *EF*: Heating increases the temperature of the $H_2O(g)$ to 125 °C.

We can calculate the enthalpy change of the system for each region of the heating curve. Lines *AB, CD,* and *EF* show the heating of a single phase from one temperature to another. As we saw in Section 5.5, the amount of heat needed to raise the temperature of a substance is given by the product of the specific heat, mass, and temperature change (Equation 5.21). The greater the specific heat of a substance, the more heat we must add to accomplish a certain temperature increase. Because the specific heat of water is greater than that of ice, the slope of line *CD* is less than that of line *AB*. This lesser slope means the amount of heat we must add to a given mass of liquid water to achieve a 1 °C temperature change is greater than the amount we must add to achieve a 1 °C temperature change in the same mass of ice.

Lines *BC* and *DE* show the conversion of one phase to another at a constant temperature. The temperature remains constant during these phase changes because the added energy is used to overcome the attractive forces between molecules rather than to increase their average kinetic energy. For line *BC*, the enthalpy change can be calculated by using ΔH_{fus}, and for line *DE* we can use ΔH_{vap}.

If we start with 1 mol of steam at 125 °C and cool it, we move right to left across Figure 11.22. We first lower the temperature of the $H_2O(g)$ ($F \longrightarrow E$), then condense it ($E \longrightarrow D$) to $H_2O(l)$, and so forth.

Sometimes as we remove heat from a liquid, we can temporarily cool it below its freezing point without forming a solid. This phenomenon, called *supercooling*, occurs when the heat is removed so rapidly that the molecules have no time to assume the ordered structure of a solid. A supercooled liquid is unstable; particles of dust entering the solution or gentle stirring is often sufficient to cause the substance to solidify quickly.

Critical Temperature and Pressure

A gas normally liquefies at some point when pressure is applied. Suppose we have a cylinder fitted with a piston and the cylinder contains water vapor at 100 °C. If we increase the pressure on the water vapor, liquid water will form when the pressure is 101.3 kPa. However, if the temperature is 110 °C, the liquid phase does not form until the pressure is 143.3 kPa. At 374 °C the liquid phase forms only at 22.06 MPa. Above this temperature, no amount of pressure causes a distinct liquid phase to form. Instead, as pressure increases, the gas becomes steadily more compressed. The highest temperature at which a distinct liquid phase can form is called the **critical temperature**. The **critical pressure** is the pressure required to bring about liquefaction at this critical temperature.

The critical temperature is the highest temperature at which a liquid can exist. Above the critical temperature, the kinetic energies of the molecules are greater than the attractive forces that lead to the liquid state regardless of how much the substance is

Sample Exercise 11.3

Calculating ΔH for Temperature and Phase Changes

Calculate the enthalpy change upon converting 1.00 mol of ice at −25 °C to steam at 125 °C under a constant pressure of 1 atm. The specific heats of ice, liquid water, and steam are 2.03, 4.18, and 1.84 J/g K, respectively. For H_2O, $\Delta H_{fus} = 6.01$ kJ/mol and $\Delta H_{vap} = 40.67$ kJ/mol.

SOLUTION

Analyze Our goal is to calculate the total heat required to convert 1 mol of ice at −25 °C to steam at 125 °C.

Plan We can calculate the enthalpy change for each segment and then sum them to get the total enthalpy change (Hess's law, Section 5.6).

Solve

For line *AB* in Figure 11.22, we are adding enough heat to ice to increase its temperature by 25 °C. A temperature change of 25 °C is the same as a temperature change of 25 K, so we can use the specific heat of ice to calculate the enthalpy change during this process:

$$AB: \Delta H = (1.00\ \cancel{\text{mol}})(18.0\ \text{g}/\cancel{\text{mol}})(2.03\ \text{J}/\cancel{\text{g}}\ \cancel{\text{K}})(25\ \cancel{\text{K}}) = 914\ \text{J} = 0.91\ \text{kJ}$$

For line *BC* in Figure 11.22, in which we convert ice to water at 0 °C, we can use the molar enthalpy of fusion directly:

$$BC: \Delta H = (1.00\ \cancel{\text{mol}})(6.01\ \text{kJ}/\cancel{\text{mol}}) = 6.01\ \text{kJ}$$

The enthalpy changes for lines *CD*, *DE*, and *EF* can be calculated in similar fashion:

$$CD: \Delta H = (1.00\ \cancel{\text{mol}})(18.0\ \text{g}/\cancel{\text{mol}})(4.18\ \text{J}/\cancel{\text{g}}\ \cancel{\text{K}})(100\ \cancel{\text{K}}) = 7520\ \text{J} = 7.52\ \text{kJ}$$

$$DE: \Delta H = (1.00\ \cancel{\text{mol}})(40.67\ \text{kJ}/\cancel{\text{mol}}) = 40.7\ \text{kJ}$$

$$EF: \Delta H = (1.00\ \cancel{\text{mol}})(18.0\ \cancel{\text{g}}/\cancel{\text{mol}})(1.84\ \text{J}/\cancel{\text{g}}\ \cancel{\text{K}})(25\ \cancel{\text{K}}) = 830\ \text{J} = 0.83\ \text{kJ}$$

The total enthalpy change is the sum of the changes of the individual steps:

$$\Delta H = 0.91\ \text{kJ} + 6.01\ \text{kJ} + 7.52\ \text{kJ} + 40.7\ \text{kJ} + 0.83\ \text{kJ} = 56.0\ \text{kJ}$$

Check The components of the total enthalpy change are reasonable relative to the horizontal lengths (heat added) of the lines in Figure 11.22. Notice that the largest component is the heat of vaporization.

Practice Exercise

What information about water is needed to calculate the enthalpy change for converting 1 mol $H_2O(g)$ at 100 °C to $H_2O(l)$ at 80 °C?
(**a**) heat of fusion (**b**) heat of vaporization (**c**) heat of vaporization and specific heat of $H_2O(g)$ (**d**) heat of vaporization and specific heat of $H_2O(l)$ (**e**) heat of fusion and specific heat of $H_2O(l)$

compressed to bring the molecules closer together. *The greater the intermolecular forces, the higher the critical temperature of a substance.*

Several experimentally determined critical temperatures and pressures are listed in Table 11.5. Notice that nonpolar, low-molecular-weight substances, which have weak intermolecular attractions, have lower critical temperatures and pressures than substances that are polar or of higher molecular weight. Notice also that water and ammonia have exceptionally high critical temperatures and pressures as a consequence of strong intermolecular hydrogen-bonding forces.

Because they provide information about the conditions under which gases liquefy, critical temperatures and pressures are often of considerable importance to engineers and other people working with gases. Sometimes we want to liquefy a gas; other times we want to avoid liquefying it. It is useless to try to liquefy a gas by applying pressure if the gas is above its critical temperature. For example, O_2 has a critical temperature of 154.4 K. It must be cooled below this temperature before it can be liquefied by pressure. In contrast, ammonia has a critical temperature of 405.6 K. Thus, it can be liquefied at room temperature (approximately 295 K) by applying sufficient pressure.

When the temperature exceeds the critical temperature and the pressure exceeds the critical pressure, the liquid and gas phases are indistinguishable from each other, and

TABLE 11.5 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (MPa)
Nitrogen, N_2	126.1	3.39
Argon, Ar	150.9	4.86
Oxygen, O_2	154.4	5.04
Methane, CH_4	190.0	4.60
Carbon dioxide, CO_2	304.3	7.40
Phosphine, PH_3	324.4	6.54
Propane, $CH_3CH_2CH_3$	370.0	4.26
Hydrogen sulfide, H_2S	373.5	9.01
Ammonia, NH_3	405.6	11.30
Water, H_2O	647.6	22.06

the substance is in a state called a **supercritical fluid**. A supercritical fluid expands to fill its container (like a gas), but the molecules are still quite closely spaced (like a liquid).

Like liquids, supercritical fluids can behave as solvents dissolving a wide range of substances. Using *supercritical fluid extraction*, the components of mixtures can be separated from one another. Supercritical fluid extraction has been successfully used to separate complex mixtures in the chemical, food, pharmaceutical, and energy industries. Supercritical CO_2 is a popular choice because it is relatively inexpensive and, if used in closed-loop systems, may be a way to reduce CO_2 emissions into the atmosphere.

Self-Assessment Exercise

11.18 What phases and enthalpy change are described by the term *deposition*?

(a) Gas to liquid, exothermic change

(b) Gas to solid, exothermic change

(a) Gas to solid, endothermic change

(b) Liquid to solid, exothermic change

Exercises

11.19 Name the phase transition in each of the following situations and indicate whether it is exothermic or endothermic: (**a**) Iodine solid turns to iodine gas when it is heated. (**b**) Snowflakes turn into water when they fall on an open palm. (**c**) Droplets of water appear on grass in a cold humid morning. (**d**) Dry ice gradually disappears when left at room temperature for some period of time.

11.20 Chloroethane (C_2H_5Cl) boils at 12 °C. When liquid C_2H_5Cl under pressure is sprayed on a room-temperature (25 °C) surface in air, the surface is cooled considerably. (**a**) What does this observation tell us about the specific heat of $C_2H_5Cl(g)$ as compared with that of $C_2H_5Cl(l)$? (**b**) Assume that the heat lost by the surface is gained by chloroethane. What enthalpies must you consider if you were to calculate the final temperature of the surface?

11.21 $CHClF_2$ is a type of hydrochlorofluorocarbon (HCFC) that has a comparatively lower damaging effect on the ozone layer. It is used as a replacement for chlorofluorocarbons (CFCs). The heat of vaporization is 233.95 kJ/g. What mass of this substance must evaporate to freeze 15 g of water initially at 15 °C? (The heat of fusion of water is 334 J/g; the specific heat of water is 4.18 J/g · K.)

11.22 Acetone, CH_3COCH_3, is a common organic solvent with relatively low melting point (178 K) and boiling point (329 K). The enthalpy of fusion of acetone is 5.72 kJ/mol, and its enthalpy of vaporization is 29.1 kJ/mol. The specific heats of solid and liquid acetone are 96 J/mol K and 125.5 J/mol K respectively. (**a**) How much heat is required to convert 23.0 g of acetone at 273 K to the vapor phase at 329 K? (**b**) How much heat is required to convert the same amount of acetone at 77 K to the vapor phase at 329 K?

11.23 Indicate whether each statement is true or false: (**a**) The critical pressure of a substance is the pressure at which it turns into a solid at room temperature. (**b**) The critical temperature of a substance is the highest temperature at which the liquid phase can form. (**c**) Generally speaking, the higher the critical temperature of a substance, the lower its critical pressure. (**d**) In general, the more intermolecular forces there are in a substance, the higher its critical temperature and pressure.

Answers to Self-Assessment Exercises

11.18 (b)

11.5 | Vapor Pressure

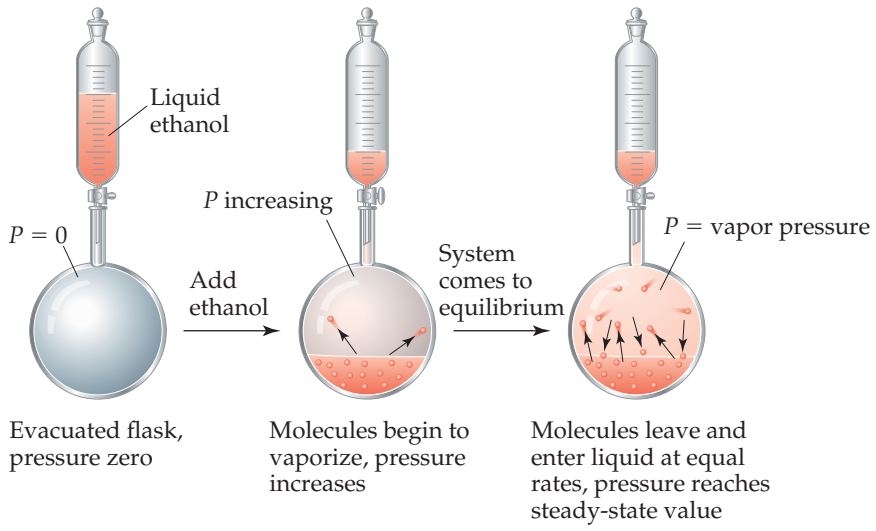


Smelling salts have a long history—there is mention of them in the writings of Pliny as well as Chaucer. Traditionally, they were used to revive someone that had fainted, but, in modern times, have been used to 'freshen up' athletes before a sporting fixture and to revive athletes on the field that have suffered an injury. This is no longer a recommended treatment as it may mask, or delay, the diagnosis of more serious neurological damage caused by concussion. The active component is ammonium carbonate, but this is often dissolved in a water–alcohol solution and accompanied by perfumes or pleasantly smelling compounds such as eucalyptus oil. The ammonium carbonate forms ammonia, which stimulates the respiratory system. It can also burn the tissue lining the nose and windpipe, so cautious use is required.

The volatility of a compound is the focus of this section, by the end of which you should be able to

- Understand what factors affect the volatility of a compound

Molecules can escape from the surface of a liquid into the gas phase by evaporation. Suppose we place a quantity of ethanol (CH_3CH_2OH) in an evacuated, closed container, as in **Figure 11.23**. The ethanol quickly begins to evaporate. As a result, the pressure



◀ **Figure 11.23** **Vapor pressure over a liquid.**

exerted by the vapor in the space above the liquid increases. After a short time, the pressure of the vapor attains a constant value, which we call the **vapor pressure**.

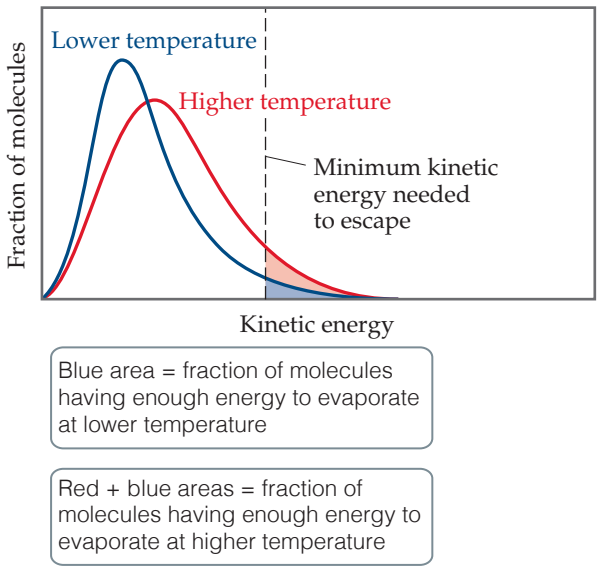
At any instant, some of the ethanol molecules at the liquid surface possess sufficient kinetic energy to overcome the attractive forces of their neighbors and, therefore, escape into the gas phase. As the number of gas-phase molecules increases, however, the probability increases that a molecule in the gas phase will strike the liquid surface and be recaptured by the liquid, as shown in the flask on the right in Figure 11.23. Eventually, the rate at which molecules return to the liquid equals the rate at which they escape. The number of molecules in the gas phase then reaches a steady value, and the pressure exerted by the vapor becomes constant.

The condition in which two opposing processes occur simultaneously at equal rates is called **dynamic equilibrium** (or simply *equilibrium*). Chemical equilibrium, which we encountered in Section 4.1, is a kind of dynamic equilibrium in which the opposing processes are chemical reactions.

A liquid and its vapor are in dynamic equilibrium when evaporation and condensation occur at equal rates. It may appear that nothing is occurring at equilibrium because there is no net change in the system. In fact, though, a great deal is happening as molecules continuously pass from liquid state to gas state and from gas state to liquid state. *The vapor pressure of a liquid is the pressure exerted by its vapor when the liquid and vapor are in dynamic equilibrium.*

Go Figure

As the temperature increases, does the rate of molecules escaping into the gas phase increase or decrease?



▲ **Figure 11.24** **The effect of temperature on the distribution of kinetic energies in a liquid.**

Volatility, Vapor Pressure, and Temperature

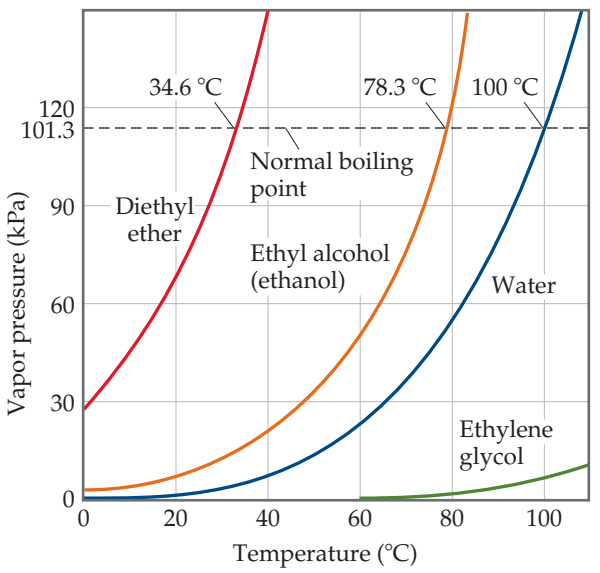
When vaporization occurs in an open container, as when water evaporates from a bowl, the vapor moves away from the liquid. Little, if any, is recaptured at the surface of the liquid. Equilibrium never occurs, and the vapor continues to form until the liquid evaporates to dryness. Substances with high vapor pressure (such as gasoline) evaporate more quickly than substances with low vapor pressure (such as motor oil). Liquids that evaporate readily are said to be **volatile**.

Hot water evaporates more quickly than cold water because vapor pressure increases with increasing temperature. To see why this statement is true, we begin with the fact that the molecules of a liquid move at various speeds. **Figure 11.24** shows the distribution of kinetic energies of the molecules at the surface of a liquid at two temperatures. (The curves are like those shown for gases in Section 10.6.) As the temperature is increased, the molecules move more energetically and more of them can break free from their neighbors and enter the gas phase, increasing the vapor pressure.

Figure 11.25 depicts the variation in vapor pressure with temperature for four common substances that differ greatly in volatility. Note that the vapor pressure in all cases increases nonlinearly with increasing temperature. The weaker the intermolecular forces in the liquid, the more easily molecules can escape and, therefore, the higher the vapor pressure at a given temperature.

Go Figure

What is the vapor pressure of ethylene glycol at its normal boiling point?



▲ **Figure 11.25** **Vapor pressure for four liquids as a function of temperature.**

Vapor Pressure and Boiling Point

The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external pressure, acting on the liquid surface. At this temperature, the thermal energy of the molecules is great enough for the molecules in the interior of the liquid to break free from their neighbors and enter the gas phase. As a result, bubbles of vapor form within the liquid. The boiling point increases as the external pressure increases. The boiling point of a liquid at 101.3 kPa pressure is called its **normal boiling point**. From Figure 11.25 we see that the normal boiling point of water is 100 °C.

The time required to cook food in boiling water depends on the water temperature. In an open container, that temperature is 100 °C, but it is possible to boil at higher temperatures. Pressure cookers work by allowing steam to escape only when it exceeds a predetermined pressure; the pressure above the water can therefore increase above atmospheric pressure. The higher pressure causes the water to boil at a higher temperature, thereby allowing the food to get hotter and to cook more rapidly.

The effect of pressure on boiling point also explains why it takes longer to cook food at high elevations than it does at sea level. The atmospheric pressure is lower at higher altitudes, so water boils at a temperature lower than 100 °C, and foods generally take longer to cook.

A CLOSER LOOK The Clausius–Clapeyron Equation

Notice that the plots in Figure 11.25 have a distinct shape: For each substance, the vapor–pressure curves sharply upward with increasing temperature. The relationship between vapor pressure and temperature is given by the *Clausius–Clapeyron equation*:

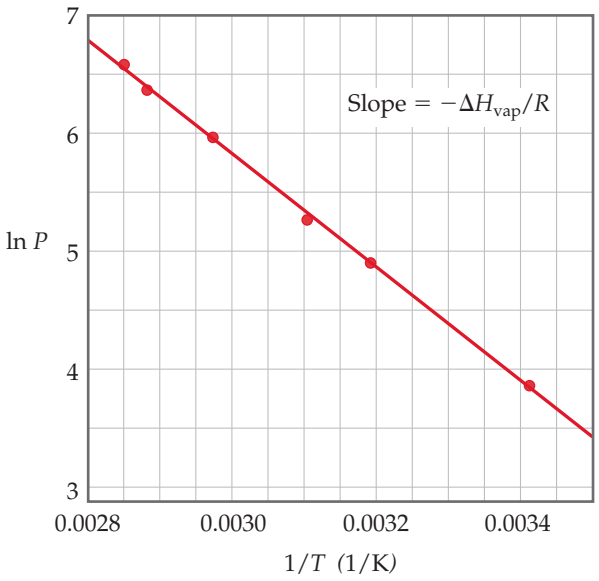
$$\ln P = \frac{-\Delta H_{vap}}{RT} + C \qquad [11.1]$$

where P is the vapor pressure, T is the absolute temperature, R is the gas constant (8.314 J/mol K), ΔH_{vap} is the molar enthalpy of vaporization, and C is a constant. This equation predicts that a graph of ln P versus $1/T$ should give a straight line with a slope equal to $\Delta H_{vap}/R$. Using this plot, we can determine the enthalpy of vaporization of a substance:

$$\Delta H_{vap} = -\text{slope} \times R$$

As an example of how we use the Clausius–Clapeyron equation, the vapor–pressure data for ethanol shown in Figure 11.25 are graphed as ln P versus $1/T$ in Figure 11.26. The data lie on a straight line with a negative slope. We can use the slope to determine ΔH_{vap} for ethanol, 38.56 kJ/mol. We can also extrapolate the line to obtain the vapor pressure of ethanol at temperatures above and below the temperature range for which we have data.

Related Exercises: 11.91–11.93



▲ **Figure 11.26** The natural logarithm of vapor pressure versus $1/T$ for ethanol.

Sample Exercise 11.4

Relating Boiling Point to Vapor Pressure

Use Figure 11.25 to estimate the boiling point of diethyl ether under an external pressure of 80 kPa atm.

SOLUTION

Analyze We are asked to read a graph of vapor pressure versus temperature to determine the boiling point of a substance at a particular pressure. The boiling point is the temperature at which the vapor pressure is equal to the external pressure.

Plan We estimate the location of that pressure on the graph, move horizontally to the vapor–pressure curve, and then drop vertically from the curve to estimate the temperature.

Solve The pressure equals 81 kPa. From Figure 11.25 we see that the boiling point at this pressure is about 27 °C, which is close to room temperature.

Comment We can make a flask of diethyl ether boil at room temperature by using a vacuum pump to lower the pressure above the liquid to about 81 kPa.

Practice Exercise

Use Figure 11.25 to determine the external pressure if ethanol boils at 60 °C.

Self-Assessment Exercise

11.24 Which compound is more volatile at 25 °C: CCl4 or CBr4?

(a) CCl_4

(b) CBr_4

Exercises

11.25 Hydrogen peroxide, H_2O_2, has a normal boiling point of 150 °C. Based on the data given in Figure 11.25, would you expect hydrogen peroxide to have a higher or lower vapor pressure than water at 25 °C?

11.26 True or false: (**a**) CBr_4 is more volatile than CCl_4. (**b**) CBr_4 has a higher boiling point than CCl_4. (**c**) CBr_4 has weaker intermolecular forces than CCl_4. (**d**) CBr_4 has a higher vapor pressure at the same temperature than CCl_4.

11.27 You are high up in the mountains and boil water to make some tea. However, when you drink your tea, it is not as hot as it should be. You try again and again, but the water is just not hot enough to make a hot cup of tea. Which is the best explanation for this result? (**a**) High in the mountains, it is probably very dry, and so the water is rapidly evaporating from your cup and cooling it. (**b**) High in the mountains, it is probably very windy, and so the water is rapidly evaporating from your cup and cooling it. (**c**) High in the mountains, the air pressure is significantly less than 101.3 kPa, so the boiling point of water is much lower than at sea level. (**d**) High in the mountains, the air pressure is significantly less than 101.3 kPa, so the boiling point of water is much higher than at sea level.

11.28 Appendix B lists the vapor pressure of water at various external pressures. (**a**) Plot the data in Appendix B, vapor pressure versus temperature (°C). From your plot, estimate the vapor pressure of water at body temperature, 37 °C. (**b**) Explain the significance of the data point at 101.3 kPa, 100 °C. (**c**) A city at an altitude of 1525 m above sea level has a barometric pressure of 84.3 kPa. To what temperature would you have to heat water to boil it in this city? (**d**) A city at an altitude of 150 m below sea level would have a barometric pressure of 103.14 kPa. To what temperature would you have to heat water to boil it in this city?

Answers to Self-Assessment Exercises

11.24 (a)

11.6 Phase Diagrams



Who would have thought that ice skating is all about the solid–liquid phase change in water! The weight of a person bearing on the thin blade of an ice skate generates a considerable pressure under the blade. Sufficient to temporarily melt the ice and drastically reduce the friction under the blade. The skater can glide fast and apparently effortlessly across the rink. As soon as the pressure on the water is released, it refreezes. By the end of this section, you should be able to

- Interpret the phase diagram of a substance

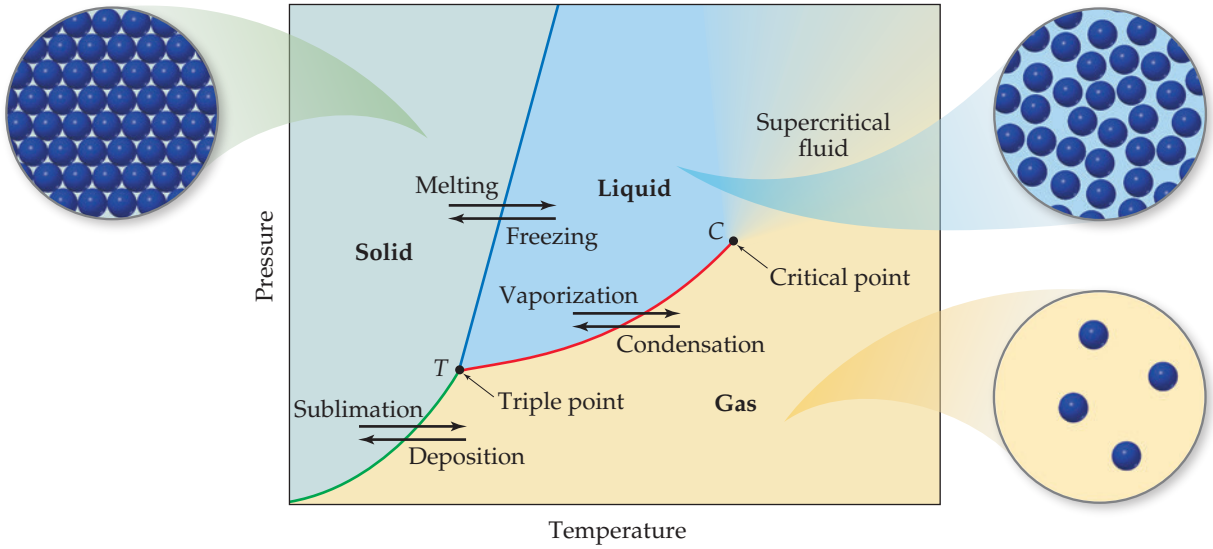
The equilibrium between a liquid and its vapor is not the only dynamic equilibrium that can exist between states of matter. Under appropriate conditions, a solid can be in equilibrium with its liquid or even with its vapor. The temperature at which solid and liquid phases coexist at equilibrium is the *melting point* of the solid or the *freezing point* of the liquid. Solids can also undergo evaporation and therefore possess a vapor pressure.

A **phase diagram** is a graphic way to summarize the conditions under which equilibria exist between the different states of matter. Such a diagram also allows us to predict which phase of a substance is present at any given temperature and pressure.

The phase diagram for any substance that can exist in all three phases of matter is shown in **Figure 11.27**. The diagram contains three important curves, each of which represents the temperature and pressure at which the various phases can coexist at equilibrium. The only substance present in the system is the one whose phase diagram is under consideration. The pressure shown in the diagram is either the pressure applied to the system or the pressure generated by the substance. The curves may be described as follows:

1. The red curve is the *vapor-pressure curve* of the liquid, representing equilibrium between the liquid and gas phases. The point on this curve where the vapor pressure is 101.3 kPa is the normal boiling point of the substance. The vapor-pressure curve ends at the **critical point** (*C*), which corresponds to the critical temperature and

Go Figure Imagine that the pressure on the solid phase in the figure is decreased at constant temperature. If the solid eventually sublimes, what must be true about the temperature?



▲ **Figure 11.27 Generic phase diagram for a pure substance.** The green line is the sublimation curve, the blue line is the melting curve, and the red line is the vapor-pressure curve.

critical pressure of the substance. At temperatures and pressures beyond the critical point, the liquid and gas phases are indistinguishable from each other, and the substance is a *supercritical fluid*.

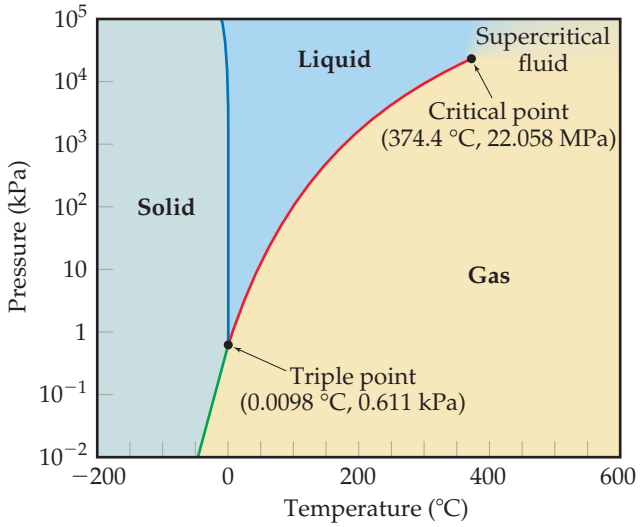
2. The green curve, the *sublimation curve*, separates the solid phase from the gas phase and represents the change in the vapor pressure of the solid as it sublimes at different temperatures. Each point on this curve represents a condition of equilibrium between the solid and the gas.
3. The blue curve, the *melting curve*, separates the solid phase from the liquid phase and represents the change in melting point of the solid with increasing pressure. Each point on this curve represents an equilibrium between the solid and the liquid. This curve usually slopes slightly to the right as pressure increases for most substances because the solid form is denser than the liquid form. An increase in pressure usually favors the more compact solid phase; thus, higher temperatures are required to melt the solid at higher pressures. The melting point at 101.3 kPa is the **normal melting point**.

Point *T,* where the three curves intersect, is the **triple point**, and here all three phases are in equilibrium. Any other point on any of the three curves represents equilibrium between two phases. Any point on the diagram that does not fall on one of the curves corresponds to conditions under which only one phase is present. The gas phase, for example, is stable at low pressures and high temperatures, whereas the solid phase is stable at low temperatures and high pressures. Liquids are stable in the region between the other two.

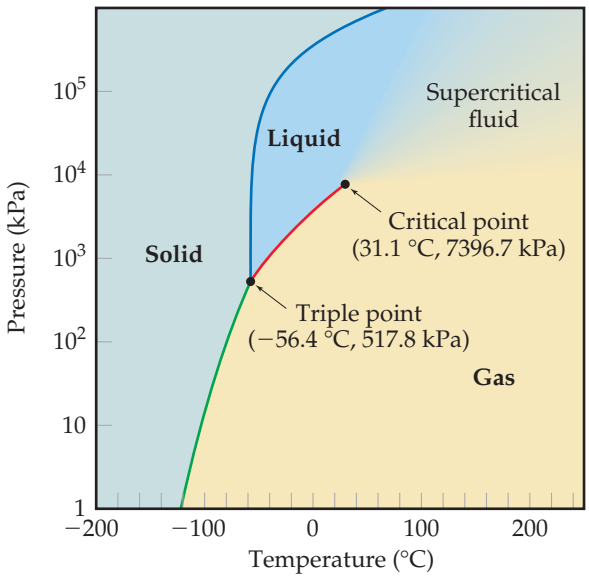
The Phase Diagrams of H_2O and CO_2

Figure 11.28 shows the phase diagram of H_2O. Because of the large range of pressures covered in the diagram, a logarithmic scale is used to represent pressure. The melting curve (blue line) of H_2O is atypical, slanting slightly to the left with increasing pressure, indicating that for water the melting point *decreases* with increasing pressure. This unusual behavior occurs because water is among the very few substances whose liquid form is more compact than its solid form, as we learned in Section 11.2.

If the pressure is held constant at 101.3 kPa, it is possible to move from the solid to liquid to gaseous regions of the phase diagram by changing the temperature, as we expect from our everyday encounters with water. The triple point of H_2O falls at a relatively low pressure, 0.611 kPa. Below this pressure, liquid water is not stable and ice sublimes to water vapor on heating. This property of water is used to "freeze-dry" foods and beverages. The food or beverage is frozen to a temperature below 0 °C. Next



▶ **Figure 11.28 Phase diagram of H_2O.** Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.



◀ **Figure 11.29 Phase diagram of CO_2.** Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.

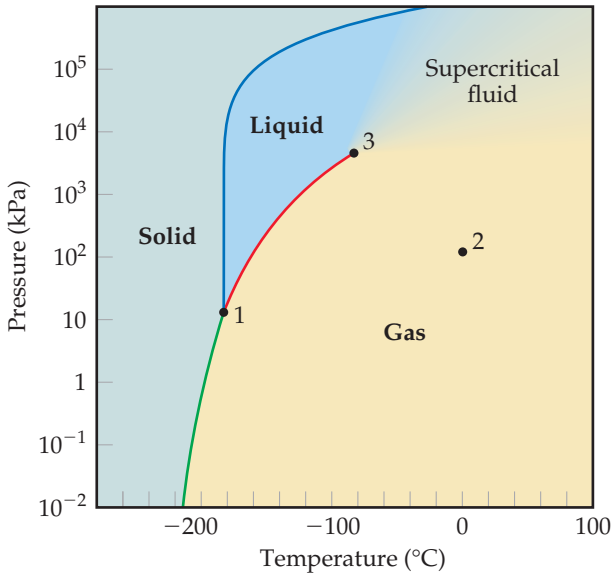
it is placed in a low-pressure chamber (below 0.611 kPa) and then warmed so that the water sublimes, leaving behind dehydrated food or beverage.

The phase diagram for CO_2 is shown in **Figure 11.29**. The melting curve (blue line) behaves typically, slanting to the right with increasing pressure, telling us that the melting point of CO_2 increases with increasing pressure. Because the pressure at the triple point is relatively high, 517.8 kPa, CO_2 does not exist as a liquid at 101.3 kPa, which means that solid CO_2 does not melt when heated, but instead sublimes. Thus, CO_2 does not have a normal melting point; instead, it has a normal sublimation point, −78.5 °C. Because CO_2 sublimes rather than melts as it absorbs energy at ordinary pressures, solid CO_2 (dry ice) is a convenient coolant.

Sample Exercise 11.5

Interpreting a Phase Diagram

Use the phase diagram for methane, CH_4, shown in **Figure 11.30** to answer the following questions. (**a**) What are the approximate temperature and pressure of the critical point? (**b**) What are the approximate temperature and pressure of the triple point? (**c**) Is methane a solid, liquid, or gas at 100 kPa and 0 °C? (**d**) If solid methane at 100 kPa is heated while the pressure is held constant, will it melt or sublime? (**e**) If methane at 100 kPa and 0 °C is compressed until a phase change occurs, in which state is the methane when the compression is complete?



▲ **Figure 11.30 Phase diagram of CH_4.** Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.

SOLUTION

Analyze We are asked to identify key features of the phase diagram and to use it to deduce what phase changes occur when specific pressure and temperature changes take place.

Plan We must identify the triple and critical points on the diagram and also identify which phase exists at specific temperatures and pressures.

Continued

Solve

(**a**) The critical point is the point where the liquid, gaseous, and supercritical fluid phases coexist. It is marked point 3 in the phase diagram and located at approximately −80 °C and 5066 kPa.

(**b**) The triple point is the point where the solid, liquid, and gaseous phases coexist. It is marked point 1 in the phase diagram and located at approximately −180 °C and 10 kPa.

(**c**) The intersection of 0 °C and 1 atm is marked point 2 in the phase diagram. It is well within the gaseous region of the phase diagram.

(**d**) If we start in the solid region at $P = 100$ kPa and move horizontally (this means we hold the pressure constant), we cross first into the liquid region, at $T \approx -180$ °C, and then into the gaseous region, at $T \approx -160$ °C. Therefore, solid methane melts when the pressure is 100 kPa. (For methane to sublime, the pressure must be below the triple point pressure.)

(**e**) Moving vertically up from point 2, which is 100 kPa and 0 °C, the first phase change we come to is from gas to supercritical fluid. This phase change happens when we exceed the critical pressure (~5066 kPa).

Check The pressure and temperature at the critical point are higher than those at the triple point, which is expected. Methane is the principal component of natural gas. So it seems reasonable that it exists as a gas at 1 atm and 0 °C.

Practice Exercise

Use the phase diagram of methane to answer the following questions. (**a**) What is the normal boiling point of methane? (**b**) Over what pressure range does solid methane sublime? (**c**) Above what temperature does liquid methane not exist?

Self-Assessment Exercise

11.29 What phases are present at the triple point of a phase diagram?

(a) solid and liquid

(b) solid and gas

(c) liquid and gas

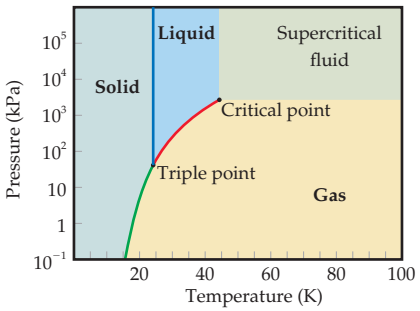
(d) solid, liquid, and gas

Exercises

11.30 (**a**) What is the significance of the critical point in a phase diagram? (**b**) Why does the line that separates the gas and liquid phases end at the critical point?

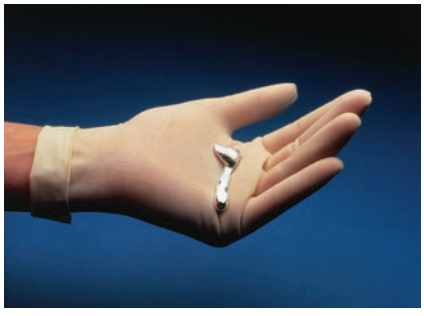
11.31 Referring to Figure 11.29, describe the phase changes (and the temperatures at which they occur) when CO_2 is heated from −80 to −20 °C at (**a**) a constant pressure of 300 kPa, (**b**) a constant pressure of 600 kPa.

11.32 The phase diagram for neon is



Use the phase diagram to answer the following questions. (**a**) What is the approximate value of the normal melting point? (**b**) Over what pressure range will solid neon sublime? (**c**) At room temperature ($T = 25$ °C) can neon be liquefied by compressing it?

11.33 At 25 °C gallium is a solid with a density of 5.91 g/cm^3. Its melting point, 29.8 °C, is low enough that you can melt it by holding it in your hand. The density of liquid gallium just above the melting point is 6.1 g/cm^3. Based on this information, what unusual feature would you expect to find in the phase diagram of gallium?



Answers to Self-Assessment Exercises

11.29 (d)

11.7 | Liquid Crystals



Electronic paper (e-paper) is based on cholesteric liquid crystal technology. It is able to mimic the appearance of ordinary ink on paper and has numerous potential uses including thin displays on walls, electronic labels, and electronic book readers. It takes very little power to change the orientation of the liquid crystal molecules and, hence, affect the optical properties of the device.

By the end of this section, you should be able to

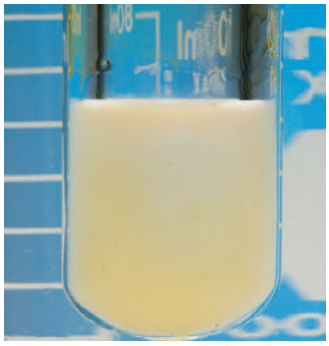
- Recognize the features of a molecule that make it a potential liquid crystal and the different liquid crystal phases that it may adopt.

In 1888, Friedrich Reinitzer, an Austrian botanist, discovered that the organic compound cholesteryl benzoate has an interesting and unusual property, shown in Figure 11.31. Solid cholesteryl benzoate melts at 145 °C, forming a viscous milky liquid; then at 179 °C the milky liquid becomes clear and remains that way at temperatures above 179 °C. When cooled, the clear liquid turns viscous and milky at 179 °C, and the milky liquid solidifies at 145 °C.

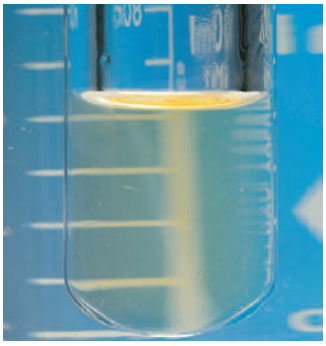
Reinitzer's work represents the first systematic report of what we call a **liquid crystal**, the term we use today for the viscous, milky state that some substances exhibit between the liquid and solid states.

This intermediate phase has some of the structure of solids and some of the freedom of motion of liquids. Because of the partial ordering, liquid crystals may be viscous and possess properties intermediate between those of solids and those of liquids. The region in which they exhibit these properties is marked by sharp transition temperatures, as in Reinitzer's sample. Just like solid, liquid, and gas phases, the liquid crystalline phase is represented by a distinct region on a phase diagram.

Today liquid crystals are used as pressure and temperature sensors and as liquid crystals displays (LCDs) in such devices as digital watches, televisions, and computers. They can be used for these applications because the weak intermolecular forces that hold the molecules together in the liquid crystalline phase are easily affected by changes in temperature, pressure, and electric fields.



145 °C < T < 179 °C
Liquid crystalline phase

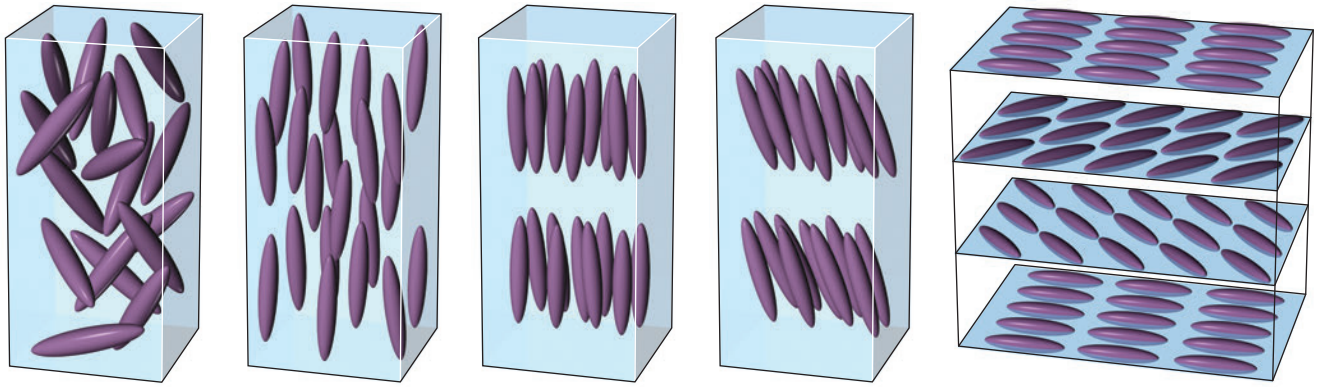


T > 179 °C
Liquid phase

▲ **Figure 11.31 Cholesteryl benzoate in its liquid and liquid crystalline states.**

Types of Liquid Crystals

Substances that form liquid crystals are often composed of rod-shaped molecules that are somewhat rigid. In the liquid phase, these molecules are oriented randomly. In the liquid crystalline phase, by contrast, the molecules are arranged in specific patterns as



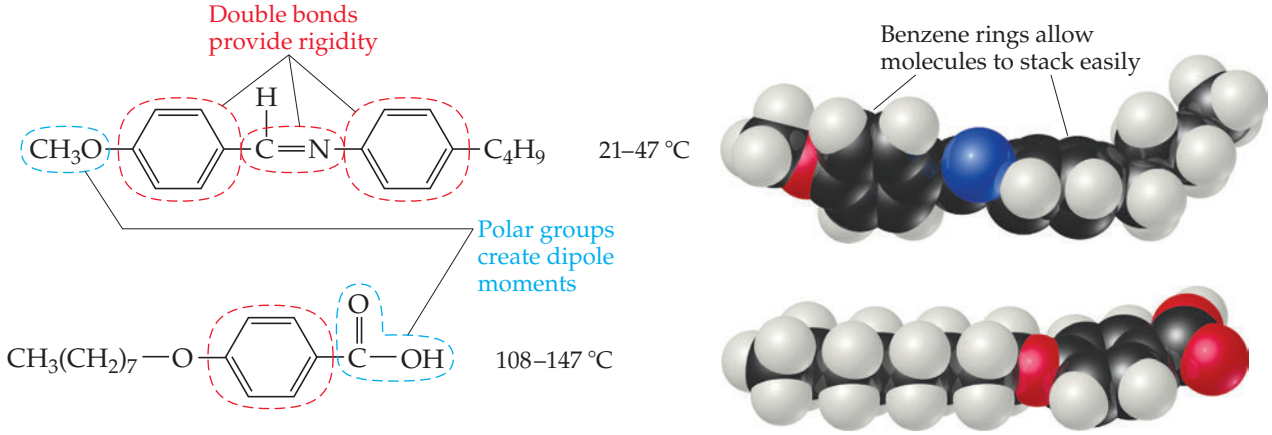
Liquid phase	Nematic liquid crystalline phase	Smectic A liquid crystalline phase	Smectic C liquid crystalline phase	Cholesteric liquid crystalline phase
Molecules arranged randomly	Long axes of molecules aligned, but ends are not aligned	Molecules aligned in layers, long axes of molecules perpendicular to layer planes	Molecules aligned in layers, long axes of molecules inclined with respect to layer planes	Molecules pack into layers, long axes of molecules in one layer rotated relative to the long axes in the layer above it

▲ **Figure 11.32 Molecular order in nematic, smectic, and cholesteric liquid crystals.** In the liquid phase of any substance, the molecules are arranged randomly, whereas in the liquid crystalline phases the molecules are arranged in a partially ordered way.

illustrated in **Figure 11.32**. Depending on the nature of the ordering, liquid crystals are classified as nematic, smectic A, smectic C, or cholesteric.

In a **nematic liquid crystal**, the molecules are aligned so that their long axes tend to point in the same direction but the ends are not aligned with one another. In **smectic A** and **smectic C liquid crystals**, the molecules maintain the long-axis alignment seen in nematic crystals, but in addition they pack into layers.

Two molecules that exhibit liquid crystalline phases are shown in **Figure 11.33**. The lengths of these molecules are much greater than their widths. The double bonds, including those in the benzene rings, add rigidity to the molecules, and the rings, because they are flat, help the molecules stack with one another. The polar —OCH_3 and —COOH groups give rise to dipole–dipole interactions and promote alignment of the molecules. Thus, the molecules order themselves quite naturally along their long axes. They can, however, rotate around their axes and slide parallel to one another. In smectic liquid crystals, the intermolecular forces (dispersion



▲ **Figure 11.33 Molecular structure and liquid crystal temperature range for two typical liquid crystalline materials.**

forces, dipole–dipole attractions, and hydrogen bonding) limit the ability of the molecules to slide past one another.

In a **cholesteric liquid crystal**, the molecules are arranged in layers, with their long axes parallel to the other molecules within the same layer.* Upon moving from one layer to the next, the orientation of the molecules rotates by a fixed angle, resulting in a spiral pattern. These liquid crystals are so named because many derivatives of cholesterol adopt this structure.

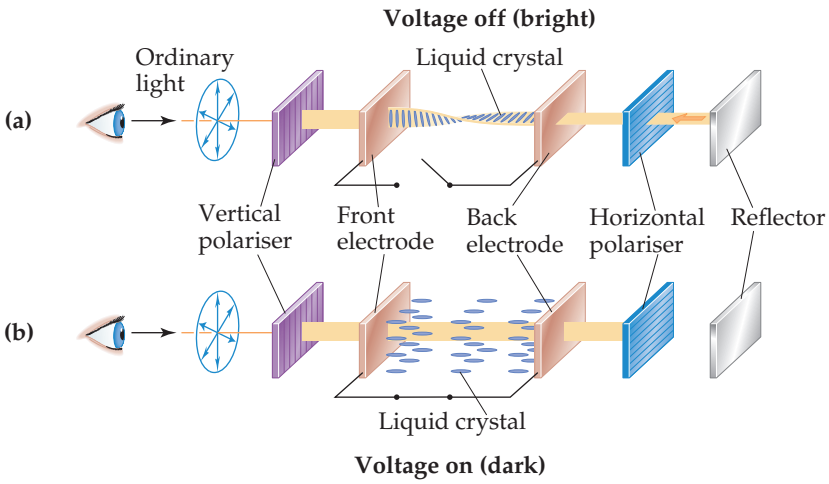
CHEMISTRY AND LIFE Liquid Crystal Displays

Liquid crystals displays (LCDs) are widely used in electronic devices such as watches, calculators and computer screens. These applications are possible because an applied electrical field changes the orientation of liquid crystal molecules and thus affects the optical properties of the device.

LCDs come in a variety of designs, but the structure illustrated in **Figure 11.34** is typical. A thin layer (5–20 μm) of liquid crystalline material is placed between electrically conducting, transparent glass electrodes. Ordinary light passes through a vertical polariser that permits light in only the vertical plane to pass. Using a special process during fabrication, the liquid crystal molecules are oriented so that the molecules at the front electrode are oriented vertically and those at the back electrode horizontally. The orientation of the molecules in between the two electrodes varies systematically from vertical to horizontal, as shown in Figure 11.34. The plane of polarisation of the light is turned by 90° as it passes through the liquid crystal layer and is thus in the correct orientation to pass through the horizontal polariser. In a watch display, a mirror reflects the light back, and the light retraces its path, allowing the device to look bright. When a voltage is applied to the plates the liquid crystalline molecules align with the voltage, as shown in Figure 11.34. The light rays thus are not properly oriented to pass through the horizontal polariser, and the device appears dark. Displays of this kind are called 'twisted nematic'. As the name implies, materials that order as nematic liquid crystals are used for this application.

Liquid crystal displays for computer and televisions employ a light source in place of the reflector, but the principle is the same. The screen is divided into a large number of tiny cells, with the voltages at points on the screen surface controlled by transistors made from thin films of amorphous silicon. Red-green-blue colour filters are employed to provide full colour. The entire display is refreshed at a frequency of about 60 Hz, so the display can change rapidly with respect to the response time of the human eye. Displays of this kind are remarkable technical achievements based on a combination of basic scientific discovery and creative engineering.

Related Exercises: 11.86, 11.87



◀ **FIGURE 11.34 Schematic illustration of the operation of a twisted nematic liquid crystal display (LCD).** (a) When the voltage is off, the molecules in the liquid crystal are aligned so that they rotate the polarisation of the light by 90°. This alignment allows light to pass through both the vertical and horizontal polarisers before being reflected and retracing its path to give a bright display. (b)When a voltage is applied to the electrodes the liquid crystal molecules align parallel to the light path. In this state the light retains the vertical polarisation and cannot pass through the horizontal polariser. The area covered by the front electrode therefore appears dark.

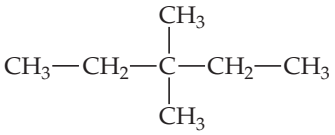
The molecular arrangement in cholesteric liquid crystals produces unusual coloring patterns with visible light. Changes in temperature and pressure change the order and, hence, the color. Cholesteric liquid crystals are used to monitor temperature changes in situations where conventional methods are not feasible. For example, they can detect hot spots in microelectronic circuits, which may signal the presence of flaws. They can also be fashioned into thermometers for measuring the skin temperature of infants. Because cholesteric liquid crystal displays can be built that draw very little power, they are also being investigated for use in electronic paper. Such applications are possible because an applied electrical field changes the orientation of liquid crystal molecules and thus affects the optical properties of the device.

*Cholesteric liquid crystals are sometimes called chiral nematic phases because the molecules within each plane adopt an arrangement similar to a nematic liquid crystal.

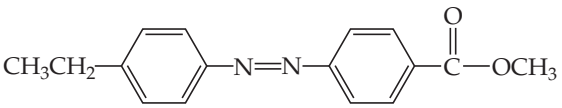
Sample Exercise 11.6

Properties of Liquid Crystals

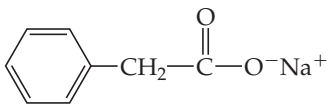
Which of these substances is most likely to exhibit liquid crystalline behavior?



(i)



(ii)



(iii)

SOLUTION

Analyze We have three molecules with different structures, and we are asked to determine which one is most likely to be a liquid crystalline substance.

Plan We need to identify all structural features that might induce liquid crystalline behavior.

Solve Molecule (i) is not likely to be liquid crystalline because the absence of double and/or triple bonds makes this molecule flexible rather than rigid. Molecule (iii) is ionic, and the generally high melting points of ionic materials make it unlikely that this substance is liquid crystalline. Molecule (ii) possesses the characteristic long axis and the kinds of structural features often seen in liquid crystals: The molecule has a rod-like shape, the double bonds and benzene rings provide rigidity, and the polar $COOCH_3$ group creates a dipole moment.

Practice Exercise

Liquid crystalline phases are produced by which of the following?
(**a**) short, flexible molecules
(**b**) complete lack of order among molecules
(**c**) three-dimensional order among molecules
(**d**) highly branched molecules
(**e**) rod-shaped molecules

Sample Integrative Exercise

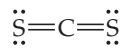
Putting Concepts Together

The substance CS_2 has a melting point of $-110.8\,°C$ and a boiling point of $46.3\,°C$. Its density at $20\,°C$ is $1.26\,g/cm^3$. It is highly flammable. (**a**) What is the name of this compound? (**b**) List the intermolecular forces that CS_2 molecules exert on one another. (**c**) Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.) (**d**) The critical temperature and pressure for CS_2 are 552 K and 7903.3 kPa, respectively. Compare these values with those for CO_2 in Table 11.5 and discuss the possible origins of the differences.

SOLUTION

(**a**) The compound is named carbon disulfide, in analogy with the naming of other binary molecular compounds such as carbon dioxide.

(**b**) Because there is no H atom, there can be no hydrogen bonding. If we draw the Lewis structure, we see that carbon forms double bonds with each sulfur:



Using the VSEPR model, we conclude that the molecule is linear and therefore has no dipole moment. Thus, there are no dipole–dipole forces. Only dispersion forces operate between the CS_2 molecules.

(**c**) The most likely products of the combustion will be CO_2 and SO_2. Under some conditions, SO_3 might be formed, but this would be the less likely outcome. Thus, we have the following equation for combustion:

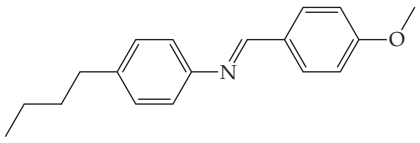
$$CS_2(l) + 3\,O_2(g) \rightarrow CO_2(g) + 2\,SO_2(g)$$

(**d**) The critical temperature and pressure of CS_2 (552 K and 7903.3 kPa, respectively) are both higher than those given for CO_2 in Table 11.5 (304 K and 7396.7 kPa, respectively). The difference in critical temperatures is especially notable. The higher values for CS_2 arise from the greater dispersion attractions between the CS_2 molecules compared with CO_2. These greater attractions are due to the larger size of the sulfur compared to oxygen and, therefore, its greater polarizability.

Self-Assessment Exercise

11.34 Which of the following substances is most likely to form a liquid crystal phase?

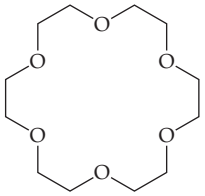
(a)



(b)



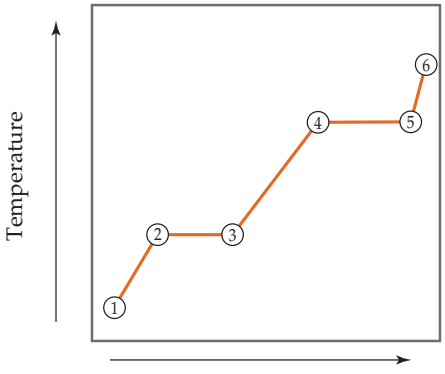
(c)



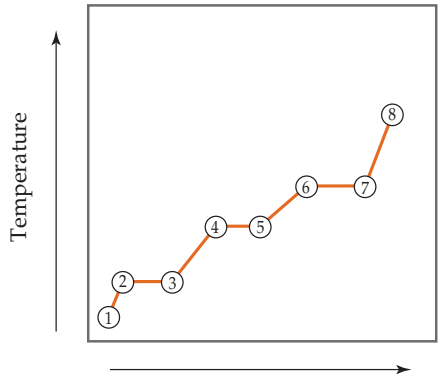
Exercises

11.35 In terms of the arrangement and freedom of motion of the molecules, how are the nematic liquid crystalline phase and an ordinary liquid phase similar? How are they different?

11.36 Two heating curves, A and B, are shown. In both cases, point 1 corresponds to the crystalline solid phase.



A



B

(**a**) One of these graphs shows data for a liquid crystalline material. Which one? (**b**) In graph A, what process does the 2–3 line segment correspond to? (**c**) In graph B, what process does the 2–3 line segment correspond to? (**d**) In graph A, what process does the 3–4 line segment correspond to? (**e**) In graph B, what process does the 3–4 line segment correspond to?

11.37 Describe how a cholesteric liquid crystalline phase differs from a smectic A liquid crystalline phase.

11.38 The smectic liquid crystalline phase can be said to be more highly ordered than the nematic phase. In what sense is this true?

Answers to Self-Assessment Exercises

11.34 (a)

Chapter Summary and Key Terms

A MOLECULAR COMPARISON OF GASES, LIQUIDS, AND SOLIDS (SECTION 11.1) Substances that are gases or liquids at room temperature are usually composed of molecules. In gases, the intermolecular attractive forces are negligible compared to the kinetic energies of the molecules; thus, the molecules are widely separated and undergo constant, chaotic motion. In liquids, the **intermolecular forces** are strong enough to keep the molecules in close proximity; nevertheless, the molecules are free to move with respect to one another. In solids, the intermolecular attractive forces are strong enough to restrain molecular motion and to force the particles to occupy specific locations in a three-dimensional arrangement.

INTERMOLECULAR FORCES (SECTION 11.2) Three types of intermolecular forces exist between neutral molecules: **dispersion forces**, **dipole–dipole interactions**, and **hydrogen bonding**. Dispersion forces operate between all molecules (and atoms, for atomic substances such as He, Ne, Ar, and so forth). As molecular weight increases, the **polarizability** of a molecule increases, which results in stronger dispersion forces. Molecular shape is also an important factor. Dipole–dipole forces increase in strength as the polarity of the molecule increases. Hydrogen bonding occurs in compounds containing O—H, N—H, and F—H bonds. Hydrogen bonds are generally stronger than dipole–dipole or dispersion forces. **Ion–dipole forces** are important in solutions in which ionic compounds are dissolved in polar solvents.

SELECT PROPERTIES OF LIQUIDS (SECTION 11.3) The stronger the intermolecular forces, the greater is the **viscosity**, or resistance to flow, of a liquid. **Surface tension** is a measure of the tendency of a liquid to maintain a minimum surface area. The surface tension of a liquid also increases as intermolecular forces increase in strength. The adhesion of a liquid to the walls of a narrow tube and the cohesion of the liquid account for **capillary action**.

PHASE CHANGES (SECTION 11.4) A substance may exist in more than one state of matter, or phase. **Phase changes** are transformations from one phase to another. Changes of a solid to liquid (melting), solid to gas (sublimation), and liquid to gas (vaporization) are all endothermic processes. Thus, the **heat of fusion** (melting), the **heat of sublimation**, and the **heat of vaporization** are all positive quantities. The reverse processes (freezing, deposition, and condensation) are exothermic.

A gas cannot be liquefied by application of pressure if the temperature is above its **critical temperature**. The pressure required to liquefy a gas at its critical temperature is called the **critical pressure**. When the temperature exceeds the critical temperature and the pressure exceeds the critical pressure, the liquid and gas phases coalesce to form a **supercritical fluid**.

VAPOR PRESSURE (SECTION 11.5) The **vapor pressure** of a liquid is the partial pressure of the vapor when it is in **dynamic equilibrium** with the liquid. At equilibrium the rate of transfer of molecules from the liquid to the vapor equals the rate of transfer from the vapor to the liquid. The higher the vapor pressure of a liquid, the more readily it evaporates and the more **volatile** it is. Vapor pressure increases with temperature. Boiling occurs when the vapor pressure equals the external pressure. Thus, the **boiling point** of a liquid depends on pressure. The **normal boiling point** is the temperature at which the vapor pressure equals 101.3 kPa.

PHASE DIAGRAMS (SECTION 11.6) The equilibria between the solid, liquid, and gas phases of a substance as a function of temperature and pressure are displayed on a **phase diagram**. A line indicates equilibria between any two phases. The line through the melting point usually slopes slightly to the right as pressure increases, because the solid is usually more dense than the liquid. The melting point at 101.3 kPa is the **normal melting point**. The point on the diagram at which all three phases coexist in equilibrium is called the **triple point**. The **critical point** corresponds to the critical temperature and critical pressure. Beyond the critical point, the substance is a supercritical fluid.

LIQUID CRYSTALS (SECTION 11.7) A **liquid crystal** is a substance that exhibits one or more ordered phases at a temperature above the melting point of the solid. In a **nematic liquid crystal** the molecules are aligned along a common direction, but the ends of the molecules are not lined up. In a **smectic liquid crystal** the ends of the molecules are lined up so that the molecules form layers. In **smectic A liquid crystals** the long axes of the molecules line up perpendicular to the layers. In **smectic C liquid crystals** the long axes of molecules are inclined with respect to the layers. A **cholesteric liquid crystal** is composed of molecules that align parallel to each other within a layer, as they do in nematic liquid crystalline phases, but the direction along which the long axes of the molecules align rotates from one layer to the next to form a helical structure. Substances that form liquid crystals are generally composed of molecules with fairly rigid, elongated shapes, as well as polar groups to help align molecules through dipole–dipole interactions.

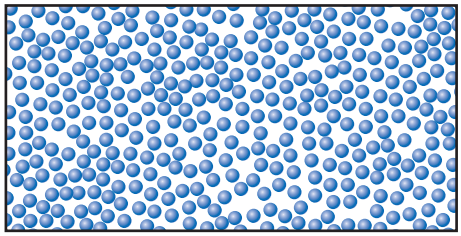
Learning Outcomes After studying this chapter, you should be able to:

- Identify the intermolecular attractive interactions (dispersion, dipole–dipole, hydrogen bonding, ion–dipole) that exist between molecules or ions based on their composition and molecular structure and compare the relative strengths of these intermolecular forces. (Section 11.2) *Related Exercises: 11.7, 11.10, 11.51, 11.56*
- Explain the concept of polarizability and how it relates to dispersion forces. (Section 11.2) *Related Exercises: 11.8, 11.9, 11.52, 11.53*
- Explain the concepts of viscosity, surface tension, and capillary action. (Section 11.3) *Related Exercises: 11.15, 11.61*
- List the names of the various changes of state for a pure substance and indicate which are endothermic and which are exothermic. (Section 11.4) *Related Exercises: 11.19, 11.75*
- Interpret heating curves and calculate the enthalpy changes related to temperature changes and phase changes. (Section 11.4) *Related Exercises: 11.22, 11.66*
- Define critical pressure, critical temperature, vapor pressure, normal boiling point, normal melting point, critical point, and triple point. (Sections 11.4, 11.5, and 11.6) *Related Exercises: 11.23, 11.26, 11.67, 11.69*
- Interpret and sketch phase diagrams. Explain how water's phase diagram differs from most other substances and why. (Section 11.6) *Related Exercises: 11.30, 11.31, 11.72, 11.73*
- Describe how the molecular arrangements characteristic of nematic, smectic, and cholesteric liquid crystals differ from ordinary liquids and from each other. Recognize the features of molecules that favor formation of liquid crystalline phases. (Section 11.7) *Related Exercises: 11.35, 11.78, 11.79*

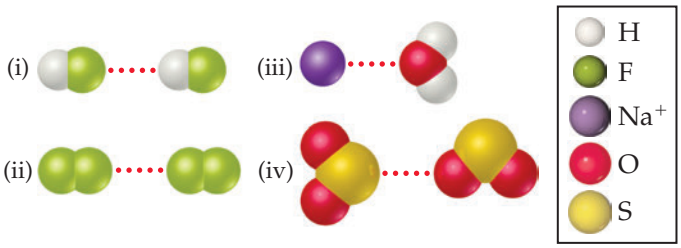
Exercises

Visualizing Concepts

11.39 (**a**) Does the diagram best describe a crystalline solid, a liquid, or a gas? (**b**) Explain. [Section 11.1]

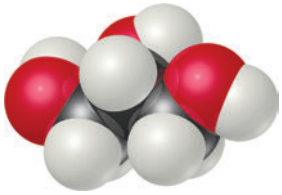


11.40 (**a**) Which kind of intermolecular attractive force is shown in each case here?

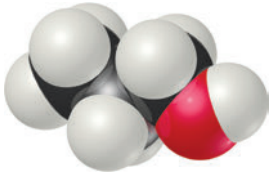


(**b**) Predict which of the four interactions is the weakest. [Section 11.2]

11.41 (**a**) Do you expect the viscosity of glycerol, $C_3H_5(OH)_3$, to be larger or smaller than that of 1-propanol, C_3H_7OH? (**b**) Explain. [Section 11.3]

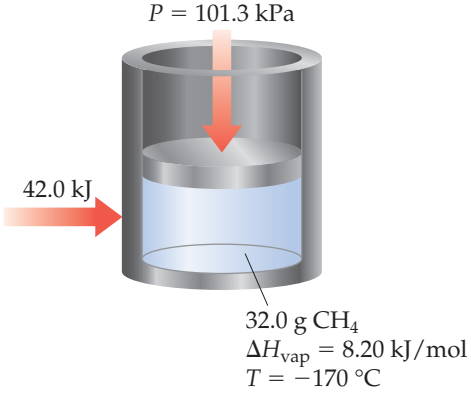


Glycerol

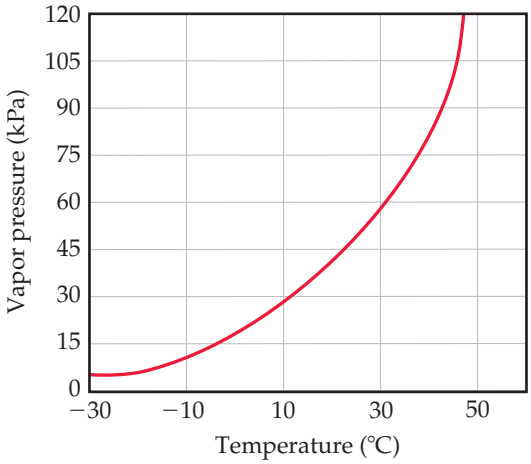


1-Propanol

11.42 If 42.0 kJ of heat is added to a 32.0 g sample of liquid methane under 101.3 kPa of pressure at a temperature of −170 °C, what are the final state and temperature of the methane once the system equilibrates? Assume no heat is lost to the surroundings. The normal boiling point of methane is −161.5 °C. The specific heats of liquid and gaseous methane are 3.48 and 2.22 J/g K, respectively. [Section 11.4]

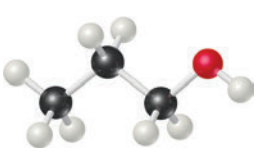


11.43 Using this graph of CS_2 data,

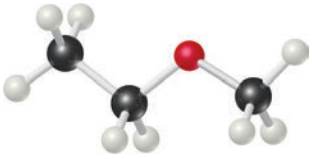


determine (**a**) the approximate vapor pressure of CS_2 at 30 °C, (**b**) the temperature at which the vapor pressure equals 45 kPa, (**c**) the normal boiling point of CS_2. [Section 11.5]

11.44 The molecules



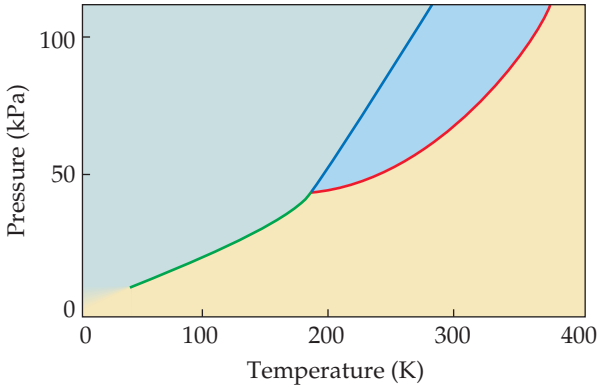
Propanol



Ethyl methyl ether

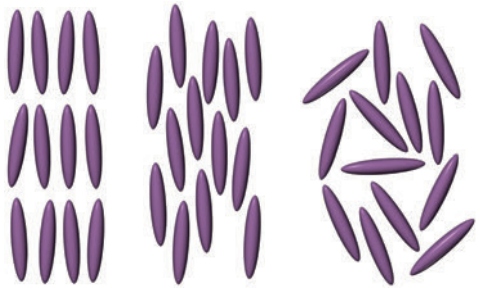
have the same molecular formula (C_3H_8O) but different chemical structures. (**a**) Which molecule(s), if any, can engage in hydrogen bonding? (**b**) Which molecule do you expect to have a larger dipole moment? (**c**) One of these molecules has a normal boiling point of 97.2 °C, while the other one has a normal boiling point of 10.8 °C. Assign each molecule to its normal boiling point. [Sections 11.2 and 11.5]

11.45 The phase diagram of a hypothetical substance is



(a) Estimate the normal boiling point and freezing point of the substance. (**b**) What is the physical state of the substance under the following conditions? (i) $T = 150$ K, $P = 20$ kPa; (ii) $T = 100$ K, $P = 80$ kPa; (iii) $T = 300$ K, $P = 100$ kPa. (**c**) What is the triple point of the substance? [Section 11.6]

11.46 At three different temperatures, T_1, T_2, and T_3, the molecules in a liquid crystal align in these ways:



T_1 T_2 T_3

(**a**) At which temperature or temperatures is the substance in a liquid crystalline state? At those temperatures, which type of liquid crystalline phase is depicted? (**b**) Which is the highest of these three temperatures? [Section 11.7]

Molecular Comparisons of Gases, Liquids, and Solids (Section 11.1)

11.47 List the three states of matter in order of (**a**) increasing molecular disorder and (**b**) increasing intermolecular attraction. (**c**) Which state of matter is most easily compressed?

11.48 As a metal such as lead melts, what happens to (**a**) the average kinetic energy of the atoms and (**b**) the average distance between the atoms?

11.49 Benzoic acid, C_6H_5COOH, melts at 122 °C. The density in the liquid state at 130 °C is 1.08 g/cm^3. The density of solid benzoic acid at 15 °C is 1.266 g/cm^3. (**a**) In which of these two states is the average distance between molecules greater? (**b**) If you converted a cubic centimeter of liquid benzoic acid into a solid, would the solid take up more, or less, volume than the original cubic centimeter of liquid?

Intermolecular Forces (Section 11.2)

11.50 (**a**) Which type of intermolecular attractive force operates between all molecules? (**b**) Which type of intermolecular attractive force operates only between polar molecules? (**c**) Which type of intermolecular attractive force operates only between the hydrogen atom of a polar bond and a nearby small electronegative atom?

11.51 Describe the intermolecular forces that must be overcome to convert these substances from a liquid to a gas: (**a**) CF_4, (**b**) NH_3, (**c**) BCl_3.

11.52 (**a**) List the following molecules in order of increasing polarizability: $GeCl_4$, CH_4, $SiCl_4$, SiH_4, and $GeBr_4$. (**b**) Predict the order of boiling points of the substances in part (a).

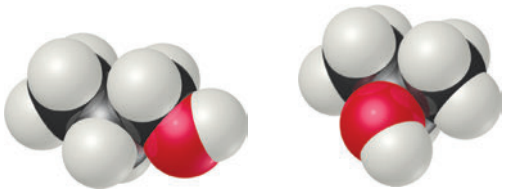
11.53 Which member in each pair has the greater dispersion forces? (**a**) CH_3OH or CH_3CH_2OH, (**b**) NH_3 or $N(CH_3)_3$, (**c**) CH_2Cl_2 or CH_2Br_2.

11.54 Butane and 2-methylpropane, whose space-filling models are shown here, are both nonpolar and have the same molecular formula, C_4H_{10}, yet butane has the higher boiling point (−0.5 °C compared to −11.7 °C). Explain.



Butane 2-Methylpropane

11.55 1-Propanol ($CH_3CH_2CH_2OH$) and 2-propanol [$(CH_3)_2CHOH$], whose space-filling models are shown, have boiling points of 97.2 and 82.5 °C, respectively. Explain why the boiling point of 1-propanol is higher, even though both have the molecular formula, C_3H_8O.



1-Propanol 2-Propanol

11.56 Rationalize the difference in boiling points in each pair: (**a**) $(CH_3)_2O$ (−23 °C) and CH_3CH_2OH (78 °C), (**b**) CO_2 (−78.5 °C) and CS_2 (46.2 °C), (**c**) CH_3COCH_3 (50.5 °C) and CH_3COOH (101 °C).

11.57 Ethylene glycol ($HOCH_2CH_2OH$), the major substance in antifreeze, has a normal boiling point of 198 °C. By comparison, ethanol (CH_3CH_2OH) boils at 78 °C at atmospheric pressure. Ethylene glycol dimethyl ether ($CH_3OCH_2CH_2OCH_3$) has a normal boiling point of 83 °C, and ethyl methyl ether ($CH_3CH_2OCH_3$) has a normal boiling point of 11 °C. (**a**) Explain why replacement of a hydrogen on the oxygen by a CH_3 group generally results in a lower boiling point. (**b**) What are the major factors responsible for the difference in boiling points of the two ethers?

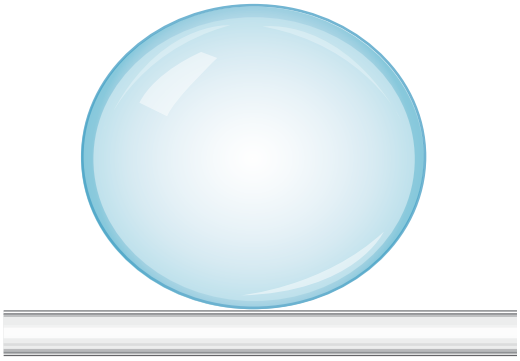
11.58 Look up and compare the normal boiling points and normal melting points of H_2O and H_2S. Based on these physical properties, which substance has stronger intermolecular forces? What kinds of intermolecular forces exist for each molecule?

11.59 A number of salts containing the tetrahedral polyatomic anion, BF_4^-, are ionic liquids, whereas salts containing the somewhat larger tetrahedral ion SO_4^{2-} do not form ionic liquids. Explain this observation.

Select Properties of Liquids (Section 11.3)

11.60 (**a**) What is the relationship between surface tension and temperature? (**b**) What is the relationship between viscosity and temperature? (**c**) Why do substances with high surface tension also tend to have high viscosities?

11.61 Liquids can interact with flat surfaces just as they can with capillary tubes; the cohesive forces within the liquid can be stronger or weaker than the adhesive forces between liquid and surface:



(i)



(ii)

(**a**) In which of these diagrams, i or ii, do the adhesive forces between surface and liquid exceed the cohesive forces within the liquid? (**b**) Which of these diagrams, i or ii, represents what happens when water is on a nonpolar surface? (**c**) Which of these diagrams, i or ii, represents what happens when water is on a polar surface?

11.62 The boiling points, surface tensions, and viscosities of water and several alcohols are as shown in this table:

	Boiling Point (°C)	Surface Tension (J/m^2)	Viscosity (kg/m s)
Water, H_2O	100	7.3×10^{-2}	0.9×10^{-3}
Ethanol, CH_3CH_2OH	78	2.3×10^{-2}	1.1×10^{-3}
1-Propanol, $CH_3CH_2CH_2OH$	97	2.4×10^{-2}	2.2×10^{-3}
1-Butanol, $CH_3CH_2CH_2CH_2OH$	117	2.6×10^{-2}	2.6×10^{-3}
Ethylene glycol, $HOCH_2CH_2OH$	197	4.8×10^{-2}	26×10^{-3}

(**a**) From ethanol to 1-propanol to 1-butanol the boiling points, surface tensions, and viscosities all increase. What is the reason for this increase? (**b**) How do you explain the fact that 1-propanol and ethylene glycol have similar molecular weights (60 versus 62 u), yet the viscosity of ethylene glycol is more than 10 times larger than 1-propanol? (**c**) How do you explain the fact that water has the highest surface tension but the lowest viscosity?

Phase Changes (Section 11.4)

11.63 Name the phase transition in each of the following situations and indicate whether it is exothermic or endothermic: (**a**) Ice-cream melts at room temperature. (**b**) Potato slices become crisp when fried. (**c**) Droplets of water appear on the lid of a food container containing freshly baked bread. (**d**) You can see your own breath on a cold day.

11.64 (**a**) What phase change is represented by the "heat of vaporization" of a substance? (**b**) Is the process of vaporization endothermic or exothermic? (**c**) If you compare a substance's heat of vaporization to the amount of heat released during condensation, which one is generally larger (consider the numerical value only)?

11.65 For many years drinking water has been cooled in hot climates by evaporating it from the surfaces of canvas bags or porous clay pots. How many grams of water can be cooled from 35 to 20 °C by the evaporation of 60 g of water? (The heat of vaporization of water in this temperature range is 2.4 kJ/g. The specific heat of water is 4.18 J/g K.)

11.66 Due to the environmental concern of fluorocarbons as refrigerants, a refrigerant based on a mixture of hydrocarbons was used as a replacement. It is a patented blend of ethane, propane, butane, and isobutane. Isobutane has a normal boiling point of −12 °C. The molar specific heat of liquid phase and gas phase isobutane are 129.7 J/mol K and 95.2 J/mol K respectively. The heat of vaporization for this compound is 21.3 kJ/mol. Calculate the heat required to convert 25.0 g of isobutane from a liquid at −50 °C to a gas at 40 °C.

11.67 The critical temperatures and pressures of a series of halogenated methanes are as follows:

Compound	CCl_3F	CCl_2F_2	$CClF_3$	CF_4
Critical temperature (K)	471	385	302	227
Critical pressure (MPa)	4.41	4.11	3.87	3.75

(**a**) List the intermolecular forces that occur for each compound. (**b**) Predict the order of increasing intermolecular attraction, from least to most, for this series of compounds. (**c**) Predict the critical temperature and pressure for CCl_4 based on the trends in this table. Look up the experimentally determined critical temperatures and pressures for CCl_4, using a source such as the *CRC Handbook of Chemistry and Physics,* and suggest a reason for any discrepancies.

Vapor Pressure (Section 11.5)

11.68 Which of the following affects the vapor pressure of a liquid? (**a**) Volume of the liquid, (**b**) surface area, (**c**) intermolecular attractive forces, (**d**) temperature, (**e**) density of the liquid.

11.69 (**a**) Place the following substances in order of increasing volatility: CH_4, CBr_4, CH_2Cl_2, CH_3Cl, $CHBr_3$, and CH_2Br_2. (**b**) How do the boiling points vary through this series? (**c**) Explain your answer to part (b) in terms of intermolecular forces.

11.70 (**a**) Two pans of water are on different burners of a stove. One pan of water is boiling vigorously, while the other is boiling gently. What can be said about the temperature of the water in the two pans? (**b**) A large container of water and a small one are at the same temperature. What can be said about the relative vapor pressures of the water in the two containers?

11.71 Using the vapor-pressure curves in Figure 11.25, (**a**) estimate the boiling point of diethyl ether at an external pressure of 133.7 kPa, (**b**) estimate the external pressure at which ethylene glycol will boil at 100 °C, (**c**) estimate the boiling point of ethanol at 26.7 kPa, (**d**) estimate the external pressure at which water will boil at 80 °C.

Phase Diagrams (Section 11.6)

11.72 (**a**) What is the significance of the triple point in a phase diagram? (**b**) Could you measure the triple point of water by measuring the temperature in a vessel in which water vapor, liquid water, and ice are in equilibrium under 101.32 kPa of air? Explain.

11.73 Referring to Figure 11.28, describe all the phase changes that would occur in each of the following cases: (**a**) Water vapor originally at 500 Pa and −0.5 °C is slowly compressed at constant temperature until the final pressure is 2000 kPa. (**b**) Water originally at 100.0 °C and 50 kPa is cooled at constant pressure until the temperature is −10 °C.

11.74 Use the phase diagram of neon to answer the following questions. (**a**) What would you observe when the pressure of neon is reduced from 101.3 kPa to 0.1013 kPa at 20 K? (**b**) What can you say about the strength of the intermolecular forces in neon and krypton based on the critical points of Ne and Kr (see Table 11.5)?

11.75 The fact that water on Earth can readily be found in all three states (solid, liquid, and gas) is in part a consequence of the fact that the triple point of water ($T = 0.01$ °C, $P = 608$ Pa) falls within a range of temperatures and pressures found on Earth. Saturn's largest moon Titan has a considerable amount of methane in its atmosphere. The conditions on the surface of Titan are estimated to be $P = 162$ kPa and $T = -178$ °C. As seen from the phase diagram of methane (Figure 11.30), these conditions are not far from the triple point of methane, raising the tantalizing possibility that solid, liquid, and gaseous methane can be found on Titan. (**a**) In what state would you expect to find methane on the surface of Titan? (**b**) On moving upward through the atmosphere, the pressure will decrease. If we assume that the temperature does not change, what phase change would you expect to see as we move away from the surface?

Liquid Crystals (Section 11.7)

11.76 What observations made by Reinitzer on cholesteryl benzoate suggested that this substance possesses a liquid crystalline phase?

11.77 Indicate whether each statement is true or false: (**a**) The liquid crystal state is another phase of matter, just like solid, liquid, and gas. (**b**) Liquid crystalline molecules are generally spherical in shape. (**c**) Molecules that exhibit a liquid crystalline phase do so at well-defined temperatures and pressures. (**d**) Molecules that exhibit a liquid crystalline phase show weaker-than-expected intermolecular forces. (**e**) Molecules containing only carbon and hydrogen are likely to form liquid crystalline phases. (**f**) Molecules can exhibit more than one liquid crystalline phase.

11.78 For a given substance, the liquid crystalline phase tends to be more viscous than the liquid phase. Why?

11.79 It often happens that a substance possessing a smectic liquid crystalline phase just above the melting point passes into a nematic liquid crystalline phase at a higher temperature. Account for this type of behavior.

Additional Exercises

11.80 As the intermolecular attractive forces between molecules increase in magnitude, do you expect each of the following to increase or decrease in magnitude? (**a**) Vapor pressure, (**b**) heat of vaporization, (**c**) boiling point, (**d**) freezing point, (**e**) viscosity, (**f**) surface tension, (**g**) critical temperature.

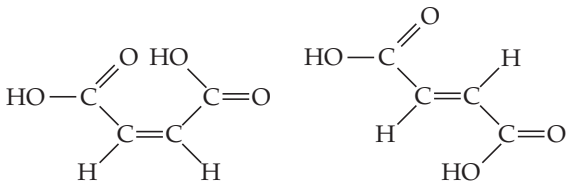
11.81 This table lists the density of substance X at various temperatures and at 101.3 kPa. The normal melting point of substance X is 80 K.

Temperature (K)	Density (mol/L)
90	35.2
100	33.8
110	32.1
120	0.136
140	0.110
160	0.0893
180	0.0796

(**a**) Over what temperature range is substance X a solid? (**b**) Over what temperature range is X a liquid? (**c**) Over what temperature range in the table is X a gas? (**d**) Estimate the normal boiling point of X. (**e**) Given that X is a nonpolar molecule, suggest the kind of intermolecular forces in X.

11.82 Suppose you have two colorless molecular liquids A and B whose boiling points are 78 °C and 112 °C respectively and both are at atmospheric pressure. Which of the following statements is correct? For each statement that is not correct, modify the statement so that it is correct. (**a**) Both A and B are liquids with identical vapor pressure at room temperature of 25 °C. (**b**) Liquid A must consist of nonpolar molecules with lower molecular weight than B. (**c**) Both liquids A and B have higher total intermolecular forces than water. (**d**) Liquid A is more volatile than liquid B because it has a lower boiling point. (**e**) At 112 °C both liquids have a vapor pressure of 1 atm.

11.83 Two isomers of butenedioic acid with the planar structures are shown here:



cis-isomer *trans*-isomer

(**a**) Which of the two isomers will have the stronger intermolecular hydrogen bonding? (**b**) One isomer has a melting point of 135 °C and the other 287 °C. Which isomer has which melting point?

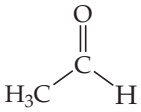
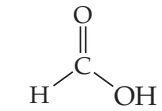
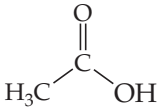
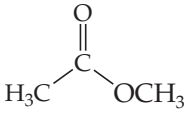
11.84 This table shows some physical properties of compounds containing O-H groups.

Liquid	Molecular Weight	Experimental Dipole Moment	Boiling Point
CH_3OH	32.04	1.7	64.7 °C
$CH_3CH_2CH_2OH$	74.12	1.66	117.7 °C
$HOCH_2CH_2OH$	62.07	1.5	197.3 °C

Which of the following statements best explains these data? (**a**) The larger the dipole moment, the stronger the intermolecular forces, and therefore the boiling point is lowest for the molecule with the largest dipole moment. (**b**) The dis-

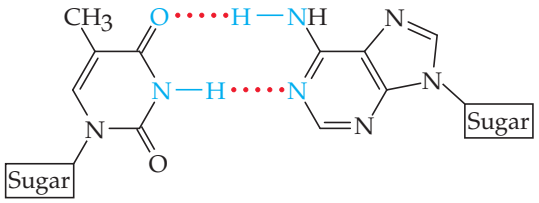
persion forces increase from CH_3OH $CH_3CH_2CH_2OH$ and $HOCH_2CH_2OH$; since the boiling point also increases in this order, the dispersion forces must be the major contributing factor for the boiling point trend; (**c**) $HOCH_2CH_2OH$ has two groups capable of hydrogen bonding per molecule, whereas CH_3OH and $CH_3CH_2CH_2OH$ have only one; therefore, $HOCH_2CH_2OH$ has the highest boiling point.

11.85 This table shows the normal boiling points of some compounds containing C=O groups.

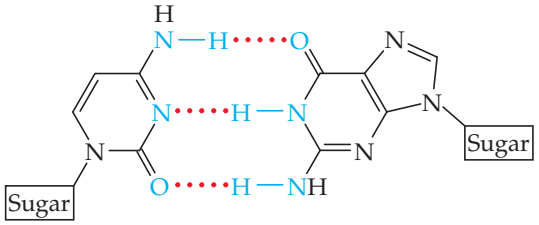
Compound	Structure	Normal Boiling Point (°C)
C_2H_4O (ethanal)		20.2
CH_2O_2 (methanoic acid)		100.8
$C_2H_4O_2$ (ethanoic acid)		118.1
$C_3H_6O_2$ (methyl ethanoate)		56.9

(**a**) Which of these compounds exhibit dispersion interactions? (**b**) Which of these compounds exhibit dipole–dipole interactions? (**c**) Which of these compounds exhibit hydrogen bonding? (**d**) Why is the boiling point of ethanoic acid higher than that of methanoic acid? (**e**) Why is the boiling point of ethanal the lowest of all?

11.86 The DNA double helix (opening picture of section 9.2) at the atomic level looks like a twisted ladder, where the "rungs" of the ladder consist of molecules that are hydrogen-bonded together. Sugar and phosphate groups make up the sides of the ladder. Shown are the structures of the adenine–thymine (AT) "base pair" and the guanine–cytosine (GC) base pair:



Thymine Adenine



Cytosine Guanine

You can see that AT base pairs are held together by two hydrogen bonds and the GC base pairs are held together by three hydrogen bonds. Which base pair is more stable to heating? Why?

11.87 Ethylene glycol ($HOCH_2CH_2OH$) and pentane (C_5H_{12}) are both liquids at room temperature and room pressure, and have about the same molecular weight. (**a**) One of these liquids is much more viscous than the other. Which one do you predict is more viscous? (**b**) One of these liquids has a much lower normal boiling point (36.1 °C) compared to the other one (198 °C). Which liquid has the lower normal boiling point? (**c**) One of these liquids is the major component in antifreeze in automobile engines. Which liquid would you expect to be used as antifreeze? (**d**) One of these liquids is used as a "blowing agent" in the manufacture of polystyrene foam because it is so volatile. Which liquid would you expect to be used as a blowing agent?

11.88 Use the normal boiling points

propane (C_3H_8)	−42.1 °C
butane (C_4H_{10})	−0.5 °C
pentane (C_5H_{12})	36.1 °C
hexane (C_6H_{14})	68.7 °C
heptane (C_7H_{16})	98.4 °C

to estimate the normal boiling point of octane (C_8H_{18}). Explain the trend in the boiling points.

11.89 One of the attractive features of ionic liquids is their low vapor pressure, which in turn tends to make them nonflammable. Why do you think ionic liquids have lower vapor pressures than most room-temperature molecular liquids?

11.90 (**a**) When you exercise vigorously, you sweat. How does this help your body cool? (**b**) A flask of water is connected to a vacuum pump. A few moments after the pump is turned on, the water begins to boil. After a few minutes, the water begins to freeze. Explain why these processes occur.

11.91 The following table gives the vapor pressure of tetrahydrofuran (C_4H_8O) as a function of temperature:

Temperature (°C)	Vapor Pressure (Pa)
−50	99
−10	3630
0	6390
30	26,800
50	58,600

(**a**) By plotting these data in a suitable fashion, determine whether the Clausius–Clapeyron equation (Equation 11.1) is obeyed. If it is obeyed, use your plot to determine ΔH_{vap} for C_4H_8O. (**b**) Use these data to determine the boiling point of the compound.

11.92 Suppose the vapor pressure of a substance is measured at two different temperatures. (**a**) By using the Clausius–Clapeyron equation (Equation 11.1) derive the following relationship between the vapor pressures, P_1 and P_2, and the absolute temperatures at which they were measured, T_1 and T_2:

$$\ln\frac{P_1}{P_2} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(b) Gasoline is a mixture of hydrocarbons, a component of which is octane ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$). Octane has a vapor pressure of 1.86 kPa at 25 °C and a vapor pressure of 19.3 kPa at 75 °C. Use these data and the equation in part (a) to calculate the heat of vaporization of octane. (**c**) By using the equation in part (a) and the data given in part (b), calculate the normal boiling point of octane. Compare your answer to the one you obtained from Exercise 11.88. (**d**) Calculate the vapor pressure of octane at −30 °C.

11.93 The following data present the temperatures at which certain vapor pressures are achieved for dichloromethane (CH_2Cl_2) and methyl iodide (CH_3I):

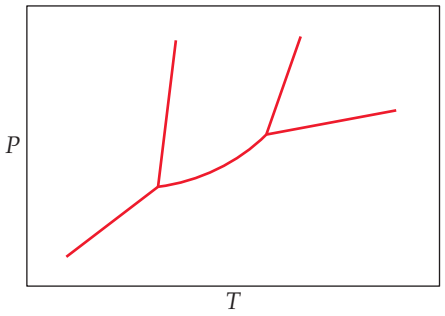
Vapor Pressure (kPa)	1.33	5.33	13.33	53.33
T for CH_2Cl_2 (°C)	−43.3	−22.3	−6.3	24.1
T for CH_3I (°C)	−45.8	−24.2	−7.0	25.3

(**a**) Which of the two substances is expected to have the greater dipole–dipole forces? Which is expected to have the greater dispersion forces? Based on your answers, explain why it is difficult to predict which compound would be more volatile. (**b**) Which compound would you expect to have the higher boiling point? Check your answer in a reference book such as the *CRC Handbook of Chemistry and Physics*. (**c**) The order of volatility of these two substances changes as the temperature is increased. What quantity must be different for the two substances for this phenomenon to occur? (**d**) Substantiate your answer for part (c) by drawing an appropriate graph.

11.94 Solid CO_2 is called dry ice. It sublimes at an atmospheric pressure of −78.5 °C. The triple point of CO_2 is −56.6 °C at 517.8 kPa. CO_2 becomes a supercritical fluid at 31 °C and 7.487 MPa. Using these data, construct a phase diagram for CO_2, labeling all the regions of your diagram.

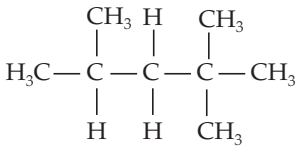
11.95 A watch with a liquid crystal display (LCD) does not function properly when it is exposed to low temperatures during a trip to Antarctica. Explain why the LCD might not function well at low temperature.

11.96 A particular liquid crystalline substance has the phase diagram shown in the figure. By analogy with the phase diagram for a nonliquid crystalline substance, identify the phase present in each area.



Integrative Exercises

11.97 In Table 11.3, we saw that the viscosity of a series of hydrocarbons increased with molecular weight, doubling from the six-carbon molecule to the ten-carbon molecule. (**a**) The eight-carbon hydrocarbon, octane, has an isomer, isooctane. Would you predict that isooctane would have a larger or smaller viscosity than octane? Why? (**b**) Predict the relative order of boiling points of the hydrocarbons in Table 11.4, from lowest to highest. (**c**) The surface tension of



2,2,4-Trimethylpentane or isooctane

the hydrocarbon liquids in Table 11.4 does increase from hexane to decane, but only by a rather small amount (20% overall, compared to the doubling of viscosity). Which of these statements is the most likely explanation for this phenomenon? (i) The flexibility of the molecules has a much larger effect on viscosity than on surface tension. (ii) Viscosity only depends on molecular weight, but surface tension depends on molecular weight and on intermolecular forces. (iii) Larger molecules can make larger liquid droplets and therefore have lower surface tension. (**d**) Nonane has a viscosity of 7.11×10^{-4} kg/m s at 20 °C. *n*-octyl alcohol, $CH_3(CH_2)_7OH$, has almost the same molecular weight as nonane, but its viscosity is 1.01×10^{-2} kg/m s at 20 °C. Which of the following statements is the most likely explanation for this phenomenon? (i) The stronger the intermolecular forces in a liquid, the smaller its viscosity. (ii) The stronger the intermolecular forces in a liquid, the larger its viscosity.

11.98 Rubbing alcohol is the common name for 2-propanol ($CH_3CH(OH)CH_3$). (**a**) Draw the three-dimensional structure of the 2-propanol molecule and predict the geometry around each carbon atom. (**b**) Is the 2-propanol molecule polar or nonpolar? (**c**) What kinds of intermolecular attractive forces exist between the 2-propanol molecules? (**d**) The isomer 1-propanol has the same molecular weight as 2-propanol, yet 2-propanol boils at 82.6 °C and 1-propanol boils at 97.2 °C. Explain the difference.

11.99 The table shown here lists the molar heats of vaporization for several organic compounds. Use specific examples from this list to illustrate how the heat of vaporization varies with (**a**) molar mass, (**b**) molecular shape, (**c**) molecular polarity, (**d**) hydrogen-bonding interactions. Explain these comparisons in terms of the nature of the intermolecular forces at work. (You may find it helpful to draw out the structural formula for each compound.)

Compound	Heat of Vaporization (kJ/mol)
$CH_3CH_2CH_3$	19.0
$CH_3CH_2CH_2CH_2CH_3$	27.6
$CH_3CHBrCH_3$	31.8
CH_3COCH_3	32.0
$CH_3CH_2CH_2Br$	33.6
$CH_3CH_2CH_2OH$	47.3

11.100 The vapor pressure of acetone (CH_3COCH_3) at 19 °C is 5.33 kPa. A 3.50-g sample of acetone is placed in a 2.00 L container at 22 °C. If the container is closed and the acetone is allowed to reach equilibrium with its vapor, how many grams of liquid acetone remain? (Assume that the vapor behaves like an ideal gas.)

11.101 Propane (C_3H_8) is pressurized into liquid and stored in cylinders to be used as a fuel. The normal boiling point of propane is listed as −42 °C. (**a**) When converting propane into liquid at room temperature of 25 °C, would you expect the pressure in the tank to be greater or less than atmospheric pressure? How does the pressure within the tank depend on how much liquid propane is in it? (**b**) Suppose the fuel tank leaks and a few liters of propane escape rapidly. What do you expect would happen to the temperature of the

remaining liquid propane in the tank? Explain. (**c**) How much heat must be added to vaporize 20 g of propane if its heat of vaporization is 18.8 kJ/mol? What volume does this amount of propane occupy at 100 kPa and 25 °C?

11.102 Using information in Appendices B and C, calculate the minimum grams of methane, CH_4, that must be combusted to provide the energy necessary to convert 0.20 kg of ice at −10 °C to liquid water at 70 °C.

11.103 The vapor pressure of a volatile liquid can be determined by slowly bubbling a known volume of gas through it at a known temperature and pressure. In an experiment, 8.00 L of argon gas is passed through 11.7872 g of liquid hexane C_6H_{14} at 30.0 °C. The mass of the remaining liquid after the experiment is 4.875 g. Assuming that the gas becomes saturated with hexane vapor and that the total gas volume and temperature remain constant, what is the vapor pressure of hexane?

11.104 The relative humidity of air is calculated by the ratio of the partial pressure of water in the air to the equilibrium vapor pressure of water at the same temperature times 100%. The average temperature and humidity of the Sahara are 40 °C and 25%, respectively. How many molecules of water are present in 1 m^3 of air in the Sahara?

Design an Experiment

Intermolecular forces are very important for predicting the physical properties of molecular substances. Sometimes, however, it is difficult to explain or predict trends in these properties because all the possible intermolecular forces can be operating at the same time, and there is a wide range of energies for these interactions. Consider ammonia, NH_3. It is a gas at $P = 101.3$ kPa, $T = 25$ °C. Ammonia can be liquefied at −33.5 °C ($P = 101.3$ kPa). Methylamine, CH_3NH_2, is a derivative of ammonia and is also a gas at $P = 101.3$ kPa, $T = 25$ °C. Methylamine can be liquefied at –6.4 °C ($P = 101.3$ kPa).

Use these experimental data to determine which molecule has the stronger intermolecular attractive interactions, ammonia or methylamine; and suggest reasons for your conclusion. Based on your reasons, what other experiments could you do with these molecules, or related molecules, to test your hypothesis?

WHAT'S AHEAD

12.1 ▶ Classification of Solids
12.2 ▶ Metallic Solids
12.3 ▶ Ionic Solids
12.4 ▶ Covalent Solids
12.5 ▶ Polymers
12.6 ▶ Nanomaterials

12

SOLIDS AND MODERN MATERIALS

12.1 | Classification of Solids



Modern devices like computers and cell phones are built from solids with very specific physical properties. For example, the integrated circuit that is at the heart of many electronic devices is built from semiconductors like silicon, metals like copper, and insulators like hafnium oxide.

Scientists and engineers turn almost exclusively to solids for materials used in many other technologies: *alloys* for magnets and airplane turbines, *semiconductors* for solar cells and light-emitting diodes, and *polymers* for packaging and biomedical applications. Chemists have contributed to the discovery and development of new materials either by inventing new substances or by developing the means to process natural materials to

form substances that have specific electrical, magnetic, optical, catalytic, or mechanical properties. In this chapter, we explore the structures and properties of solids. As we do so, we will examine some of the solid materials used in modern technology.

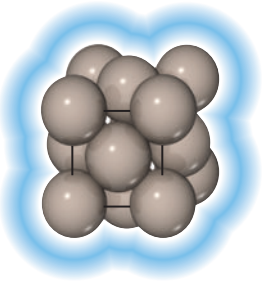
By the end of this section, you should be able to

- Classify solids based on their bonding/intermolecular forces and understand how differences in bonding relate to physical properties.
- Describe the difference between crystalline and amorphous solids.
- Understand the terms used to describe a crystal lattice, recognize the five two-dimensional and the seven three-dimensional primitive lattices, and describe the locations of lattice points for body-centered and face-centered lattices.

Solids can be as hard as diamond or as soft as wax. Some readily conduct electricity, whereas others do not. The shapes of some solids can easily be manipulated, while others are brittle and resistant to any change in shape. The physical properties as well as the structures of solids are dictated by the types of bonds that hold the atoms in place. We can classify solids according to those bonds (**Figure 12.1**).

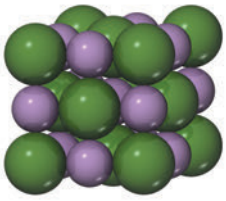
Metallic solids are held together by a delocalized "sea" of collectively shared valence electrons. This form of bonding allows metals to conduct electricity. It is also responsible for the fact that most metals are relatively strong without being brittle. **Ionic solids** are held together by the mutual electrostatic attraction between cations and anions. Differences between ionic and metallic bonding make the electrical and mechanical properties of ionic solids very different from those of metals: Ionic solids do not conduct electricity well and are brittle. **Covalent-network solids** are held together by an extended network of covalent bonds. This type of bonding can result in materials that are extremely hard, like diamond, and it is also responsible for the unique properties of semiconductors. **Molecular solids** are held together by the intermolecular forces we studied in Chapter 11: dispersion forces, dipole–dipole interactions, and hydrogen bonds. Because these forces are relatively weak, molecular solids tend to be soft and have low melting points.

We will also consider two classes of solids that do not fall neatly into the preceding categories: polymers and nanomaterials. **Polymers** contain long chains of atoms (usually carbon), where the atoms within a given chain are connected by covalent bonds and adjacent chains are held to one another largely by weaker intermolecular forces. Polymers are normally stronger and have higher melting points than molecular solids, and they



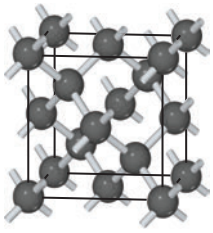
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



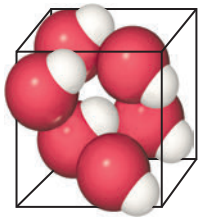
Ionic solids

Extended networks of ions held together by cation–anion interactions (NaCl, MgO)



Covalent-network solids

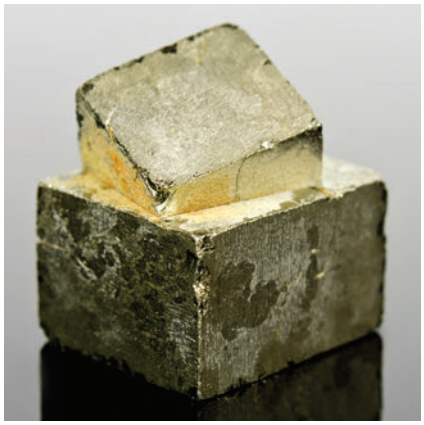
Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H_2O)

▲ **Figure 12.1** **Classification and examples of solids according to predominant bonding type.**

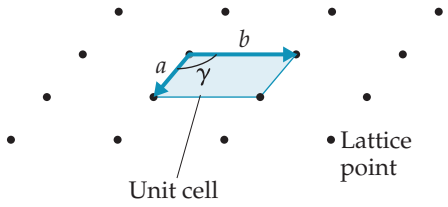


Iron pyrite (FeS_2), a crystalline solid



Obsidian (*ca.* 70% SiO_2), an amorphous solid

▲ **Figure 12.2 Examples of crystalline and amorphous solids.** The atoms in crystalline solids repeat in an orderly, periodic fashion that leads to well-defined faces at the macroscopic level. This order is lacking in amorphous solids like obsidian (volcanic glass).



▲ **Figure 12.3 A crystalline lattice in two dimensions.** An infinite array of lattice points is generated by adding together the lattice vectors *a* and *b*. The unit cell is a parallelogram defined by the lattice vectors.

are more flexible than metallic, ionic, or covalent-network solids. **Nanomaterials** are solids in which the dimensions of individual crystals have been reduced to the order of 1–100 nm. As we will see, the properties of conventional materials change when their crystals become this small.

Crystalline and Amorphous Solids

Solids contain large numbers of atoms. For example, a 1-carat diamond has a volume of 57 mm^3 and contains 1.0×10^{22} carbon atoms. How can we hope to describe such a large collection of atoms? Fortunately, the structures of many solids have patterns that repeat over and over in three dimensions. We can visualize the solid as being formed by stacking a large number of small, identical structural units, much like a wall can be built by stacking identical bricks.

Solids in which atoms are arranged in an orderly repeating pattern are called **crystalline solids**. These solids usually have flat surfaces, or *faces*, that make definite angles with one another. The orderly arrangements of atoms that produce these faces also cause the solids to have highly regular shapes (**Figure 12.2**). Examples of crystalline solids include sodium chloride, quartz, and diamond.

Amorphous solids (from the Greek words for "without form") lack the order found in crystalline solids. At the atomic level the structures of amorphous solids are similar to the structures of liquids, but the molecules, atoms, and/or ions lack the freedom of motion they have in liquids. Amorphous solids do not have the well-defined faces and shapes of a crystal. Familiar amorphous solids are rubber, glass, and obsidian (volcanic glass).

Unit Cells and Crystal Lattices

In a crystalline solid, there is a relatively small repeating unit, called a **unit cell**, that is made up of a unique arrangement of atoms and embodies the structure of the solid. The structure of the crystal can be built by stacking this unit over and over in all three dimensions. Thus, the structure of a crystalline solid is defined by (a) the size and shape of the unit cell and (b) the locations of atoms within the unit cell.

The geometrical pattern of points on which the unit cells are arranged is called a **crystal lattice**. The crystal lattice is, in effect, an abstract (that is, not real) scaffolding for the crystal structure. We can imagine forming the entire crystal structure by first building the scaffolding and then filling in each unit cell with the same atom or group of atoms.

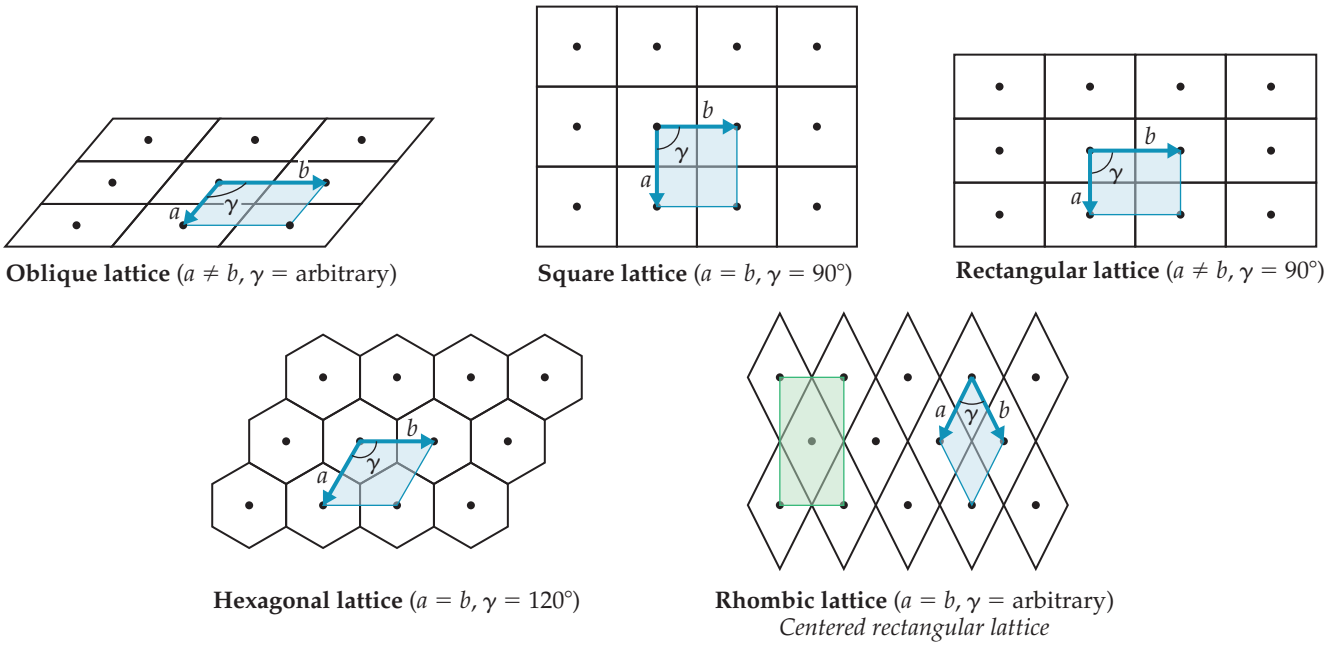
Before describing the structures of solids, we need to understand the properties of crystal lattices. It is useful to begin with two-dimensional lattices because they are simpler to visualize than three-dimensional ones. **Figure 12.3** shows a two-dimensional array of **lattice points**. Each lattice point has an identical environment. The positions of the lattice points are defined by the **lattice vectors** *a* and *b*. Beginning from any lattice point, it is possible to move to any other lattice point by adding together whole-number multiples of the two lattice vectors.*

The parallelogram formed by the lattice vectors, the shaded region in Figure 12.3, defines the unit cell. In two dimensions the unit cells must *tile*, or fit together in space, in such a way that they completely cover the area of the lattice with no gaps. In three dimensions, the unit cells must stack together to fill all space.

In a two-dimensional lattice, the unit cells can take only one of the five shapes shown in **Figure 12.4**. The most general type of lattice is the *oblique lattice*. In this lattice, the lattice vectors are of different lengths and the angle γ between them is of arbitrary size, which makes the unit cell an arbitrarily shaped parallelogram. The *square lattice, rectangular lattice, hexagonal lattice*,** and *rhombic lattice* have a unique combination

*A vector is a quantity involving both a direction and a magnitude. The magnitudes of the vectors in Figure 12.3 are indicated by their lengths, and their directions are indicated by the arrowheads.

**You may wonder why the hexagonal unit cell is not shaped like a hexagon. Remember that the unit cell is by definition a *parallelogram* whose size and shape are defined by the lattice vectors *a* and *b*.



▲ **Figure 12.4 The five two-dimensional lattices.** The primitive unit cell for each lattice is shaded in blue. For the rhombic lattice the centered rectangular unit cell is shaded in green. Unlike the primitive rhombic unit cell, the centered cell has two lattice points per unit cell.

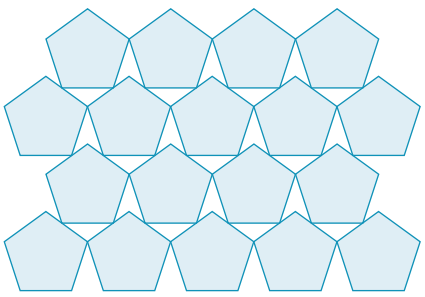
of γ angle and relationship between the lengths of lattice vectors a and b (shown in Figure 12.4). For a rhombic lattice an alternative unit cell can be drawn, a rectangle with lattice points on its corners *and* its center (shown in green in Figure 12.4). Because of this, the rhombic lattice is commonly referred to as a *centered rectangular lattice*. The lattices in Figure 12.4 represent five basic shapes: squares, rectangles, hexagons, rhombuses (diamonds), and arbitrary parallelograms. Other polygons, such as pentagons, cannot cover space without leaving gaps, as **Figure 12.5** shows.

To understand real crystals, we must consider three dimensions. A three-dimensional lattice is defined by *three* lattice vectors a, b, and c (**Figure 12.6**). These lattice vectors define a unit cell that is a parallelepiped (a six-sided figure whose faces are all parallelograms) and is described by the lengths a, b, c of the cell edges and the angles α, β, γ between these edges. There are seven possible shapes for a three-dimensional unit cell, as shown in Figure 12.6.

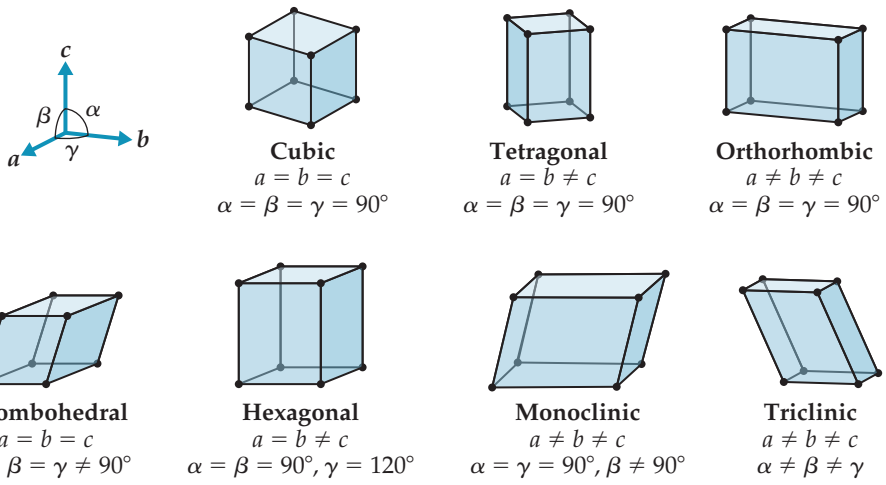
If we place a lattice point at each corner of a unit cell, we get a **primitive lattice**. All seven lattices in Figure 12.6 are primitive lattices. It is also possible to generate

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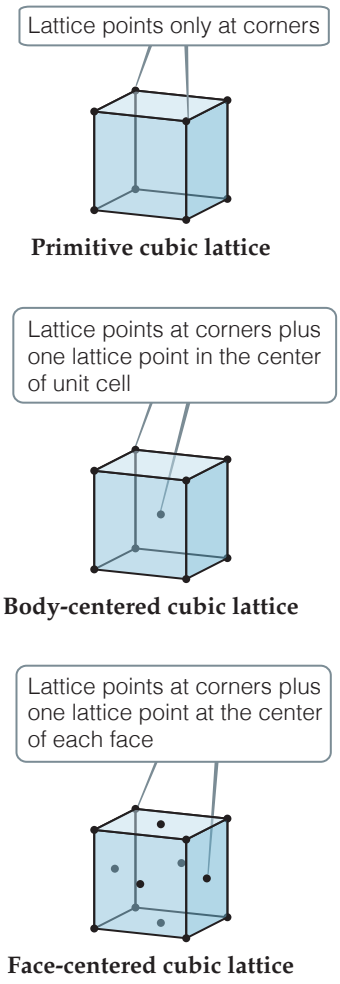
Why is there a centered rectangular lattice but not a centered square lattice?



▲ **Figure 12.5 Not all shapes tile space.** Tiling means covering a surface entirely, which is impossible for some geometric shapes, as shown here for pentagons.



▲ **Figure 12.6 The seven three-dimensional primitive lattices.**



▲ **Figure 12.7** **The three types of cubic lattices.**

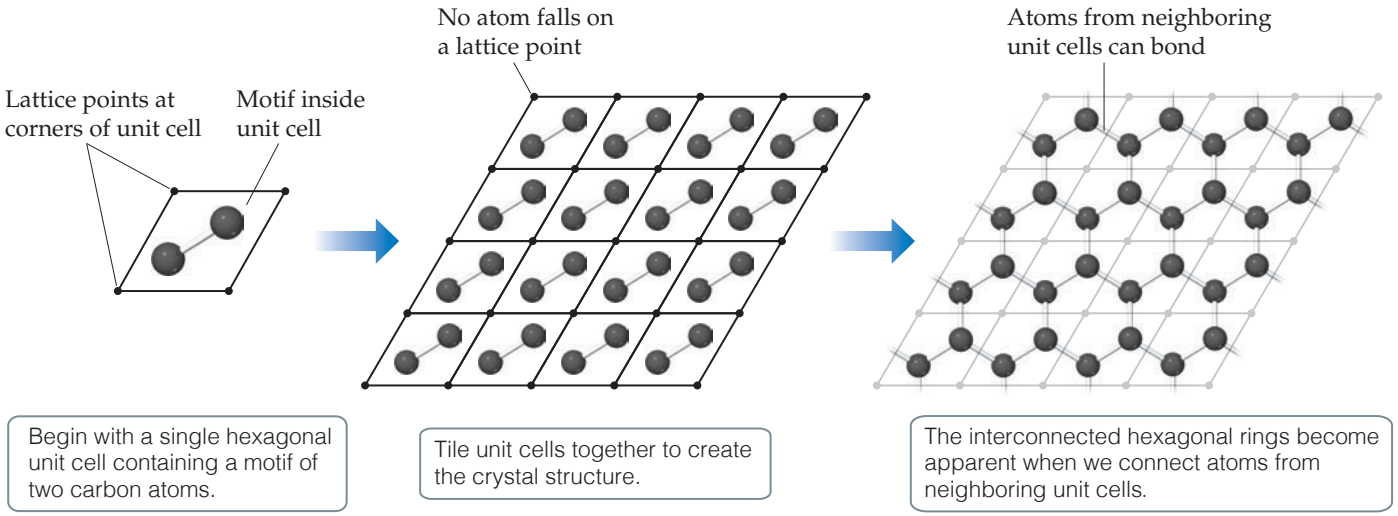
what are called *centered lattices* by placing additional lattice points in specific locations in the unit cell. This is illustrated for a cubic lattice in **Figure 12.7**. A **body-centered cubic lattice** has one lattice point at the center of the unit cell in addition to the lattice points at the eight corners. A **face-centered cubic lattice** has one lattice point at the center of each of the six faces of the unit cell in addition to the lattice points at the eight corners. Centered lattices exist for other types of unit cells as well. For the crystals discussed in this chapter we need consider only the lattices shown in Figures 12.6 and 12.7.

Filling the Unit Cell

The lattice by itself does not define a crystal structure. To generate a crystal structure, we need to associate an atom or group of atoms with each lattice point. In the simplest case, the crystal structure consists of identical atoms, and each atom lies directly on a lattice point. When this happens, the crystal structure and the lattice points have identical patterns. Many metallic elements adopt such structures, as we will see in Section 12.2. Only for solids in which all the atoms are identical can this occur; in other words, *only elements* can form structures of this type. For compounds, even if we were to put an atom on every lattice point, the points would not be identical because the atoms are not all the same.

In most crystals, the atoms are not exactly coincident with the lattice points. Instead, a group of atoms, called a **motif**, is associated with each lattice point. The unit cell contains a specific motif of atoms, and the crystal structure is built up by repeating the unit cell over and over. This process is illustrated in **Figure 12.8** for a two-dimensional crystal based on a hexagonal unit cell and a two-carbon-atom motif. The resulting infinite two-dimensional honeycomb structure is a two-dimensional crystal called *graphene*, a material that has so many interesting properties that its modern discoverers won the Nobel Prize in Physics in 2010. Each carbon atom is covalently bonded to three neighboring carbon atoms in what amounts to an infinite sheet of interconnected hexagonal rings.

The crystal structure of graphene illustrates two important characteristics of crystals. First, we see that no atoms lie on the lattice points. While most of the structures we discuss in this chapter do have atoms on the lattice points, there are many examples, like graphene, where this is not the case. Thus, to build up a structure you must know the location and orientation of the atoms in the motif with respect to the lattice points. Second, we see that bonds can be formed between atoms in neighboring unit cells and the bonds between atoms need not be parallel to the lattice vectors.



▲ **Figure 12.8** **Two-dimensional structure of graphene built up from a single unit cell.**

A CLOSER LOOK X-ray Diffraction

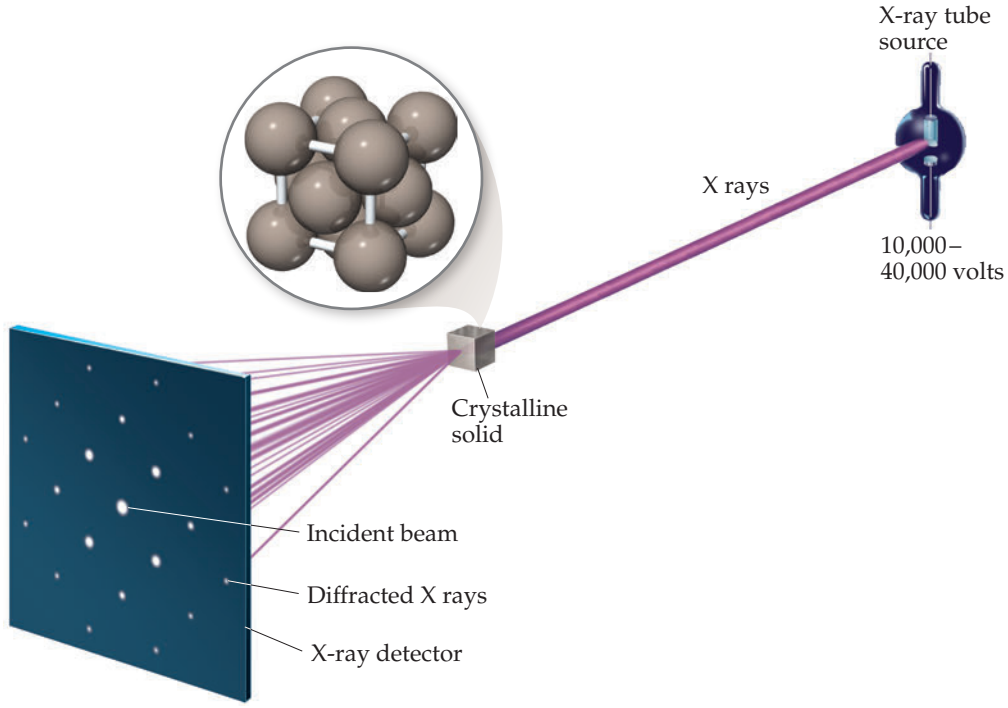
When light waves pass through a narrow slit, they are scattered in such a way that the wave seems to spread out. This physical phenomenon is called *diffraction*. When light passes through many evenly spaced narrow slits (a *diffraction grating*), the scattered waves interact to form a series of bright and dark bands, known as a diffraction pattern. The bright bands correspond to constructive overlapping of the light waves, and the dark bands correspond to destructive overlapping of the light waves. The most effective diffraction of light occurs when the wavelength of the light and the width of the slits are similar in magnitude.

The spacing of the layers of atoms in solid crystals is usually about 0.2–2 nm. The wavelengths of X rays are also in this range. Thus, a crystal can serve as an effective diffraction grating for X rays. X-ray diffraction results from the scattering of X rays by a regular arrangement of atoms, molecules, or ions. Much of what we know about crystal structures has been obtained by looking at the diffraction patterns that result when X rays pass through a crystal, a technique known as *X-ray crystallography*. As shown in **Figure 12.9** a monochromatic beam of X rays is passed through a crystal. The diffraction pattern that results is recorded. For many years the diffracted X rays were detected by photographic film. Today, crystallographers use an *array detector*, a device analogous to that used in digital cameras, to capture and measure the intensities of the diffracted rays.

The pattern of spots on the detector in Figure 12.9 depends on the particular arrangement of atoms in the crystal. The spacing and symmetry of the bright spots, where constructive interference occurs, provide information about the size and shape of the unit cell. The intensities of the spots provide information that can be used to determine the locations of the atoms within the unit cell. When combined, these two pieces of information give the atomic structure that defines the crystal.

X-ray crystallography is used extensively to determine the structures of molecules in crystals. The instruments used to measure X-ray diffraction, known as *X-ray diffractometers*, are now computer controlled, making the collection of diffraction data highly automated. The diffraction pattern of a crystal can be determined very accurately and quickly (sometimes in a matter of hours), even though thousands of diffraction spots are measured. Computer programs are then used to analyze the diffraction data and determine the arrangement and structure of the molecules in the crystal. X-ray diffraction is an important technique in industries ranging from steel and cement manufacture to pharmaceuticals.

Related Exercises: 12.120–12.122



▲ **Figure 12.9 Diffraction of X rays by a crystal.** A monochromatic X-ray beam is passed through a crystal. The X rays are diffracted, and the resulting interference pattern is recorded. The crystal is rotated and another diffraction pattern recorded. Analysis of many diffraction patterns gives the positions of the atoms in the crystal.

Self-Assessment Exercises

12.1 How would you classify wax?
- **(a)** Metallic solid
- **(b)** Ionic solid
- **(c)** Molecular solid
- **(d)** Covalent-network solid

12.2 Is soot an amorphous or crystalline form of carbon?
- **(a)** Amorphous
- **(b)** Crystalline

12.3 How would you describe the lattice portrayed for the metallic solid in Figure 12.1?
- **(a)** Body-centered cubic lattice
- **(b)** Face-centered cubic lattice

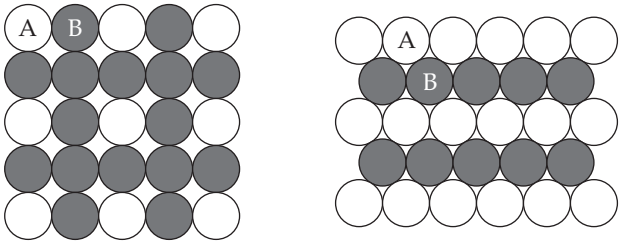
Exercises

12.4 Silicon is the fundamental component of integrated circuits. Si has the same structure as diamond. (**a**) Is Si a molecular, metallic, ionic, or covalent-network solid? (**b**) Silicon readily reacts to form silicon dioxide, SiO_2, which is quite hard and is insoluble in water. Is SiO_2 most likely a molecular, metallic, ionic, or covalent-network solid?

12.5 Which type (or types) of crystalline solid is characterized by each of the following? (**a**) High mobility of electrons throughout the solid; (**b**) softness, relatively low melting point; (**c**) high melting point and poor electrical conductivity; (**d**) network of covalent bonds.

12.6 You are given a white substance that melts at 1500 °C. The substance is brittle and soluble in water. Both the molten solid and the solution is a conductor of electricity. Which type of solid (molecular, metallic, covalent-network, or ionic) might this substance be?

12.7 Two patterns of packing two different circles of the same size are shown here. For each structure (**a**) draw the two-dimensional unit cell; (**b**) determine the angle between the lattice vectors, γ, and determine whether the lattice vectors are of the same length or of different lengths; (**c**) determine the type of two-dimensional lattice (from Figure 12.4).



(i) **(ii)**

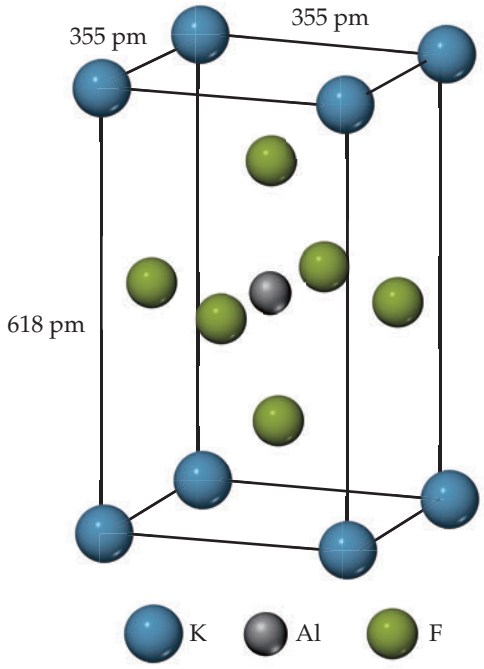
12.8 Imagine the primitive cubic lattice. Now imagine grabbing opposite corners and stretching it along the body diagonal while keeping the edge lengths equal. The three angles between the lattice vectors remain equal but are no longer 90°. What kind of primitive lattice have you made?



12.9 Besides the cubic unit cell, which other unit cell(s) has edge lengths that are all equal to each other? (**a**) Orthorhombic, (**b**) hexagonal, (**c**) rhombohedral, (**d**) triclinic, (**e**) both rhombohedral and triclinic.

12.10 What is the minimum number of atoms that could be contained in the unit cell of an element with a face-centered cubic lattice? (**a**) 1, (**b**) 2, (**c**) 3, (**d**) 4, (**e**) 5.

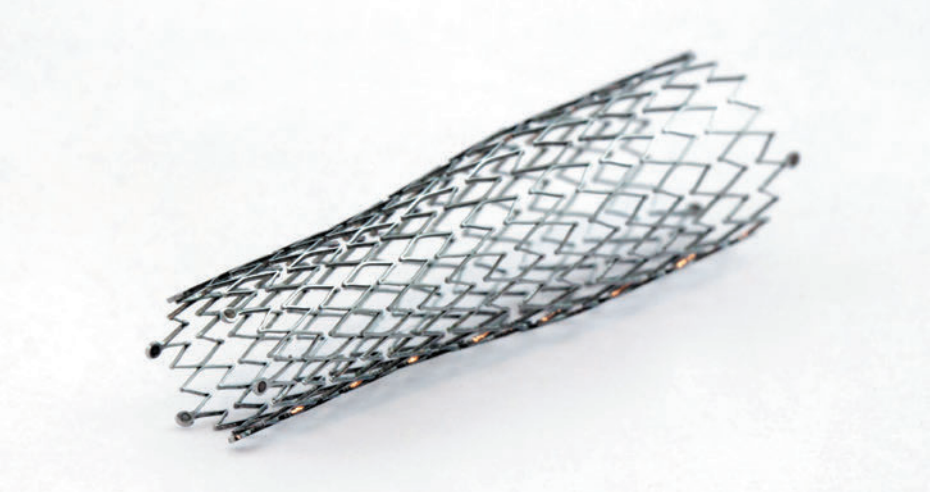
12.11 The unit cell of a compound containing potassium, aluminum, and fluorine is shown here. (**a**) What type of lattice does this crystal possess (all three lattice vectors are mutually perpendicular)? (**b**) What is the empirical formula?



Answers to Self-Assessment Exercises

12.1 (c) **12.2** (a) **12.3** (b)

12.2 | Metallic Solids



Nitinol is a 1:1 nickel–titanium alloy that has 'shape memory'. This remarkable property was discovered by accident when the alloy was presented to a management meeting of the US Naval Ordnance Laboratory (from where it derived its name: Ni-Ti-N-O-L) in 1961. The folded wire was passed around the room and one of the participants used a cigarette lighter to heat the sample. To the astonishment of those present, the wire uncoiled and took on its original shape. The wire has two crystal structures that are easily interconverted but that are stable at different temperatures. Heating the wire while holding the desired shape fixes the shape and crystal structure. On cooling, the wire may be deformed into another shape and transform to a more complicated crystal structure. Subsequent warming reforms the original crystal lattice and shape.

There are several applications of nitinol in dentistry and medicine. For example, stents used to treat heart conditions can be 'set' in their open, functioning shape before cooling and compacting for easy insertion into a blocked coronary artery. At body temperature, the nitinol reforms its open shape, allowing blood to flow more freely.

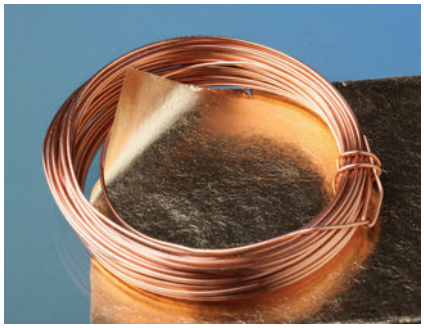
By the end of this section, you should be able to

- Describe the lattice structure of metals and alloys
- Relate the physical properties of metals to the bonding present

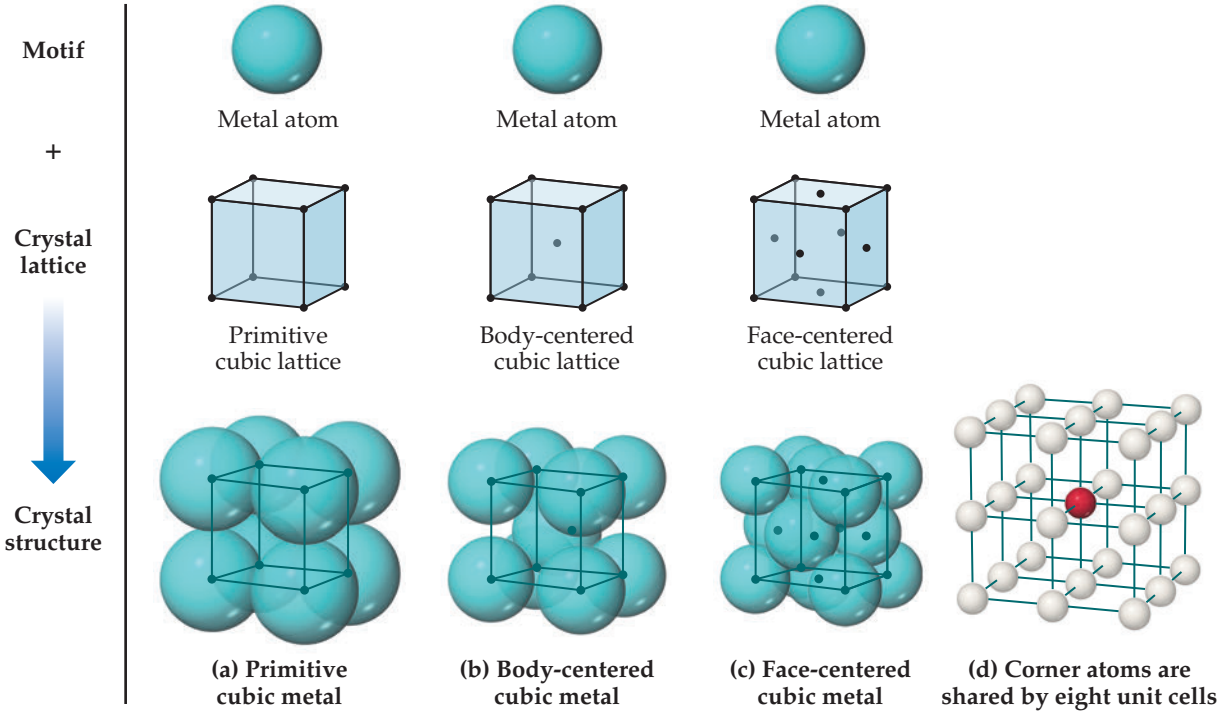
Metallic solids, also simply called *metals*, consist entirely of metal atoms. The bonding in metals is too strong to be due to dispersion forces, and yet there are not enough valence electrons to form covalent bonds between atoms. The bonding, called *metallic bonding*, happens because the valence electrons are *delocalized* throughout the entire solid. That is, the valence electrons are not associated with specific atoms or bonds but are spread throughout the solid. In fact, we can visualize a metal as an array of positive ions immersed in a "sea" of delocalized valence electrons.

The chemical bonding in metals is reflected in their properties. You have probably held a length of copper wire or an iron bolt. Perhaps you have even seen the surface of a freshly cut piece of sodium metal. These substances, though distinct from one another, share certain similarities that enable us to classify them as metallic. A clean metal surface has a characteristic luster. Metals have a cold feeling when you touch them, related to their high thermal conductivity (ability to conduct heat). Metals also have high electrical conductivity, which means that electrically charged particles flow easily through them. The thermal conductivity of a metal usually parallels its electrical conductivity. Silver and copper, for example, which possess the highest electrical conductivities among the elements, also possess the highest thermal conductivities.

Most metals are *malleable*, which means that they can be hammered into thin sheets, and *ductile*, which means that they can be drawn into wires (**Figure 12.10**). These properties indicate that the atoms are capable of slipping past one another. Ionic and covalent-network solids do not exhibit such behavior; they are typically brittle.



▲ **Figure 12.10 Malleability and ductility.** Gold leaf demonstrates the characteristic malleability of metals, and copper wire demonstrates their ductility.



▲ **Figure 12.11 The structures of (a) primitive cubic, (b) body-centered cubic, and (c) face-centered cubic metals.** Each structure can be generated by the combination of a single-atom motif and the appropriate lattice. (**d**) Corner atoms (one shown in red) are shared among eight neighboring cubic unit cells.

The Structures of Metallic Solids

The crystal structures of many metals are simple and can be generated by placing a single atom on each lattice point. The structures corresponding to the three cubic lattices are shown in **Figure 12.11**. Metals with a primitive cubic structure are rare, one of the few examples being the radioactive element polonium. Body-centered cubic metals include iron, chromium, sodium, and tungsten. Examples of face-centered cubic metals include aluminum, lead, copper, silver, and gold.

Notice in the bottom row of Figure 12.11 that the atoms on the corners and faces of a unit cell do not lie wholly within the unit cell. These corner and face atoms are shared by neighboring unit cells. An atom that sits at the corner of a unit cell is shared among eight unit cells, and only $1/8$ of the atom is in one particular unit cell. Because a cube has eight corners, each primitive cubic unit cell contains $(1/8) \times 8 = 1$ atom, as shown in **Figure 12.12**(**a**). Similarly, each body-centered cubic unit cell [Figure 12.12(**b**)] contains two atoms, $(1/8) \times 8 = 1$ from the corners and 1 at the center of the unit cell. Atoms that lie on the face of a unit cell, as they do in a face-centered cubic metal, are shared by two unit cells so that only one-half of the atom belongs to each unit cell. Therefore, a face-centered cubic unit cell [Figure 12.12(**c**)] contains four atoms, $(1/8) \times 8 = 1$ atom from the corners and $(1/2) \times 6 = 3$ atoms from the faces.

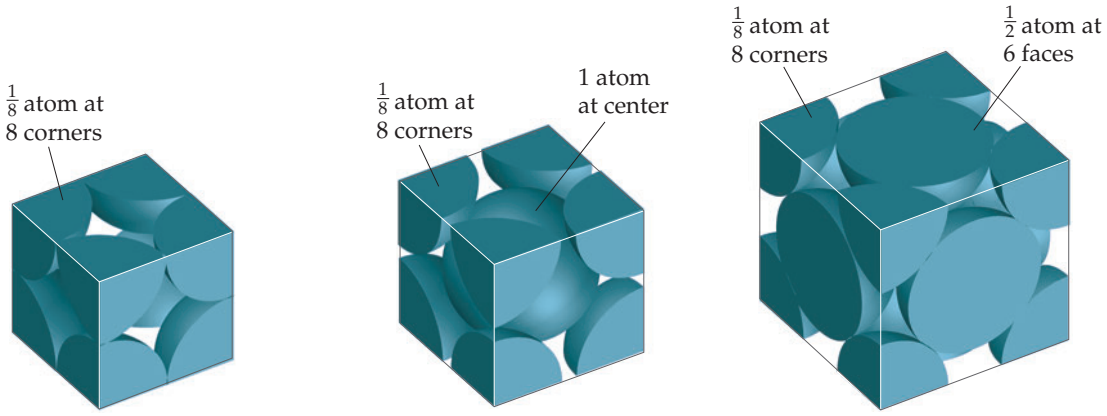
Table 12.1 summarizes how the fractional part of each atom that resides within a unit cell depends on the atom's location within the cell.

Close Packing

The shortage of valence electrons and the fact that they are collectively shared make it favorable for the atoms in a metal to pack together closely. Because we can consider the shape of an atom to be a sphere, we can understand the structures of metals by considering how spheres pack. The most efficient way to pack one layer of equal-sized spheres is to surround each sphere by six neighbors, as shown at the top of **Figure 12.13**. To form a three-dimensional structure, we need to stack additional layers on top of this base layer. To maximize packing efficiency, the second layer of spheres must sit in the depressions

Go Figure

Which one of these unit cells would you expect to represent the densest packing of spheres?



(a) Primitive cubic metal
1 atom per unit cell

(b) Body-centered cubic metal
2 atoms per unit cell

(c) Face-centered cubic metal
4 atoms per unit cell

▲ **Figure 12.12 A space-filling view of unit cells for metals with a cubic structure.** Only the portion of each atom that falls within the unit cell is shown.

TABLE 12.1 Fraction of Any Atom as a Function of Location within the Unit Cell*

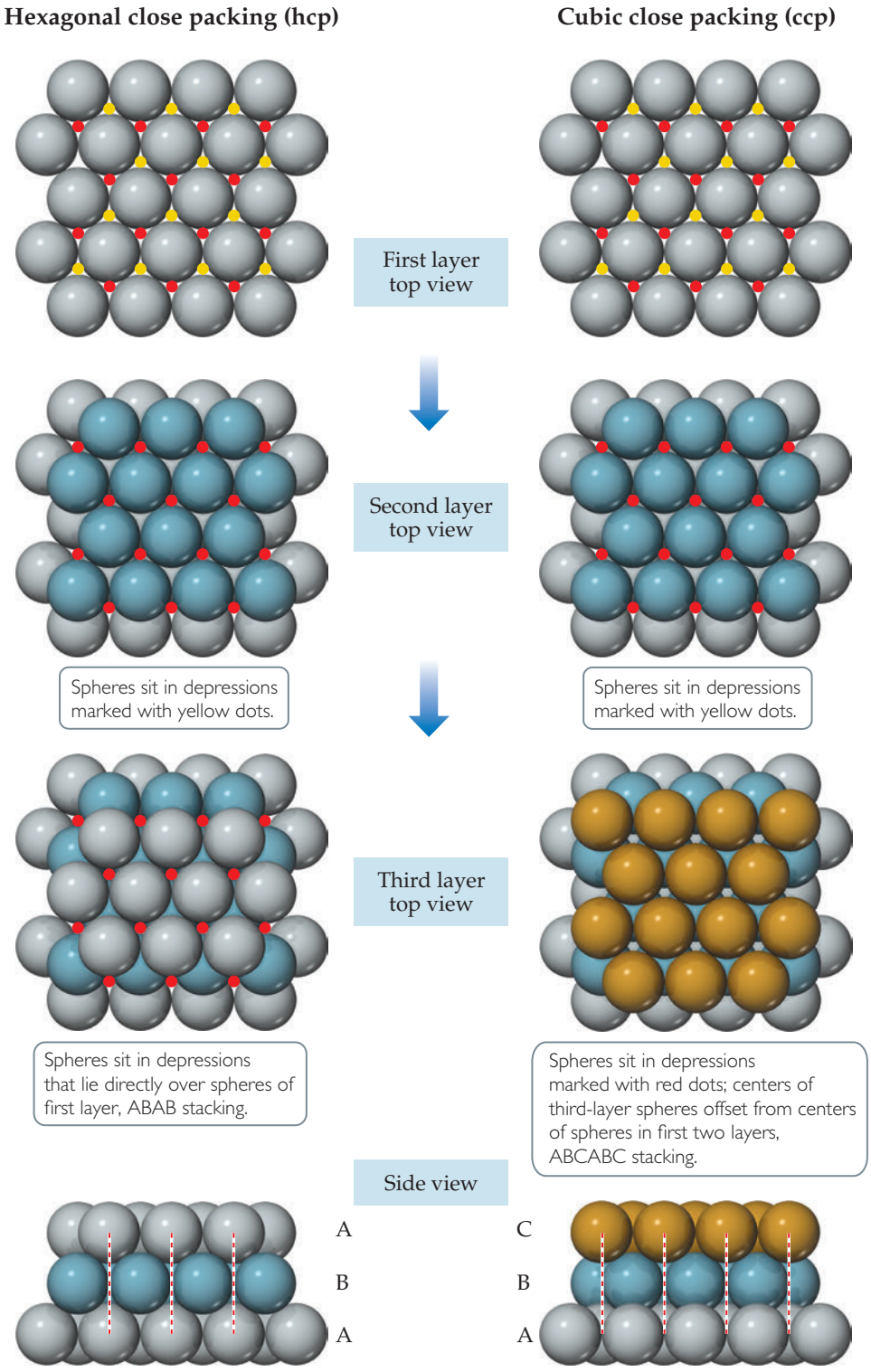
Atom Location	Number of Unit Cells Sharing Atom	Fraction of Atom within Unit Cell
Corner	8	1/8 or 12.5%
Edge	4	1/4 or 25%
Face	2	1/2 or 50%
Anywhere else	1	1 or 100%

*It is only the position of the center of the atom that matters. Atoms that reside near the boundary of the unit cell but not on a corner, edge, or face are counted as residing 100% within the unit cell.

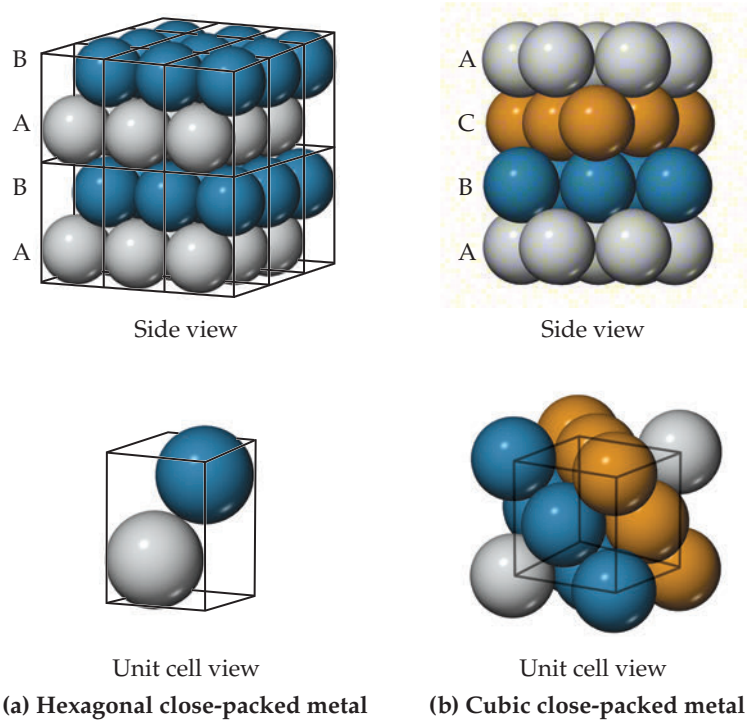
formed by the spheres in the first layer. We can either put the next layer of atoms into the depressions marked by the yellow dot or the depressions marked by the red dot (realizing that the spheres are too large to simultaneously fill both sets of depressions). For the sake of discussion we arbitrarily put the second layer in the yellow depressions.

For the third layer, we have two choices for where to place the spheres. One possibility is to put the third layer in the depressions that lie directly over the spheres in the first layer. This is done on the left-hand side of Figure 12.13, as shown by the dashed red lines in the side view. Continuing with this pattern, the fourth layer would lie directly over the spheres in the second layer, leading to the ABAB stacking pattern seen on the left, which is called **hexagonal close packing** (hcp). Alternatively, the third-layer spheres could lie directly over the depressions that were marked with red dots in the first layer. In this arrangement, the spheres in the third layer do not sit directly above the spheres in either of the first two layers, as shown by the dashed red lines on the lower right-hand side of Figure 12.13. If this sequence is repeated in subsequent layers, we derive an ABCABC stacking pattern shown on the right known as **cubic close packing** (ccp). In both hexagonal close packing and cubic close packing, each sphere has 12 equidistant nearest neighbors: six neighbors in the same layer, three from the layer above, and three from the layer below. We say that each sphere has a **coordination number** of 12. The coordination number is the number of atoms immediately surrounding a given atom in a crystal structure.

Go Figure What type of two-dimensional lattice describes the structure of a single layer of close-packed atoms?



▲ **Figure 12.13 Close packing of equal-sized spheres.** Hexagonal (left) close packing and cubic (right) close packing are equally efficient ways of packing spheres. The red and yellow dots indicate the positions of depressions between atoms.



(a) Hexagonal close-packed metal **(b) Cubic close-packed metal**

◀ **Figure 12.14 The unit cells for (a) a hexagonal close-packed metal and (b) a cubic close-packed metal.** The solid lines indicate the unit cell boundaries. Colors are used to distinguish one layer of atoms from another.

The extended structure of a hexagonal close-packed metal is shown in Figure 12.14(**a**). There are two atoms in the primitive hexagonal unit cell, one from each layer. Neither atom sits directly on the lattice points, which are located at the corners of the unit cell. The presence of two atoms in the unit cell is consistent with the two-layer ABAB stacking sequence associated with hcp packing.

Although it is not immediately obvious, the structure that results from cubic close packing possesses a unit cell that is identical to the face-centered cubic unit cell we encountered earlier [Figure 12.11(**c**)]. The relationship between the ABC layer stacking and the face-centered cubic unit cell is shown in Figure 12.14(**b**). In this figure, we see that the layers stack perpendicular to the body diagonal of the cubic unit cell.

Sample Exercise 12.1

Calculating Packing Efficiency

It is not possible to pack spheres together without leaving some void spaces between the spheres. *Packing efficiency* is the fraction of space in a crystal that is actually occupied by atoms. Determine the packing efficiency of a face-centered cubic metal.

SOLUTION

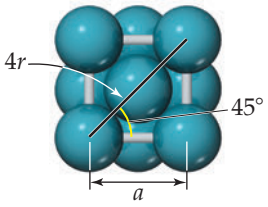
Analyze We must determine the volume taken up by the atoms that reside in the unit cell and divide this number by the volume of the unit cell.

Plan We can calculate the volume taken up by atoms by multiplying the number of atoms per unit cell by the volume of a sphere, $4\pi r^3/3$. To determine the volume of the unit cell, we must first identify the direction along which the atoms touch each other. We can then use geometry to express the length of the cubic unit cell edge, a, in terms of the radius of the atoms. Once we know the edge length, the cell volume is simply a^3.

Solve As shown in Figure 12.12, a face-centered cubic metal has four atoms per unit cell. Therefore, the volume occupied by the atoms is

$$\text{Occupied volume} = 4 \times \left(\frac{4\pi r^3}{3}\right) = \frac{16\pi r^3}{3}$$

For a face-centered cubic metal, the atoms touch along the diagonal of a face of the unit cell:



Therefore, a diagonal across a face of the unit cell is equal to four times the atomic radius, r. Using simple trigonometry, and the identity $\cos(45°) = \sqrt{2}/2$, we can show that

$$a = 4r\cos(45°) = 4r(\sqrt{2}/2) = (2\sqrt{2})r$$

Finally, we calculate the packing efficiency by dividing the volume occupied by atoms by the volume of the cubic unit cell, a^3:

$$\text{Packing efficiency} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{(\frac{16}{3})\pi r^3}{(2\sqrt{2})^3 r^3}$$

$$= 0.74 \text{ or } 74\%$$

Continued

Practice Exercise

Consider the two-dimensional square lattice of Figure 12.4. The "packing efficiency" for a two-dimensional structure would be the area of the atoms divided by the area of the unit cell, times 100%. What is the packing efficiency for a square lattice for atoms of radius $a/2$ that are centered at the lattice points?

(**a**) 3.14% (**b**) 15.7% (**c**) 31.8% (**d**) 74.0% (**e**) 78.5%

Alloys

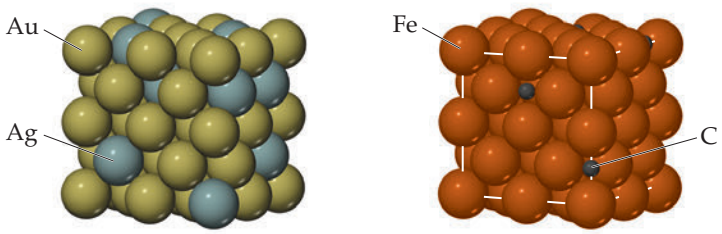
An **alloy** is a material that contains more than one element and has the characteristic properties of a metal. The alloying of metals is of great importance because it is one of the primary ways of modifying the properties of pure metallic elements. Nearly all the common uses of iron, for example, involve alloy compositions (for example, stainless steel). Bronze is formed by alloying copper and tin, while brass is an alloy of copper and zinc. Pure gold is too soft to be used in jewelry, but alloys of gold are much harder (see "Chemistry Put to Work: Alloys of Gold"). Other common alloys are described in **Table 12.2**.

Alloys can be divided into four categories: substitutional alloys, interstitial alloys, heterogeneous alloys, and intermetallic compounds. Substitutional and interstitial alloys are both homogeneous mixtures in which components are dispersed randomly and uniformly (**Figure 12.15**). Solids that form homogeneous mixtures are called solid solutions. When atoms of the solute in a solid solution occupy positions normally occupied by a solvent atom, we have a **substitutional alloy**. When the solute atoms occupy interstitial positions in the "holes" between solvent atoms, we have an **interstitial alloy** (Figure 12.15).

TABLE 12.2 Some Common Alloys

Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood's metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber's solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

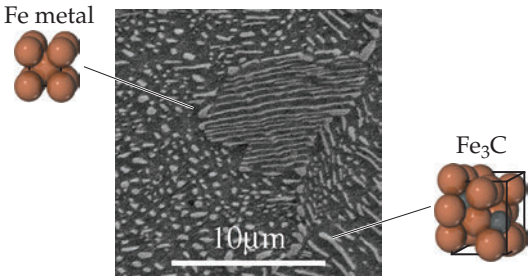
Go Figure What determines which species in a solid solution is the solute and which is the solvent?



Substitutional alloy
14-karat gold

Interstitial alloy
Steel

▲ **Figure 12.15 The distribution of solute and solvent atoms in a substitutional alloy and an interstitial alloy.** Both types of alloys are solid solutions and, therefore, homogeneous mixtures.



◀ **Figure 12.16 Microscopic view of the structure of the heterogeneous alloy pearlite.** The dark regions are body-centered cubic iron metal, and the lighter regions are cementite, Fe_3C.

Substitutional alloys are formed when the two metallic components have similar atomic radii and chemical-bonding characteristics. For example, silver and gold form such an alloy over the entire range of possible compositions. When two metals differ in radii by more than about 15%, solubility is generally more limited.

For an interstitial alloy to form, the solute atoms must have a much smaller bonding atomic radius than the solvent atoms. Typically, the interstitial element is a nonmetal that makes covalent bonds to the neighboring metal atoms. The presence of the extra bonds provided by the interstitial component causes the metal lattice to become harder, stronger, and less ductile. For example, steel, which is much harder and stronger than pure iron, is an alloy of iron that contains up to 3% carbon. Other elements may be added to form *alloy steels*. Vanadium and chromium may be added to impart strength, for instance, and to increase resistance to fatigue and corrosion.

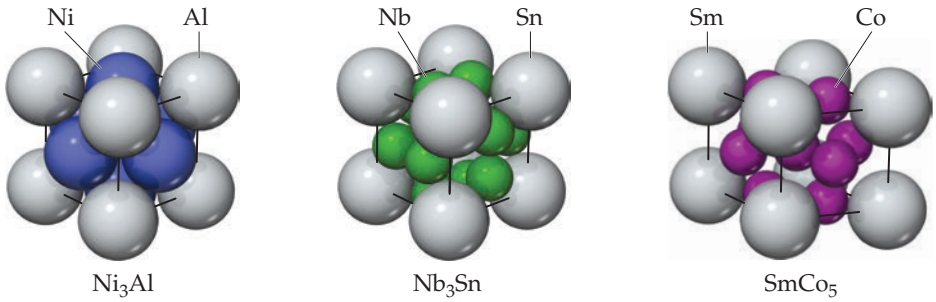
One of the most important iron alloys is stainless steel, which contains about 0.4% carbon, 18% chromium, and 1% nickel. The ratio of elements present in the steel may vary over a wide range, imparting a variety of specific physical and chemical properties to the materials.

In a **heterogeneous alloy**, the components are not dispersed uniformly. For example, the heterogeneous alloy pearlite contains two phases (**Figure 12.16**). One phase is essentially pure body-centered cubic iron, and the other is the compound Fe_3C, known as cementite. In general, the properties of heterogeneous alloys depend on both the composition and the manner in which the solid is formed from the molten mixture. The properties of a heterogeneous alloy formed by rapid cooling of a molten mixture, for example, are distinctly different from the properties of an alloy formed by slow cooling of the same mixture.

Intermetallic compounds are compounds rather than mixtures. Because they are compounds, they have definite properties and their composition cannot be varied. Furthermore, the different types of atoms in an intermetallic compound are ordered rather than randomly distributed. The ordering of atoms in an intermetallic compound generally leads to better structural stability and higher melting points than what is observed in the constituent metals. These features can be attractive for high-temperature applications. On the negative side, intermetallic compounds are often more brittle than substitutional alloys.

Intermetallic compounds play many important roles in modern society. The intermetallic compound Ni_3Al is a major component of jet aircraft engines because of

Go Figure In the unit cell drawing on the right, why do we see eight Sm atoms and nine Co atoms if the empirical formula is $SmCo_5$?



▲ **Figure 12.17 Three examples of intermetallic compounds.**

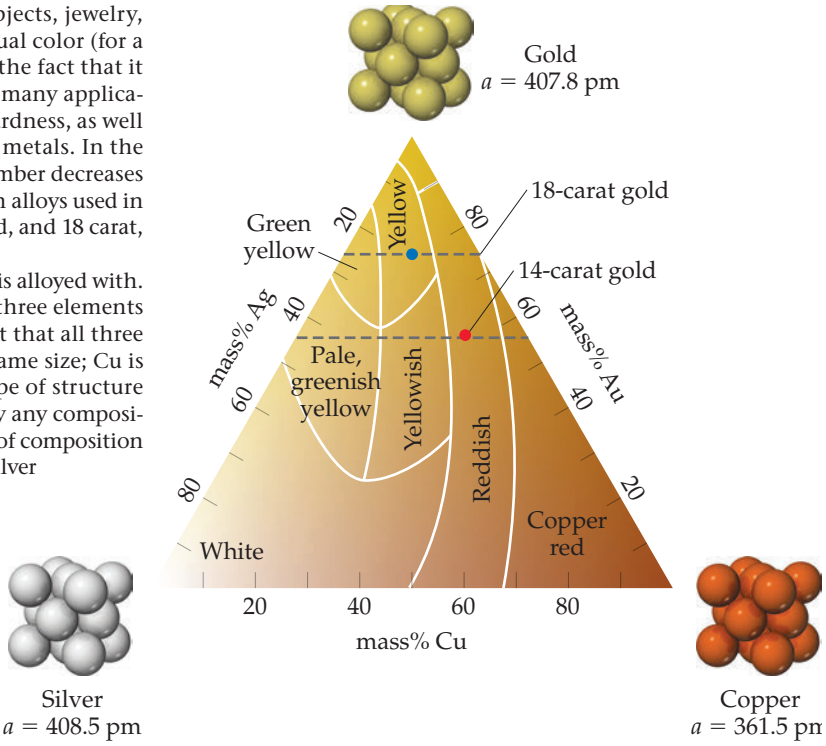
its strength at high temperature and its low density. Razor blades are often coated with Cr_3Pt, which adds hardness, allowing the blade to stay sharp longer. Both compounds have the structure shown on the left-hand side of **Figure 12.17**. The compound Nb_3Sn, also shown in Figure 12.17, is a superconductor, a substance that, when cooled below a critical temperature, conducts electricity with no resistance. In the case of Nb_3Sn superconductivity is observed only when the temperature falls below 18 K. Superconductors are used in the magnets in MRI scanners widely employed for medical imaging. The need to keep the magnets cooled to such a low temperature is part of the reason why MRI devices are expensive to operate. The hexagonal intermetallic compound $SmCo_5$, shown on the right-hand side of Figure 12.17, is used to make the permanent magnets found in lightweight headsets and high-fidelity speakers. A related compound with the same structure, $LaNi_5$, is used as the anode in nickel-metal hydride batteries.

CHEMISTRY PUT TO WORK Alloys of Gold

Gold has long been a metal of choice for decorative objects, jewelry, and coins. The popularity of gold is driven by its unusual color (for a metal), its resistance to many chemical reactions, and the fact that it can easily be worked. However, pure gold is too soft for many applications, including jewelry. To increase its strength and hardness, as well as to modify its color, gold is often alloyed with other metals. In the jewelry trade pure gold is termed 24 carat. The carat number decreases as the mass percent of gold decreases. The most common alloys used in jewelry are 14 carat, which is $(14/24) \times 100 = 58\%$ gold, and 18 carat, which is $(18/24) \times 100 = 75\%$ gold.

The color of gold varies depending on the metals it is alloyed with. Gold is typically alloyed with silver and/or copper. All three elements crystallize with a face-centered cubic structure. The fact that all three elements have similar radii (Au and Ag are nearly the same size; Cu is roughly 11% smaller) and crystallize with the same type of structure make it possible to form substitutional alloys with nearly any composition. The variations in color of these alloys as a function of composition are shown in **Figure 12.18**. Gold alloyed with equal parts silver and copper (blue dot) takes on the golden yellow color we associate with 18-carat gold jewelry. Red (14-carat) or rose gold is a copper-rich alloy (red dot). Silver-rich alloys take on a greenish hue, eventually giving way to silvery-white colors as silver becomes the majority constituent.

Related Exercises: 12.17, 12.78, 12.124



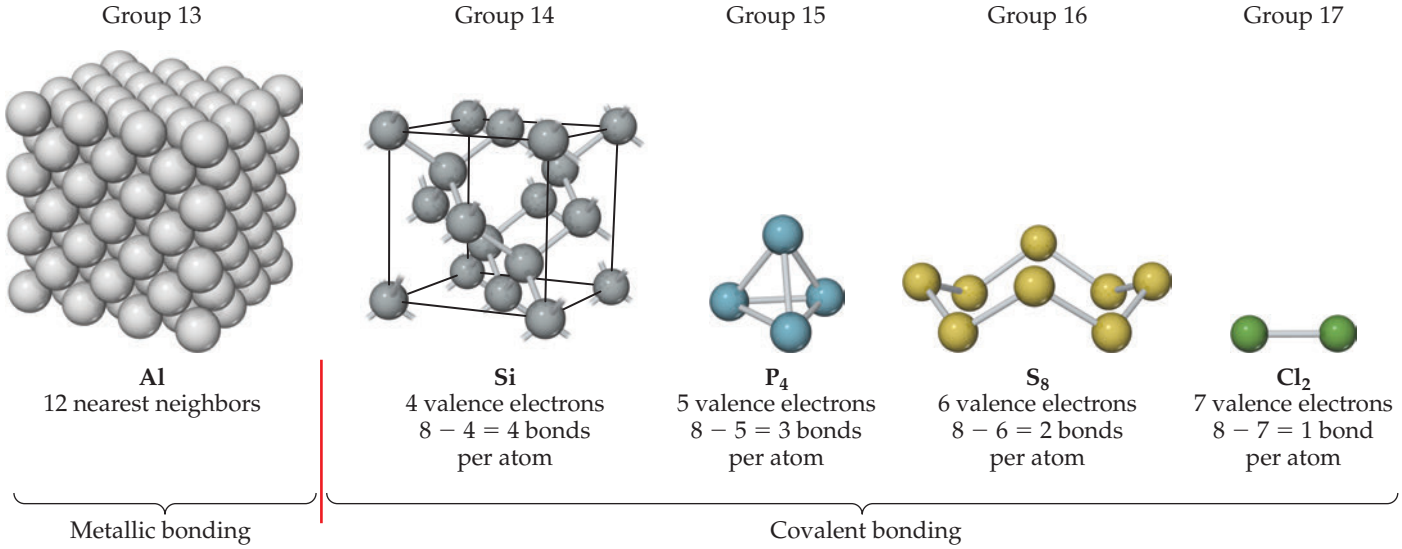
▶ **Figure 12.18** Colors of Au–Ag–Cu alloys as a function of composition.

Metallic Bonding

Consider the elements of the third period of the periodic table (Na–Ar). Argon with eight valence electrons has a complete octet; as a result it does not form any bonds. Chlorine, sulfur, and phosphorus form molecules (Cl_2, S_8, and P_4) in which the atoms make one, two, and three bonds, respectively (**Figure 12.19**). Silicon forms an extended network solid in which each atom is bonded to four equidistant neighbors. Each of these elements forms $8 - N$ bonds, where N is the number of valence electrons. This behavior can easily be understood through the application of the octet rule.

If the $8 - N$ trend continued as we move left across the periodic table, we would expect aluminum (three valence electrons) to form five bonds. Like many other metals, however, aluminum adopts a close-packed structure with 12 nearest neighbors. Magnesium and sodium also adopt metallic structures. What is responsible for this abrupt change in the preferred bonding mechanism? The answer, as noted earlier, is that metals do not have enough valence-shell electrons to satisfy their bonding requirements by forming localized electron-pair bonds. In response to this deficiency, the valence electrons are collectively shared. A structure in which the atoms are close-packed facilitates this delocalized sharing of electrons.

Go Figure Which of these drawings represent molecules?



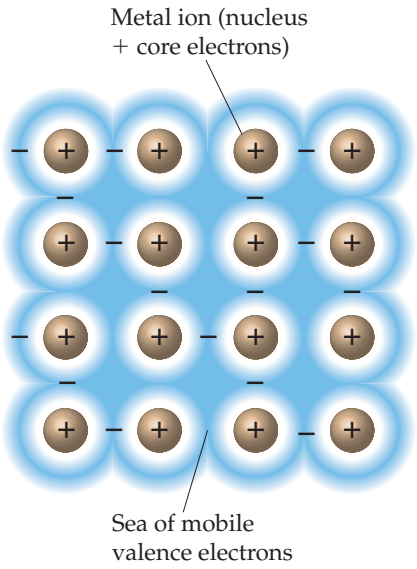
▲ **Figure 12.19 Bonding in Period 3 elements.**

Electron-Sea Model

A simple model that accounts for some of the most important characteristics of metals is the **electron-sea model**, which pictures the metal as an array of metal cations in a "sea" of valence electrons (Figure 12.20). The electrons are confined to the metal by electrostatic attractions to the cations, and they are uniformly distributed throughout the structure. The electrons are mobile, however, and no individual electron is confined to any particular metal ion. When a voltage is applied to a metal wire, the electrons, being negatively charged, flow through the metal toward the positively charged end of the wire.

The high thermal conductivity of metals is also accounted for by the presence of mobile electrons. The movement of electrons in response to temperature gradients permits ready transfer of kinetic energy throughout the solid.

The ability of metals to deform (their malleability and ductility) can be explained by the fact that metal atoms form bonds to many neighbors. Changes in the positions of the atoms brought about in reshaping the metal are partly accommodated by a redistribution of electrons.



▲ **Figure 12.20 Electron-sea model of metallic bonding.** The valence electrons delocalize to form a sea of mobile electrons that surrounds and binds together an extended array of metal ions.

Molecular Orbital Model

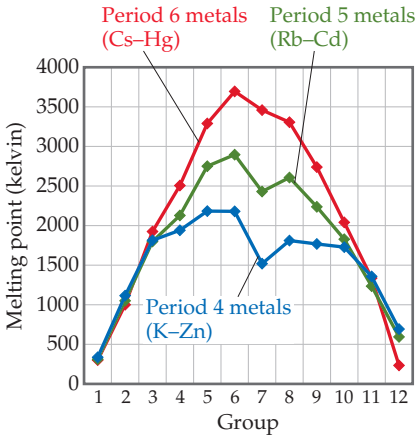
Although the electron-sea model works surprisingly well given its simplicity, it does not adequately explain many properties of metals. According to the model, for example, the strength of bonding between metal atoms should steadily increase as the number of valence electrons increases, resulting in a corresponding increase in the melting points. However, elements near the middle of the transition metal series, rather than those at the end, have the highest melting points in their respective periods (Figure 12.21). This trend implies that the strength of metallic bonding first increases with increasing number of electrons and then decreases. Similar trends are seen in other physical properties of the metals, such as the boiling point, heat of fusion, and hardness.

To obtain a more accurate picture of the bonding in metals, we must turn to molecular orbital theory. In Sections 9.7 and 9.8, we learned how molecular orbitals are created from the overlap of atomic orbitals. Let's briefly review some of the rules of molecular orbital theory:

1. Atomic orbitals combine to make molecular orbitals that can extend over the entire molecule.
2. A molecular orbital can contain zero, one, or two electrons.

Go Figure

Which element in each period has the highest melting point? In each case, is the element you named at the beginning, middle, or end of its period?



▲ **Figure 12.21 The melting points of metals from Periods 4, 5, and 6.**

3. The number of molecular orbitals in a molecule equals the number of atomic orbitals that combine to form molecular orbitals.
4. Adding electrons to a bonding molecular orbital strengthens bonding, while adding electrons to antibonding molecular orbitals weakens bonding.

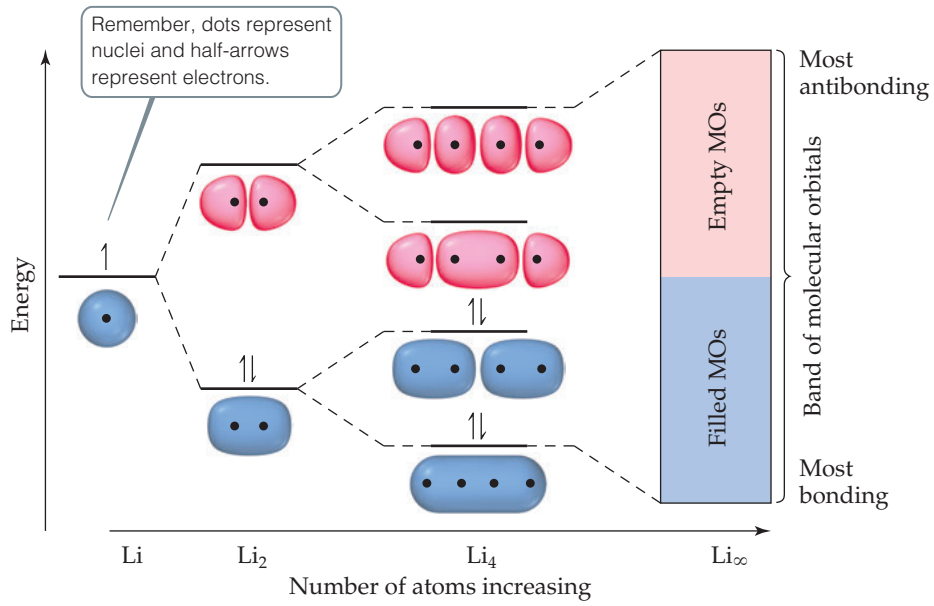
The electronic structures of crystalline solids and small molecules have similarities as well as differences. To illustrate, consider how the molecular orbital diagram for a chain of lithium atoms changes as we increase the length of the chain (**Figure 12.22**). Each lithium atom contains a half-filled 2*s* orbital in its valence shell. The molecular-orbital diagram for Li_2 is analogous to that of an H_2 molecule: one filled bonding molecular orbital and one empty antibonding molecular orbital with a nodal plane between the atoms. For Li_4, there are four molecular orbitals, ranging from the lowest-energy orbital, where the orbital interactions are completely bonding (zero nodal planes), to the highest-energy orbital, where all interactions are antibonding (three nodal planes).

As the length of the chain increases, the number of molecular orbitals increases. Regardless of chain length, the lowest-energy orbitals are always the most bonding and the highest-energy orbitals always the most antibonding. Furthermore, because each lithium atom has only one valence shell atomic orbital, the number of molecular orbitals is equal to the number of lithium atoms in the chain. Because each lithium atom has one valence electron, half of the molecular orbitals are fully occupied and the other half are empty, regardless of chain length.*

Electronic Band Structure If the chain becomes very long, there are so many molecular orbitals that the energy separation between them becomes vanishingly small. As the chain length goes to infinity, the allowed energy states become a continuous **band**. For a crystal large enough to see with the eye (or even an optical microscope), the number of atoms is extremely large. Consequently, the electronic structure of the crystal is like that of the infinite chain, consisting of bands, as shown on the right-hand side of Figure 12.22.

Go Figure

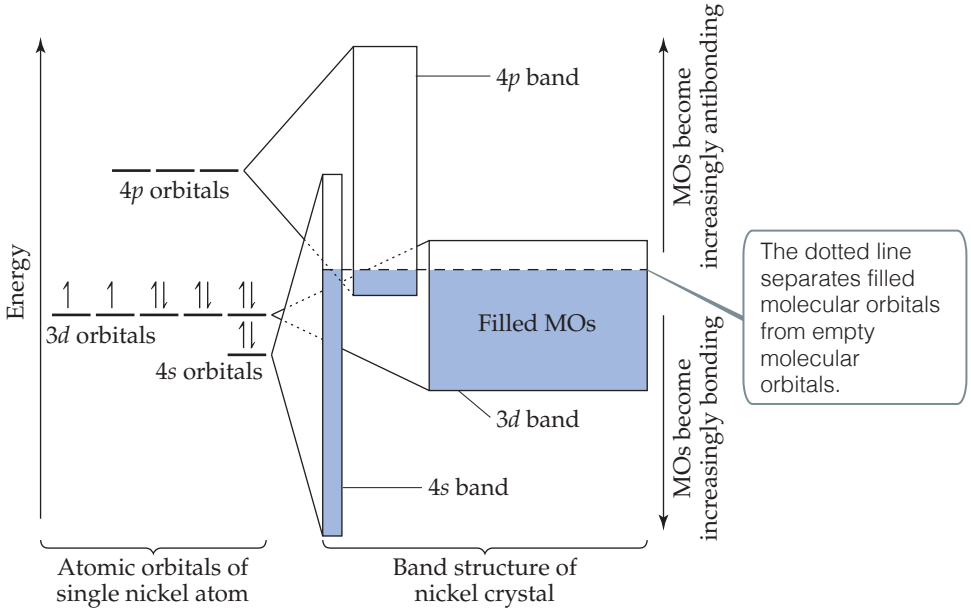
How does the energy spacing between molecular orbitals change as the number of atoms in the chain increases?



▲ **Figure 12.22 Discrete energy levels in individual molecules become continuous energy bands in a solid.** Occupied orbitals are shaded blue, and empty orbitals pink.

*This is strictly true only for chains with an even number of atoms.

Go Figure If the metal were potassium rather than nickel, which bands—4*s*, 4*p*, and/or 3*d*—would be partially occupied?



▲ **Figure 12.23** **The electronic band structure of nickel.**

The electronic structures of most metals are more complicated than those shown in Figure 12.22 because we have to consider more than one type of atomic orbital on each atom. Because each type of orbital can give rise to its own band, the electronic structure of a solid usually consists of a series of bands. The electronic structure of a bulk solid is referred to as a **band structure**.

The band structure of a typical metal is shown schematically in **Figure 12.23**. The electron filling depicted corresponds to nickel metal, but the basic features of other metals are similar. The electron configuration of a nickel atom is $[Ar]4s^2 3d^8$, as shown on the left side of the figure. The energy bands that form from each of these orbitals are shown on the right side. The 4*s*, 4*p*, and 3*d* orbitals are treated independently, each giving rise to a band of molecular orbitals. In practice, these overlapping bands are not completely independent of each other, but for our purposes this simplification is reasonable.

The 4*s*, 4*p*, and 3*d* bands differ from one another in the energy range they span (represented by the heights of the rectangles on the right side of Figure 12.23) and in the number of electrons they can hold (represented by the area of the rectangles). The 4*s*, 4*p*, and 3*d* bands can hold 2, 6, and 10 electrons per atom, respectively, corresponding to two per orbital, as dictated by the Pauli exclusion principle. The energy range spanned by the 3*d* band is smaller than the range spanned by the 4*s* and 4*p* bands because the 3*d* orbitals are smaller and, therefore, overlap with orbitals on neighboring atoms less effectively.

Many properties of metals can be understood from Figure 12.23. We can think of the energy band as a partially filled container for electrons. The incomplete filling of the energy band gives rise to characteristic metallic properties. The electrons in orbitals near the top of the occupied levels require very little energy input to be "promoted" to higher-energy orbitals that are unoccupied. Under the influence of any source of excitation, such as an applied electrical potential or an input of thermal energy, electrons move into previously vacant levels and are thus freed to move through the lattice, giving rise to electrical and thermal conductivity.

Without the overlap of energy bands, the periodic properties of metals could not be explained. In the absence of the *d*- and *p*-bands, we would expect the *s*-band to be half-filled for the alkali metals (Group 1) and completely filled for the alkaline-earth metals (Group 2). If that were true, metals like magnesium, calcium, and strontium would

not be good electrical and thermal conductors, in disagreement with experimental observations.

While the conductivity of metals can be qualitatively understood using either the electron-sea model or the molecular orbital model, many physical properties of transition metals, such as the melting points plotted in Figure 12.21, can be explained only with the latter model. The molecular orbital model predicts that bonding first becomes stronger as the number of valence electrons increases and the bonding orbitals are increasingly populated. Upon moving past the middle elements of the transition metal series, the bonds grow weaker as electrons populate antibonding orbitals. Strong bonds between atoms lead to metals with higher melting and boiling points, higher heats of fusion, higher hardness, and so forth.

Self-Assessment Exercises

12.12 Sterling silver is 92.5% silver and 7.5% copper. Both pure metals crystalize with a face-centered cubic structure. What sort of alloy is sterling silver?

(a) Substitution alloy

(b) Interstitial alloy

(c) Heterogeneous alloy

(d) Intermetallic compound

12.13 Which element, Pt or Re, has the greater number of electrons in antibonding orbitals? Which one would you expect to have the higher melting point?

(a) Pt has the greater number of electrons in antibonding orbitals and the lower melting point

(b) Pt has the greater number of electrons in antibonding orbitals and the higher melting point

(c) Re has the greater number of electrons in antibonding orbitals and the lower melting point

(d) Re has the greater number of electrons in antibonding orbitals and the higher melting point

Exercises

12.14 The densities of the elements Cr, Mn, Fe, and Cu are 7.15, 7.30, 7.87, and 8.96 g/cm^3, respectively. One of these elements crystallizes in a face-centered cubic structure; the other three crystallize in a body-centered cubic structure. Which one crystallizes in the face-centered cubic structure? Justify your answer.

12.15 Barium crystallizes in a body-centered cubic structure. (**a**) How many Ba atoms are contained in each unit cell? (**b**) How many nearest neighbors does each Ba atom possess? (**c**) Estimate the length of the unit cell edge, a, from the atomic radius of barium (0.215 nm). (**d**) Estimate the density of Ba metal at this temperature.

12.16 Determine if each statement is true or false: (**a**) Substitutional alloys are solid solutions, but interstitial alloys are heterogenous alloys. (**b**) Substitutional alloys have "solute" atoms that replace "solvent" atoms in a lattice, but interstitial alloys have "solute" atoms that are in between the "solvent" atoms in a lattice. (**c**) The atomic radii of the atoms in a substitutional alloy are similar to each other, but in an interstitial alloy, the interstitial atoms are a lot smaller than the host lattice atoms.

12.17 For each of the following alloy compositions, indicate whether you would expect it to be a substitutional alloy, an interstitial alloy, or an intermetallic compound:

(**a**) $Cu_{0.66}Zn_{0.34}$, (**b**) Ag_3Sn, (**c**) $Ti_{0.99}O_{0.01}$.

12.18 Indicate whether each statement is true or false:

(**a**) Intermetallic compounds have a fixed composition.

(**b**) Copper is the majority component in both brass and bronze.

(**c**) In stainless steel, the chromium atoms occupy interstitial positions.

12.19 Imagine that you have a metal bar sitting half in the sun and half in the dark. On a sunny day, the part of the metal that has been sitting in the sun feels hot. If you touch the part of the metal bar that has been sitting in the dark, will it feel hot or cold? Justify your answer in terms of thermal conductivity.

12.20 The molecular-orbital diagrams for two- and four-atom linear chains of lithium atoms are shown in Figure 12.22. Construct a molecular-orbital diagram for a chain containing six lithium atoms and use it to answer the following questions: (**a**) How many molecular orbitals are there in the diagram? (**b**) How many nodes are in the lowest-energy molecular orbital? (**c**) How many nodes are in the highest-energy molecular orbital? (**d**) How many nodes are in the highest-energy occupied molecular orbital (HOMO)? (**e**) How many nodes are in the lowest-energy unoccupied molecular orbital (LUMO)? (**f**) How does the HOMO–LUMO energy gap for this case compare to that of the four-atom case?

12.21 Which would you expect to be the more ductile element, (**a**) Ag or Cr, (**b**) Zn or Ge? In each case, explain your reasoning.

Answers to Self-Assessment Exercises

12.12 (a) **12.13** (a)

12.3 | Ionic Solids



A piezoelectric crystal responds to applied pressure by generating a voltage difference across two crystal faces. The effect works in both directions as an applied voltage can cause a deformation of the crystal structure by up to 0.1%. There are many applications that utilize the piezoelectric effect including gas ignition lighters, sonar, balances for weighing, ultrasound nozzles, ink-jet printers, amplification 'pick-ups' for musical instruments, clock generators to synchronize computer circuit boards and probes for scanning microscopes. While there is a wide range of types of material that show a piezoelectric effect, Rochelle salt (potassium sodium tartrate) was used in the early days for gramophone pick-ups as well as microphones and earpieces where the crystal could have an output of as much as 2 V. Unfortunately, the salt absorbs water easily and deteriorated quickly in humid climates.

In this section, we examine the crystal structures of ionic solids, and, by the end of the section, you should be able to

- Relate the structure of an ionic solid to its empirical formula

Ionic solids are held together by the electrostatic attraction between cations and anions: ionic bonds. The high melting and boiling points of ionic compounds are a testament to the strength of the ionic bonds. The strength of an ionic bond depends on the charges and sizes of the ions. As discussed in Chapters 8 and 11, the attractions between cations and anions increase as the charges of the ions increase. Thus NaCl, where the ions have charges of 1+ and 1−, melts at 801 °C, whereas MgO, where the ions have charges of 2+ and 2−, melts at 2852 °C. The interactions between cations and anions also increase as the ions get smaller, as we see from the melting points of the alkali metal halides in **Table 12.3**. These trends mirror the trends in lattice enthalpy discussed in Section 8.2.

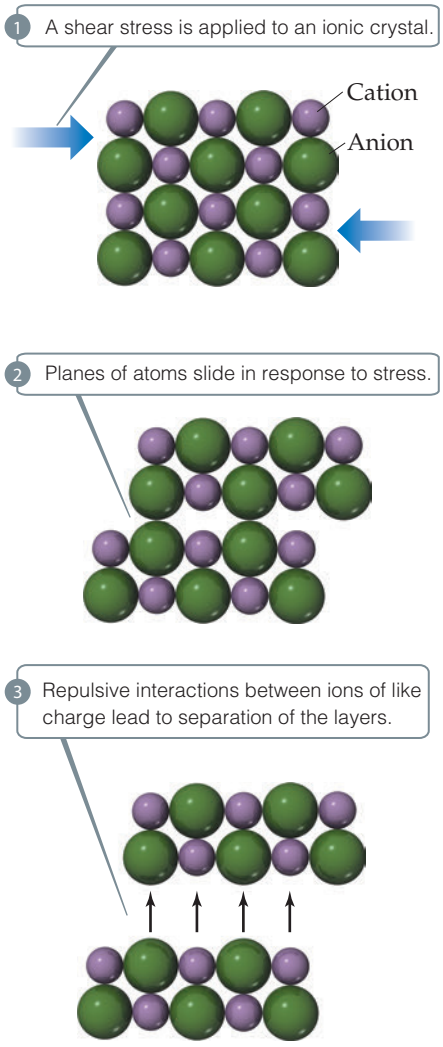
Although ionic and metallic solids both have high melting and boiling points, the differences between ionic and metallic bonding are responsible for important differences in their properties. Because the valence electrons in ionic compounds are confined to the anions, rather than being delocalized, ionic compounds are typically electrical insulators. They tend to be brittle, a property explained by repulsive interactions between ions of like charge. When stress is applied to an ionic solid, as in **Figure 12.24**, the planes of

TABLE 12.3 Properties of the Alkali Metal Halides

Compound	Cation–Anion Distance (pm)	Lattice Enthalpy (kJ/mol)	Melting Point (°C)
LiF	201	1030	845
NaCl	283	788	801
KBr	330	671	734
RbI	367	632	674

Go Figure

Why don't metals cleave in the way depicted here for ionic substances?



(a)



(b)

▲ **Figure 12.24 Brittleness and faceting in ionic crystals. (a)** When a shear stress (blue arrows) is applied to an ionic solid, the crystal separates along a plane of atoms as shown. **(b)** This property of ionic crystals is used to facet gemstones, such as rubies.

atoms, which before the stress were arranged with cations next to anions, shift so that the alignment becomes cation–cation, anion–anion. The resulting repulsive interaction causes the planes to split away from each other, a property that lends itself to the carving of certain gemstones (such as ruby, composed principally of Al_2O_3).

Structures of Ionic Solids

Like metallic solids, ionic solids tend to adopt structures with symmetric, close-packed arrangements of atoms. However, important differences arise because we now have to pack together spheres that have different radii and opposite charges. Because cations are often considerably smaller than anions, the coordination numbers in ionic compounds are smaller than those in close-packed metals. Even if the anions and cations were the same size, the close-packed arrangements seen in metals cannot be replicated without letting ions of like charge come in contact with each other. The repulsions between ions of the same type make such arrangements unfavorable. The most favorable structures are those where the cation–anion distances are as close as those permitted by ionic radii, but the anion–anion and cation–cation distances are maximized.

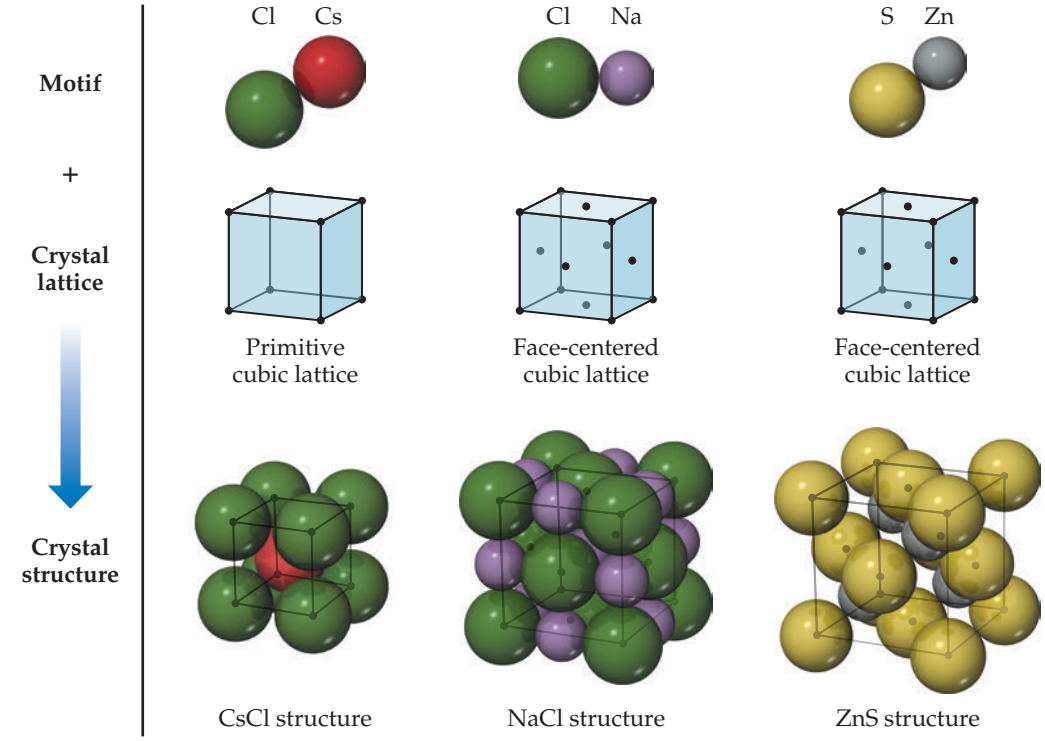
Three common ionic structure types are shown in **Figure 12.25**. The cesium chloride (CsCl) structure is based on a primitive cubic lattice. Anions sit on the lattice points at the corners of the unit cell, and a cation sits at the center of each cell. (Remember, there is no lattice point inside a primitive unit cell.) With this arrangement, both cations and anions are surrounded by a cube of eight ions of the opposite type.

The sodium chloride (NaCl; also called the rock salt structure) and zinc blende (ZnS) structures are based on a face-centered cubic lattice. In both structures the anions sit on the lattice points that lie on the corners and faces of the unit cell, but the two-atom motif is slightly different for the two structures. In NaCl the Na^+ ions are displaced from the Cl^- ions along the edge of the unit cell, whereas in ZnS the Zn^{2+} ions are displaced from the S^{2-} ions along the body diagonal of the unit cell. This difference leads to different coordination numbers. In sodium chloride, each cation and each anion are surrounded by six ions of the opposite type, leading to an octahedral coordination environment. In zinc blende, each cation and each anion are surrounded by four ions of the opposite type, leading to a tetrahedral coordination geometry. The cation coordination environments can be seen in **Figure 12.26**.

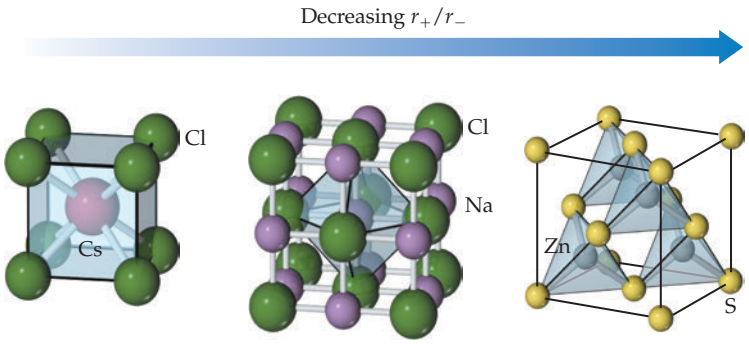
For a given ionic compound, we might ask which type of structure is most favorable. A number of factors come into play, but two of the most important are the relative sizes of the ions and the stoichiometry. Consider first ion size. Notice in Figure 12.26 that the coordination number changes from 8 to 6 to 4 on moving from CsCl to NaCl to ZnS. This trend is driven in part by the fact that for these three compounds the ionic radius of the cation gets smaller while the ionic radius of the anion changes very little. When the cation and anion are similar in size, a large coordination number is favored and the CsCl structure is often realized. As the relative size of the cation gets smaller, eventually it is no longer possible to maintain the cation–anion contacts and simultaneously keep the anions from touching each other. When this occurs, the coordination number drops from 8 to 6, and the sodium chloride structure becomes more favorable. As the cation size decreases further, eventually the coordination number must be reduced again, this time from 6 to 4, and the zinc blende structure becomes favored. Remember that, in ionic crystals, ions of opposite charge touch each other but ions of the same charge should not touch.

The relative number of cations and anions also helps determine the most stable structure type. All the structures in Figure 12.26 have equal numbers of cations and anions. These structure types (cesium chloride, sodium chloride, zinc blende) can be realized only for ionic compounds in which the number of cations and anions is equal. When this is not the case, other crystal structures must result.

Go Figure Do the anions touch each other in any of these three structures? If not, which ions do touch each other?



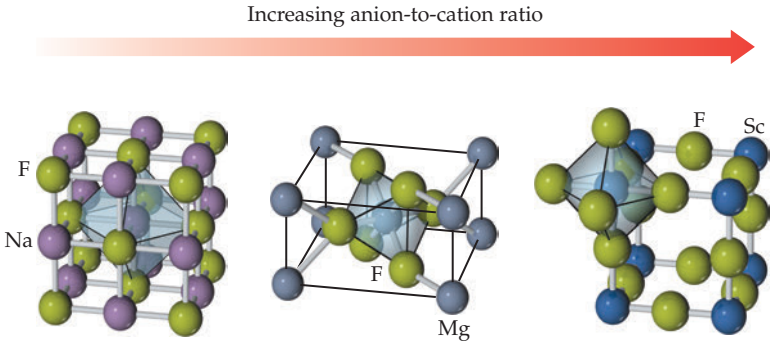
▲ **Figure 12.25 The structures of CsCl, NaCl, and ZnS.** Each structure type can be generated by the combination of a two-atom motif and the appropriate lattice.



	CsCl	NaCl	ZnS
Cation radius, r_+ (pm)	181	116	88
Anion radius, r_- (pm)	167	167	170
r_+/r_-	1.08	0.69	0.52
Cation coordination number	8	6	4
Anion coordination number	8	6	4

▲ **Figure 12.26 Coordination environments in CsCl, NaCl, and ZnS.** The sizes of the ions have been reduced to show the coordination environments clearly.

Go Figure How many cations are there per unit cell for each of these structures? How many anions per unit cell?



	NaF	MgF_2	ScF_3
Cation coordination number	6	6	6
Cation coordination geometry	Octahedral	Octahedral	Octahedral
Anion coordination number	6	3	2
Anion coordination geometry	Octahedral	Trigonal planar	Linear

▲ **Figure 12.27 Coordination numbers depend on stoichiometry.** The sizes of the ions have been reduced to show the coordination environments clearly.

As an example, consider NaF, MgF_2, and ScF_3 (**Figure 12.27**). Sodium fluoride has the sodium chloride structure with a coordination number of 6 for both cation and anion, as you might expect since NaF and NaCl are quite similar. Magnesium fluoride, however, has two anions for every cation, resulting in a tetragonal crystal structure called the *rutile structure*. The cation coordination number is still 6, but the fluoride coordination number is now only 3. In the scandium fluoride structure, there are three anions for every cation; the cation coordination number is still 6, but the fluoride coordination number has dropped to 2. As the cation/anion ratio goes down, there are fewer cations to surround each anion, and so the anion coordination number must decrease. The empirical formula of an ionic compound can be described quantitatively by the relationship

$$\frac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \frac{\text{anion coordination number}}{\text{cation coordination number}} \qquad [12.1]$$

Sample Exercise 12.2

Calculating the Density of an Ionic Solid

Rubidium iodide crystallizes with the same structure as sodium chloride. (**a**) How many iodide ions are there per unit cell? (**b**) How many rubidium ions are there per unit cell? (**c**) Use the ionic radii and molar masses of Rb^+ (166 pm, 85.47 *g/mol*) and I^- (206 pm, 126.90 g/mol) to estimate the density of rubidium iodide in g/cm^3.

SOLUTION

Analyze and Plan

(**a**) We need to count the number of anions in the unit cell of the sodium chloride structure, remembering that ions on the corners, edges, and faces of the unit cell are only partially inside the unit cell.

(**b**) We can apply the same approach to determine the number of cations in the unit cell. We can double-check our answer by writing the empirical formula to make sure the charges of the cations and anions are balanced.

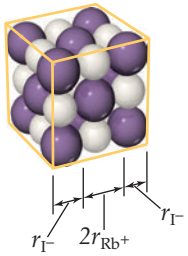
(**c**) Because density is an intensive property, the density of the unit cell is the same as the density of a bulk crystal. To calculate the density we must divide the mass of the atoms per unit cell by the volume of the unit cell. To determine the volume of the unit cell, we need to estimate the length of the unit cell edge by first identifying the direction along which the ions touch and then using ionic radii to estimate the length. Once we have the length of the unit cell edge, we can cube it to determine its volume.

Solve

(**a**) The crystal structure of rubidium iodide looks just like NaCl with Rb^+ ions replacing Na^+ and I^- ions replacing Cl^-. From the views of the NaCl structure in Figures 12.25 and 12.26, we see that there is an anion at each corner of the unit cell and at the center of each face. From Table 12.1 we see that the ions sitting on the corners are equally shared by eight unit cells ($\frac{1}{8}$ ion per unit cell), while those ions sitting on the faces are equally shared by two unit cells ($\frac{1}{2}$ ion per unit cell). A cube has eight corners and six faces, so the total number of I^- ions is $8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$ per unit cell.

(**b**) Using the same approach for the rubidium cations, we see that there is a rubidium ion on each edge and one at the center of the unit cell. Using Table 12.1 again, we see that the ions sitting on the edges are equally shared by four unit cells (1/4 ion per unit cell), whereas the cation at the center of the unit cell is not shared. A cube has 12 edges, so the total number of rubidium ions is $12\left(\frac{1}{4}\right) + 1 = 4$. This answer makes sense because the number of Rb^+ ions must be the same as the number of I^- ions to maintain charge balance.

(**c**) In ionic compounds, cations and anions touch each other. In RbI the cations and anions touch along the edge of the unit cell as shown in the following figure.



The length of the unit cell edge is equal to $r(I^-) + 2r(Rb^+) + r(I^-) = 2r(I^-) + 2r(Rb^+)$. Plugging in the ionic radii we get $2(206\text{ pm}) + 2(166\text{ pm}) = 744\text{ pm}$. The volume of a cubic unit cell is just the edge length cubed. Converting from pm to cm and cubing we get

$$\text{Volume} = (7.44 \times 10^{-8}\,\text{cm})^3 = 4.12 \times 10^{-22}\,\text{cm}^3.$$

From parts (a) and (b) we know that there are four rubidium and four iodide ions per unit cell. Using this result and the molar masses, we can calculate the mass per unit cell

$$\text{Mass} = \frac{4(85.47\,\text{g/mol}) + 4(126.90\,\text{g/mol})}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 1.411 \times 10^{-21}\,\text{g}$$

The density is the mass per unit cell divided by the volume of a unit cell

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{1.411 \times 10^{-21}\,\text{g}}{4.12 \times 10^{-22}\,\text{cm}^3} = 3.43\,\text{g/cm}^3$$

Check The densities of most solids fall between the density of lithium (0.5 g/cm^3) and that of iridium (22.6 g/cm^3), so this value is reasonable.

Practice Exercise

Estimate the length of the cubic unit cell edge and the density of CsCl (Figure 12.25) from the ionic radii of cesium, 181 pm, and chloride, 167 pm. (*Hint*: Ions in CsCl touch along the body diagonal, a vector running from one corner of a cube through the body center to the opposite corner. Using trigonometry it can be shown that the body diagonal of a cube is $\sqrt{3}$ times longer than the edge.)

Self-Assessment Exercise

12.22 In the crystal of titanium dioxide, the oxide ions are coordinated by three titanium ions. What is the coordination number of titanium?

(a) 1

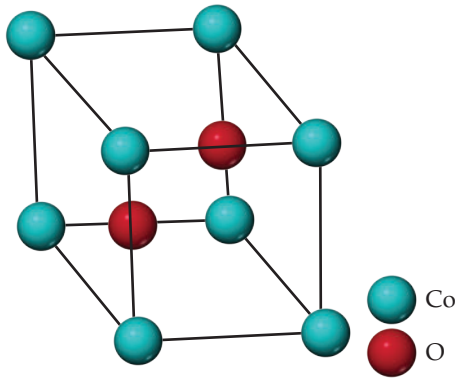
(b) 2

(c) 3

(d) 6

Exercises

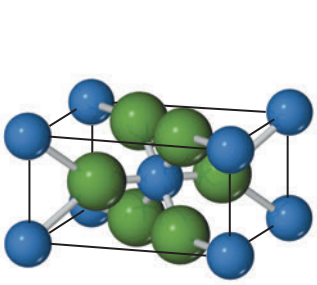
12.23 The unit cell of a compound containing Co and O has a unit cell as illustrated here. The Co atoms are on the corners, and the O atoms are completely within the unit cell. What is the empirical formula of this compound? What is the oxidation state of the metal?



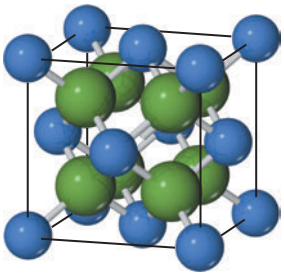
12.24 Silver chloride (AgCl) adopts the rock salt structure. The density of AgCl at 25 °C is 5.56 g/cm^3. Calculate the length of an edge of the AgCl unit cell.

12.25 At room temperature and pressure RbCl crystallizes with the NaCl-type structure. (**a**) Use ionic radii to predict the length of the cubic unit cell edge. (**b**) Use this value to estimate the density. (**c**) At high temperature and pressure, the structure transforms to one with a CsCl-type structure. Use ionic radii to predict the length of the cubic unit cell edge for the high-pressure form of RbCl. (**d**) Use this value to estimate the density. How does this density compare with the density you calculated in part (b)?

12.26 The rutile and fluorite structures, shown here (anions are colored green), are two of the most common structure types of ionic compounds where the cation to anion ratio is 1:2. (**a**) For CaF_2 and ZnF_2 use ionic radii, Ca^{2+} (r = 114 pm), Zn^{2+} (r = 88 pm), and F^- (r = 119 pm), to predict which compound is more likely to crystallize with the fluorite structure and which with the rutile structure. (**b**) What are the coordination numbers of the cations and anions in each of these structures?



Rutile



Fluorite

12.27 The coordination number for the Al^{3+} ion is typically between four and six. Use the anion coordination number to determine the Al^{3+} coordination number in the following compounds: (**a**) AlF_3 where the fluoride ions are two coordinate, (**b**) Al_2O_3 where the oxygen ions are six coordinate, (**c**) AlN where the nitride ions are four coordinate.

Answers to Self-Assessment Exercise

12.22 (d)

12.4 | Covalent Solids



Diamond was long considered the hardest known substance, but that does not appear to be the case anymore. If you were to investigate very hard substances, you might start by looking at ones that have a similar structure to that of diamond. We have seen that the structure depends on bonding and size. Boron nitride (BN) is a material that is both isostructural and isoelectronic with diamond. Calculations suggest it can withstand about 18% more stress than diamond, but it occurs rarely in nature, so this has yet to be verified on a natural sample. It can be manufactured in the lab and the strength of BN, coupled with a resistance to oxidation at high temperatures, makes it an ideal candidate for cutting and grinding tools and other high-temperature applications.

There are two classes of covalent solid with very different properties. By the end of this section, you should be able to

- Interpret melting point and boiling point data in terms of crystal structure
- Predict how n-type and p-type doping can be used to control the conductivity of semiconductors

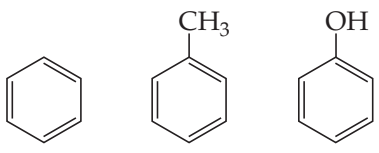
Molecular Solids

Molecular solids consist of atoms or neutral molecules held together by dipole–dipole forces, dispersion forces, and/or hydrogen bonds. Because these intermolecular forces are weak, molecular solids are soft and have relatively low melting points (usually below 200 °C). Most substances that are gases or liquids at room temperature form molecular solids at low temperature. Examples include Ar, H_2O, and CO_2.

The properties of molecular solids depend in large part on the strengths of the forces between molecules. Consider, for example, the properties of sucrose (table sugar, $C_{12}H_{22}O_{11}$). Each sucrose molecule has eight —OH groups, which allow for the formation of multiple hydrogen bonds. Consequently, sucrose exists as a crystalline solid at room temperature, and its melting point, 184 °C, is relatively high for a molecular solid.

Molecular shape is also important because it dictates how efficiently molecules pack together in three dimensions. Benzene (C_6H_6), for example, is a highly symmetrical planar molecule. It has a higher melting point than toluene, a compound in which one of the hydrogen atoms of benzene has been replaced by a CH_3 group (**Figure 12.28**). The lower symmetry of toluene molecules prevents them from packing in a crystal as efficiently as benzene molecules. As a result, the intermolecular forces that depend on close contact are not as effective and the melting point is lower. In contrast, the boiling point of toluene is *higher* than that of benzene, indicating that the intermolecular attractive forces are larger in liquid toluene than in liquid benzene. The melting and boiling points of phenol, another substituted benzene shown in Figure 12.28, are higher than those of benzene because the OH group of phenol can form hydrogen bonds.

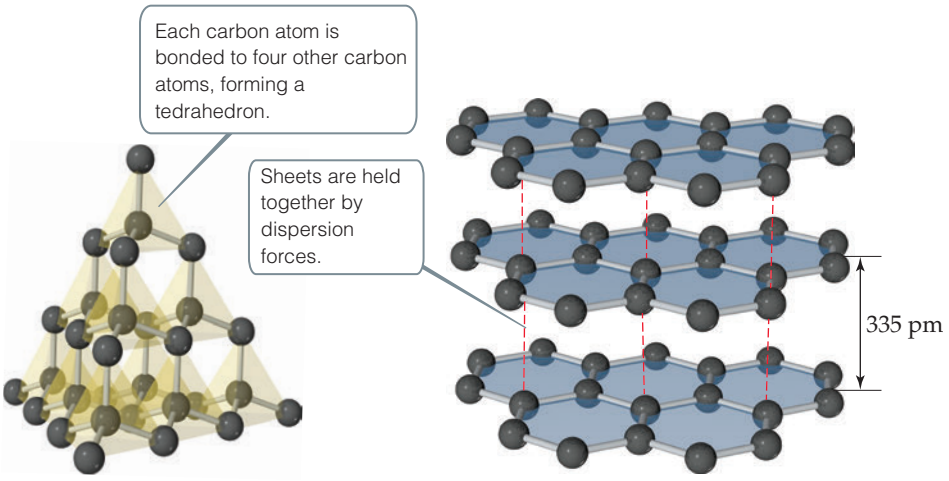
Go Figure In which substance, benzene or toluene, are the intermolecular forces stronger? In which substance do the molecules pack more efficiently?



	Benzene	Toluene	Phenol
Melting point (°C)	5	−95	43
Boiling point (°C)	80	111	182

▲ **Figure 12.28** **Melting and boiling points for benzene, toluene, and phenol.**

▶ **Figure 12.29** **The structures of (a) diamond and (b) graphite.**



(a) Diamond **(b) Graphite**

Covalent-Network Solids

Covalent-network solids consist of atoms held together in large networks by covalent bonds. Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids. Diamond and graphite, two allotropes of carbon, are two of the most familiar covalent-network solids. Other examples are silicon, germanium, quartz (SiO_2), silicon carbide (SiC), and boron nitride (BN). In all cases, the bonding between atoms is either completely covalent or more covalent than ionic.

In diamond, each carbon atom is bonded tetrahedrally to four other carbon atoms (**Figure 12.29**). The structure of diamond can be derived from the zinc blende structure (Figure 12.26) if carbon atoms replace both the zinc and sulfide ions. The carbon atoms are sp^3 hybridized and held together by strong carbon–carbon single covalent bonds. The strength and directionality of these bonds make diamond one of the hardest known material. For this reason, industrial-grade diamonds are employed in saw blades used for the most demanding cutting jobs. The stiff, interconnected bond network also explains why diamond is one of the best-known thermal conductors, yet is not electrically conductive. Diamond has a high melting point, 3550 °C.

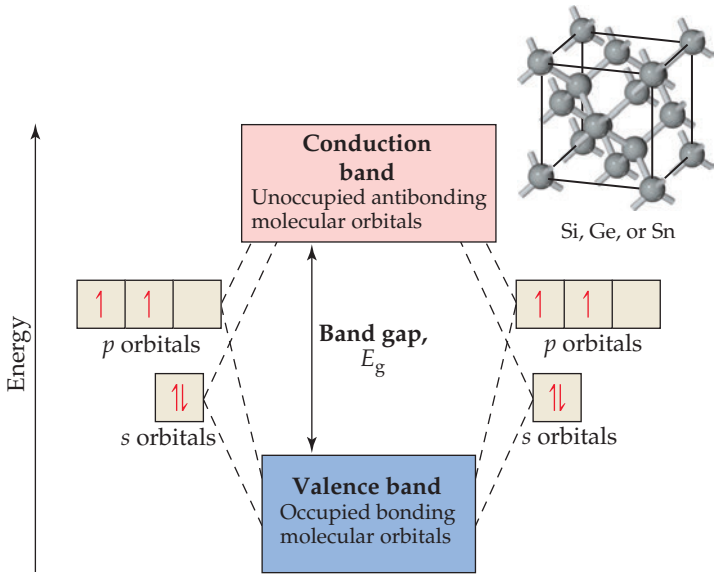
In graphite, [Figure 12.29(b)], the carbon atoms form covalently bonded layers that are held together by intermolecular forces. The layers in graphite are the same as those in the graphene sheet shown in Figure 12.8. Graphite has a hexagonal unit cell containing two layers offset so that the carbon atoms in a given layer sit over the middle of the hexagons of the layer below. Each carbon is covalently bonded to three other carbons in the same layer to form interconnected hexagonal rings. The distance between adjacent carbon atoms in the plane, 142 pm, is very close to the C—C distance in benzene, 140 pm. In fact, the bonding resembles that of benzene, with delocalized π bonds extending over the layers. Electrons move freely through the delocalized orbitals, making graphite a good electrical conductor along the layers. (In fact, graphite is used as a conducting electrode in batteries.) These sp^2 hybridized sheets of carbon atoms are separated by 335 pm from one another, and the sheets are held together only by dispersion forces. Thus, the layers readily slide past one another when rubbed, giving graphite a greasy feel. This tendency is enhanced when impurity atoms are trapped between the layers, as is typically the case in commercial forms of the material.

Graphite is used as a lubricant and as the "lead" in pencils. The enormous differences in physical properties of graphite and diamond—both of which are pure carbon—arise from differences in their three-dimensional structure and bonding.

Semiconductors

Metals conduct electricity extremely well. Many solids, however, conduct electricity somewhat, but nowhere near as well as metals, which is why such materials are called **semiconductors**. Two examples of semiconductors are silicon and germanium, which

Go Figure If you draw a second diagram next to this one to represent an insulator, what aspect of the second diagram would be different?



▲ **Figure 12.30** **The electronic band structure of semiconductors that have the diamond crystal structure.**

lie immediately below carbon in the periodic table. Like carbon, each of these elements has four valence electrons, just the right number to satisfy the octet rule by forming single covalent bonds with four neighbors. Hence, silicon and germanium, as well as the gray form of tin, crystallize with the same infinite network of covalent bonds as diamond.

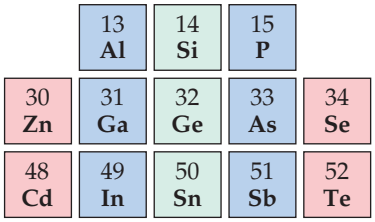
When atomic *s* and *p* orbitals overlap, they form bonding molecular orbitals and antibonding molecular orbitals. Each pair of *s* orbitals overlaps to give one bonding and one antibonding molecular orbital, whereas the *p* orbitals overlap to give three bonding and three antibonding molecular orbitals. The extended network of bonds leads to the formation of the same type of bands we saw for metals in Section 12.2. However, unlike metals, in semiconductors an energy gap develops between the filled and empty states, much like the energy gap between bonding and antibonding orbitals. The band that forms from bonding molecular orbitals is called the **valence band**, and the band that forms the antibonding orbitals is called the **conduction band** (Figure 12.30). In a semiconductor, the valence band is filled with electrons and the conduction band is empty. These two bands are separated by the energy **band gap** E_g. In the semiconductor community, energies are given in electron volts (eV); $1\text{ eV} = 1.602 \times 10^{-19}\text{ J}$. Band gaps greater than ~3.5 eV are so large that the material is not a semiconductor; it is an **insulator** and does not conduct electricity.

Semiconductors can be divided into two classes: elemental semiconductors, which contain only one type of atom, and compound semiconductors, which contain two or more elements. The elemental semiconductors all come from Group 14. As we move down the periodic table, bond distances increase, which decreases orbital overlap. This decrease in overlap reduces the energy difference between the top of the valence band and the bottom of the conduction band. As a result, the band gap decreases on going from diamond (5.5 eV, an insulator) to silicon (1.11 eV) to germanium (0.67 eV) to gray tin (0.08 eV). In the heaviest Group 14 element, lead, the band gap collapses altogether. As a result, lead has the structure and properties of a metal.

Compound semiconductors maintain the same *average* valence electron count as elemental semiconductors—four per atom. For example, in gallium arsenide, GaAs, each Ga atom contributes three electrons and each As atom contributes five, which averages out to four per atom—the same number as in silicon or germanium. Hence, GaAs is a semiconductor. Other examples are InP, where indium contributes three valence electrons

TABLE 12.4 Band Gaps of Select Elemental and Compound Semiconductors

Material	Structure Type	E_g, eV[†]
Si	Diamond	1.11
AlP	Zinc blende	2.43
Ge	Diamond	0.67
GaAs	Zinc blende	1.43
ZnSe	Zinc blende	2.58
Sn[‡]	Diamond	0.08
InSb	Zinc blende	0.18
CdTe	Zinc blende	1.50



[†] Band gap energies are room temperature values, 1 eV = 1.602×10^{-19} J.
[‡] These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

and phosphorus contributes five, and CdTe, where cadmium provides two valence electrons and tellurium contributes six. In both cases, the average is again four valence electrons per atom. GaAs, InP, and CdTe all crystallize with a zinc blende structure.

The band gap of a compound semiconductor tends to increase as the difference in group numbers increases. For example, $E_g = 0.67$ eV in Ge, but $E_g = 1.43$ eV in GaAs. If we increase the difference in group number to four, as in ZnSe (Groups 12 and 16), the band gap increases to 2.70 eV. This progression is a result of the transition from pure covalent bonding in elemental semiconductors to polar covalent bonding in compound semiconductors. As the difference in electronegativity of the elements increases, the bonding becomes more polar and the band gap increases.

Electrical engineers manipulate both the orbital overlap and the bond polarity to control the band gaps of compound semiconductors for use in a wide range of electrical and optical devices. The band gaps of several elemental and compound semiconductors are given in Table 12.4.

Sample Exercise 12.3

Qualitative Comparison of Semiconductor Band Gaps

Will GaP have a larger or smaller band gap than ZnS? Will it have a larger or smaller band gap than GaN?

SOLUTION

Analyze The size of the band gap depends on the vertical and horizontal positions of the elements in the periodic table. The band gap will increase when either of the following conditions is met: (1) The elements are located higher up in the periodic table, where enhanced orbital overlap leads to a larger splitting between bonding and antibonding orbital energies, or (2) the horizontal separation between the elements increases, which leads to an increase in the electronegativity difference and bond polarity.

Plan We must look at the periodic table and compare the relative positions of the elements in each case.

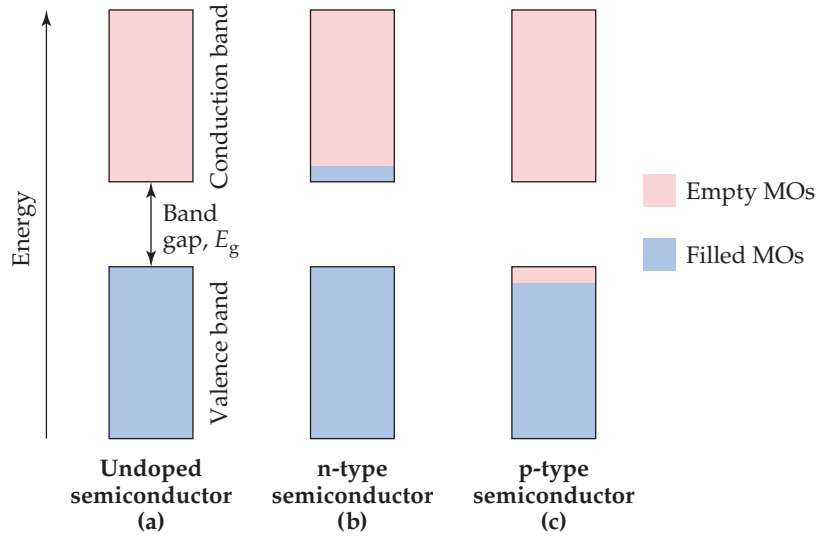
Solve Gallium is in the fourth period and Group 13. Phosphorus is in the third period and Group 15. Zinc and sulfur are in the same periods as gallium and phosphorus, respectively. However, zinc, in Group 12, is one element to the left of gallium; sulfur in Group 16 is one element to the right of phosphorus. Thus, we would expect the electronegativity difference to be larger for ZnS, which should result in ZnS having a larger band gap than GaP.

For both GaP and GaN the more electropositive element is gallium. So we need only compare the positions of the more electronegative elements, P and N. Nitrogen is located above phosphorus in Group 15. Therefore, based on increased orbital overlap, we would expect GaN to have a larger band gap than GaP.

Check External references show that the band gap of GaP is 2.26 eV, ZnS is 3.6 eV, and GaN is 3.4 eV.

▶ Practice Exercise
Will ZnSe have a larger or smaller band gap than ZnS?

Go Figure Predict what would happen in panel (**b**) if you doubled the amount of doping shown in the n-type semiconductor.



▲ **Figure 12.31** **The addition of small amounts of impurities (doping) to a semiconductor changes the electronic properties of the material.**

Semiconductor Doping

The electrical conductivity of a semiconductor is influenced by the presence of small numbers of impurity atoms. The process of adding controlled amounts of impurity atoms to a material is known as **doping**. Consider what happens when a few phosphorus atoms (known as dopants) replace silicon atoms in a silicon crystal. In pure Si, all of the valence-band molecular orbitals are filled and all of the conduction-band molecular orbitals are empty, as **Figure 12.31**(**a**) shows. Because phosphorus has five valence electrons but silicon has only four, the "extra" electrons that come with the dopant phosphorus atoms are forced to occupy the conduction band [Figure 12.31(**b**)]. The doped material is called an *n-type* semiconductor, *n* signifying that the number of *n*egatively charged electrons in the conduction band has increased. These extra electrons can move very easily in the conduction band. Thus, just a few parts per million (ppm) of phosphorus in silicon can increase silicon's intrinsic conductivity by a factor of a million!

The dramatic change in conductivity in response to the addition of a trace amount of a dopant means that extreme care must be taken to control the impurities in semiconductors. The semiconductor industry uses "nine-nines" silicon to make integrated circuits; what this means is that Si must be 99.999999999% pure (nine nines after the decimal place) to be technologically useful! Doping provides an opportunity for controlling the electrical conductivity through precise control of the type and concentration of dopants.

It is also possible to dope semiconductors with atoms that have fewer valence electrons than the host material. Consider what happens when a few aluminum atoms replace silicon atoms in a silicon crystal. Aluminum has only three valence electrons compared to silicon's four. Thus, there are electron vacancies, known as **holes**, in the valence band when silicon is doped with aluminum [Figure 12.31(**c**)]. Since the negatively charged electron is not there, the hole can be thought of as having a positive charge. Any adjacent electron that jumps into the hole leaves behind a new hole. Thus, the positive hole moves about in the lattice like a particle.* A material like this is called a *p-type* semiconductor, *p* signifying that the number of *p*ositive holes in the material has increased.

*This movement is analogous to watching people changing seats in a classroom; you can watch the people (electrons) move about the seats (atoms), or you can watch the empty seats (holes) "move."

As with n-type conductivity, p-type dopant levels of only parts per million can lead to a millionfold increase in conductivity—but in this case, the holes in the valence band are doing the conduction [Figure 12.31(c)].

The junction of an n-type semiconductor with a p-type semiconductor forms the basis for diodes, transistors, solar cells, and other devices.

Sample Exercise 12.4

Identifying Types of Semiconductors

Which of the following elements, if doped into silicon, would yield an n-type semiconductor: Ga, As, or C?

SOLUTION

Analyze An n-type semiconductor means that the dopant atoms must have more valence electrons than the host material. Silicon is the host material in this case.

Plan We must look at the periodic table and determine the number of valence electrons associated with Si, Ga, As, and C. The elements with more valence electrons than silicon are the ones that will produce an n-type material upon doping.

Solve Si is in column 14, and so has four valence electrons. Ga is in column 13, and so has three valence electrons. As is in column 15, and so has five valence electrons; C is in column 14, and so has four valence electrons. Therefore, As, if doped into silicon, would yield an n-type semiconductor.

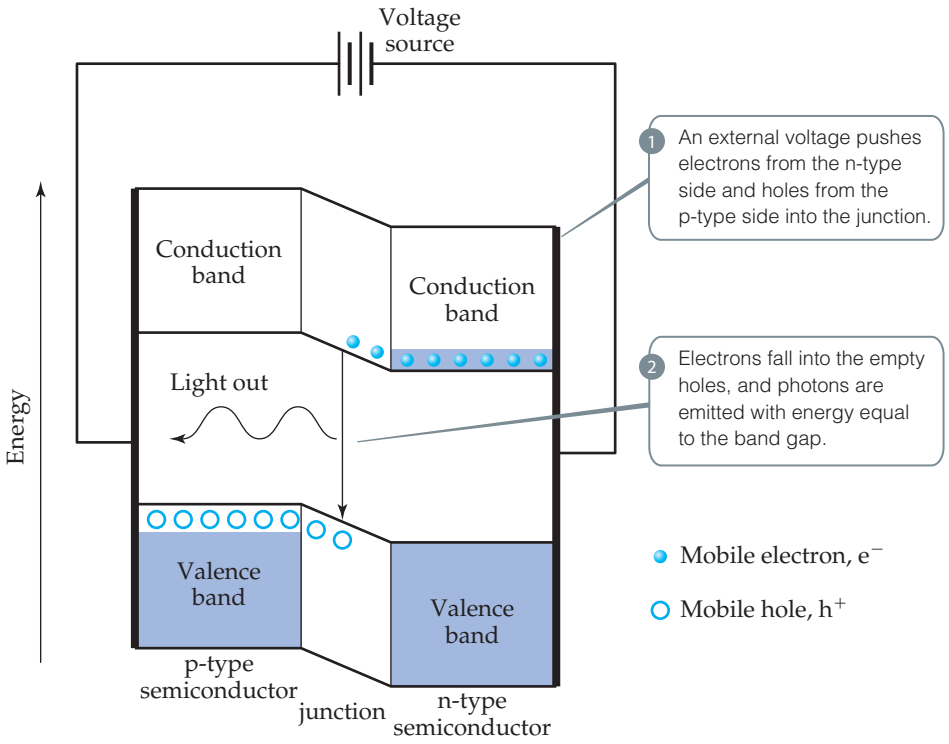
Practice Exercise

Compound semiconductors can be doped to make n-type and p-type materials, but the scientist has to make sure that the proper atoms are substituted. For example, if Ge were doped into GaAs, Ge could substitute for Ga, making an n-type semiconductor; but if Ge substituted for As, the material would be p-type. Suggest a way to dope CdSe to create a p-type material.

CHEMISTRY PUT TO WORK Solid-State Lighting

Artificial lighting is so widespread we take it for granted. Major savings in energy would be realized if incandescent lights could be replaced by light-emitting diodes (LEDs). Because LEDs are made from semiconductors, this is an appropriate place to take a closer look at the operation of an LED.

The heart of an LED is a p–n diode, which is formed by bringing an n-type semiconductor into contact with a p-type semiconductor. In the junction where they meet, there are very few electrons or holes to carry the charge across the interface between them, and the conductivity decreases. When an appropriate voltage is applied, electrons are driven from the conduction band of the n-doped side into the junction, where they meet holes that have been driven from the valence band of the p-doped side. The electrons fall into the empty holes, and their energy is converted into light whose photons have energy equal to the band gap (**Figure 12.32**). In this way electrical energy is converted into optical energy.

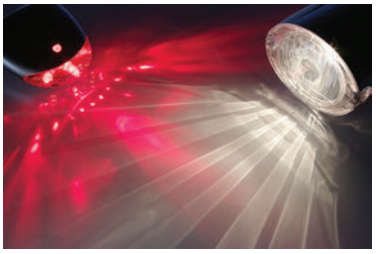


▲ **Figure 12.32 Light-emitting diodes.** The heart of a light-emitting diode is a p–n junction in which an applied voltage drives electrons and holes together, where they combine and give off light.

Because the wavelength of light that is emitted depends on the band gap of the semiconductor, the color of light produced by the LED can be controlled by appropriate choice of semiconductor. Most red LEDs are made of a mixture of GaP and GaAs. The band gap of GaP is 2.26 eV (3.62×10^{-19} J), which corresponds to a green photon with a wavelength of 549 nm, while GaAs has a band gap of 1.43 eV (2.29×10^{-19} J), which corresponds to an infrared photon with a wavelength of 867 nm. By forming solid solutions of these two compounds, with stoichiometries of $GaP_{1-x}As_x$, the band gap can be adjusted to any intermediate value. Thus, $GaP_{1-x}As_x$ is the solid solution of choice for red, orange, and yellow LEDs. Green LEDs are made from mixtures of GaP and AlP ($E_g = 2.43$ eV, $\lambda = 510$ nm).

Red LEDs have been in the market for decades, but to make white light, an efficient blue LED was needed. The first prototype bright blue LED was demonstrated in a Japanese laboratory in 1993. In 2010, less than 20 years later, over $10 billion worth of blue LEDs were sold worldwide. The blue LEDs are based on combinations of GaN (E_g = 3.4 eV, λ = 365 nm) and InN (E_g = 2.4 eV, λ = 517 nm). Many colors of LEDs are now available and are used in everything from barcode scanners to traffic lights (Figure 12.33). Because the light emission results from semiconductor structures that can be made extremely small and because they emit little heat, LEDs are replacing standard incandescent and fluorescence light bulbs in many applications.

Related Exercises: 12.29, 12.33, 12.94, 12.95



▲ **Figure 12.33** LEDs are all around us.

Self-Assessment Exercises

12.28 Sulfur has a melting point of 115 °C. How would you classify the solid?

(a) Molecular solid

(b) Covalent-network solid

12.29 If you want to dope GaAs to make a p-type semiconductor with an element to replace As, which element(s) would you pick?

(a) Si

(b) P

(c) Se

Exercises

12.30 Classify each of the following statements as true or false:

(**a**) For molecular solids, the melting point generally increases as the strengths of the covalent bonds increase.

(**b**) For molecular solids, the melting point generally increases as the strengths of the intermolecular forces increase.

12.31 Which of the following properties are typical characteristics of a covalent-network solid, a metallic solid, or both: (**a**) ductility, (**b**) hardness, (**c**) high melting point?

12.32 For each of the following pairs of semiconductors, which one will have the larger band gap: (**a**) InP or InAs, (**b**) Ge or AlP, (**c**) AgI or CdTe?

12.33 Cadmium telluride is an important material for solar cells. (**a**) What is the band gap of CdTe? (**b**) What wavelength of light would a photon of this energy correspond to? (**c**) Draw a vertical line at this wavelength in the figure shown in Exercise 12.95, (towards the end of this chapter) which shows the light output of the sun as a function of wavelength. (**d**) With respect to silicon, does CdTe absorb a larger or smaller portion of the solar spectrum?

12.34 The first LEDs were made from GaAs, which has a band gap of 1.43 eV. What wavelength of light would be emitted from an LED made from GaAs? What region of the electromagnetic spectrum does this light correspond to: ultraviolet, visible, or infrared?

Answers to Self-Assessment Exercises

12.28 (a) **12.29** (a)

12.5 | Polymers



Silicone is a polymer composed of an alternating chain of Si and O atoms with two carbon groups (typically CH_3- groups) attached to each Si atom. The polymer is resistant to water and inert under normal circumstances making it useful as a sealant and in medicine. For example, breast implants, used for reconstructive or cosmetic surgery can be made of silicone.

By the end of this section, you should be able to

- Define the terms relating to polymers.
- Explain how the interactions between polymer chains impact the physical properties of polymers.

In nature we find many substances of very high molecular weight, running up to millions of u, that make up much of the structure of living organisms and tissues. Some examples are starch and cellulose, which abound in plants, as well as proteins, which are found in both plants and animals. In 1827, Jöns Jakob Berzelius coined the word **polymer** (from the Greek *polys*, "many," and *meros*, "parts") to denote molecular substances of high molecular weight formed by the *polymerization* (joining together) of **monomers**, molecules with low molecular weight.

Historically, natural polymers, such as wool, leather, silk, and natural rubber, were processed into usable materials. During the past 70 years or so, chemists have learned to form synthetic polymers by polymerizing monomers through controlled chemical reactions. A great many of these synthetic polymers have a backbone of carbon–carbon bonds because carbon atoms have an exceptional ability to form strong stable bonds with one another.

Plastics are polymeric solids that can be formed into various shapes, usually by the application of heat and pressure. There are several types of plastics.

Thermoplastics can be reshaped. For example, plastic milk containers are made from the thermoplastic polymer *polyethene* (polyethylene). These containers can be melted down and the polymer recycled for some other use. If you look at the bottom of a plastic container, you are likely to see a recycle symbol containing a number, as shown in Figure 12.34. The number and the letter abbreviation below it indicate the kind of polymer from which the container is made, as summarized in Table 12.5. These symbols make it possible to sort containers by composition. In general, the lower the number, the greater the ease with which the material can be recycled.



▲ **Figure 12.34 Recycling symbols.** Most plastic containers manufactured today carry a recycling symbol indicating the type of polymer used to make the container and the polymer's suitability for recycling.

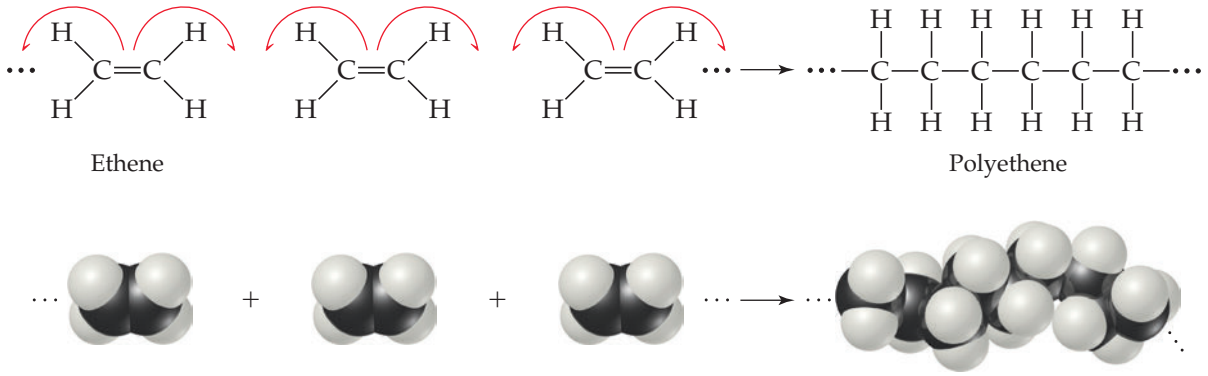
Unlike a thermoplastic, a **thermosetting plastic** (also called a *thermoset*) is shaped through irreversible chemical processes and, therefore, cannot be reshaped readily. Vulcanized rubber and polyurethanes found in commercial products including insulating foams and mattresses are familiar examples of thermosetting plastics.

Another type of plastic is the **elastomer**, which is a material that exhibits rubbery or elastic behavior. When subjected to stretching or bending, an elastomer regains its original shape upon removal of the distorting force, if it has not been distorted beyond some elastic limit. Rubber is the most familiar example of an elastomer.

Some polymers, such as nylon and polyesters, both of which are thermosetting plastics, can be formed into fibers that, like hair, are very long relative to their

TABLE 12.5 Categories Used for Recycling Polymeric Materials in the United States

Number	Abbreviation	Polymer
1	PET or PETE	Polyethene terephthalate
2	HDPE	High-density polyethene
3	PVC	Polyvinyl chloride
4	LDPE	Low-density polyethene
5	PP	Polypropene
6	PS	Polystyrene
7	None	Other



▲ **Figure 12.35** **The polymerization of ethene monomers to make the polymer polyethene.**

cross-sectional area. These fibers can be woven into fabrics and cords and fashioned into clothing, tire cord, and other useful objects.

Making Polymers

A good example of a polymerization reaction is the formation of polyethene from ethene molecules (**Figure 12.35**). In this reaction, the double bond in each ethene molecule "opens up," and two of the electrons originally in this bond are used to form new C—C single bonds with two other ethene molecules. This type of polymerization, in which monomers are coupled through their multiple bonds, is called **addition polymerization**.

We can write the equation for the polymerization reaction as follows:

$$n\ CH_2{=}CH_2 \longrightarrow \left[\begin{array}{cc} H & H \\ | & | \\ C & C \\ | & | \\ H & H \end{array}\right]_n$$

Here n represents the large number—ranging from hundreds to many thousands—of monomer molecules (ethene in this case) that react to form one polymer molecule. Within the polymer, a repeat unit (the unit shown in brackets in the previous equation) appears over and over along the entire chain. The ends of the chain are capped by carbon–hydrogen bonds or by some other bond, so that the end carbons have four bonds.

Polyethene is an important material; its annual production exceeds 190 billion pounds each year. Although its composition is simple, the polymer is not easy to make. The right manufacturing conditions were identified only after many years of research. Today many forms of polyethene, varying widely in physical properties, are known.

Polymers of other chemical compositions provide still greater variety in physical and chemical properties. **Table 12.6** lists several other common polymers obtained by addition polymerization.

A second general reaction used to synthesize commercially important polymers is **condensation polymerization**. In a condensation reaction two molecules are joined to form a larger molecule by elimination of a small molecule, such as H_2O. For example, an amine (a compound containing $—NH_2$) reacts with a carboxylic acid (a compound containing —COOH) to form a bond between N and C plus an H_2O molecule (**Figure 12.36**).

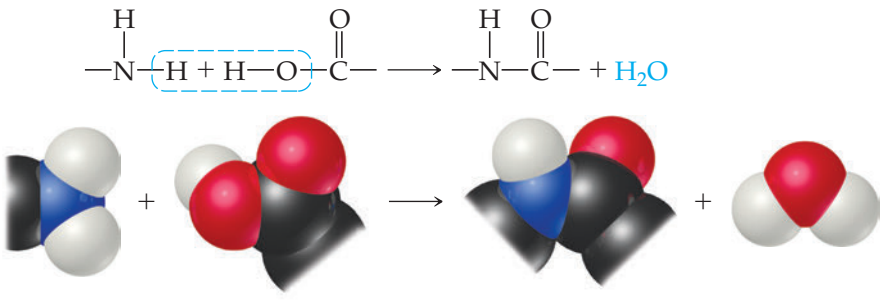
Polymers formed from two different monomers are called **copolymers**. In the formation of many nylons, a *diamine*, a compound with the $—NH_2$ group at each end, is reacted with a *diacid*, a compound with the —COOH group at each end. For example, the copolymer nylon 6,6 is formed when a diamine that has six carbon atoms and an amino group on each end is reacted with adipic acid, which also has six carbon atoms (**Figure 12.37**). A condensation reaction occurs on each end of the diamine and the acid. Water is released, and N—C bonds are formed between molecules.

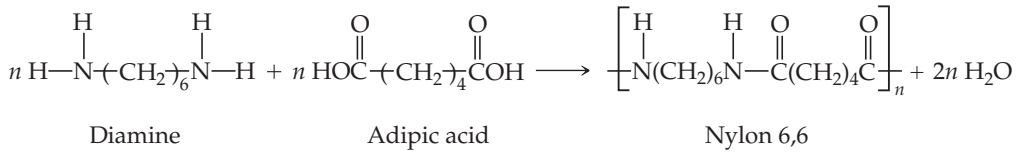
TABLE 12.6 Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethene	$-(CH_2-CH_2)_n-$	Films, packaging, bottles
Polypropene	$-[CH_2-CH(CH_3)]_n-$	Kitchenware, fibers, appliances
Polystyrene	$-[CH_2-CH(C_6H_5)]_n-$	Packaging, disposable food containers, insulation
Polyvinyl chloride (PVC)	$-[CH_2-CH(Cl)]_n-$	Pipe fittings, plumbing
Condensation Polymers		
Polyurethane	$-[NH-R-NH-C(=O)-O-R'-O-C(=O)]_n-$ R, R′ = —CH_2—CH_2— (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethene terephthalate (a polyester)	$-[O-CH_2-CH_2-O-C(=O)-C_6H_4-C(=O)]_n-$	Tire cord, magnetic tape, apparel, soft-drink bottles
Nylon 6,6	$-[NH-(CH_2)_6-NH-C(=O)-(CH_2)_4-C(=O)]_n-$	Home furnishings, apparel, carpet, fishing line, toothbrush bristles
Polycarbonate	$-[O-C_6H_4-C(CH_3)_2-C_6H_4-O-C(=O)]_n-$	Shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows, greenhouses

Table 12.6 lists nylon 6,6 and some other common polymers obtained by condensation polymerization. Notice that these polymers have backbones containing N or O atoms as well as C atoms.

▶ **Figure 12.36** A condensation polymerization.



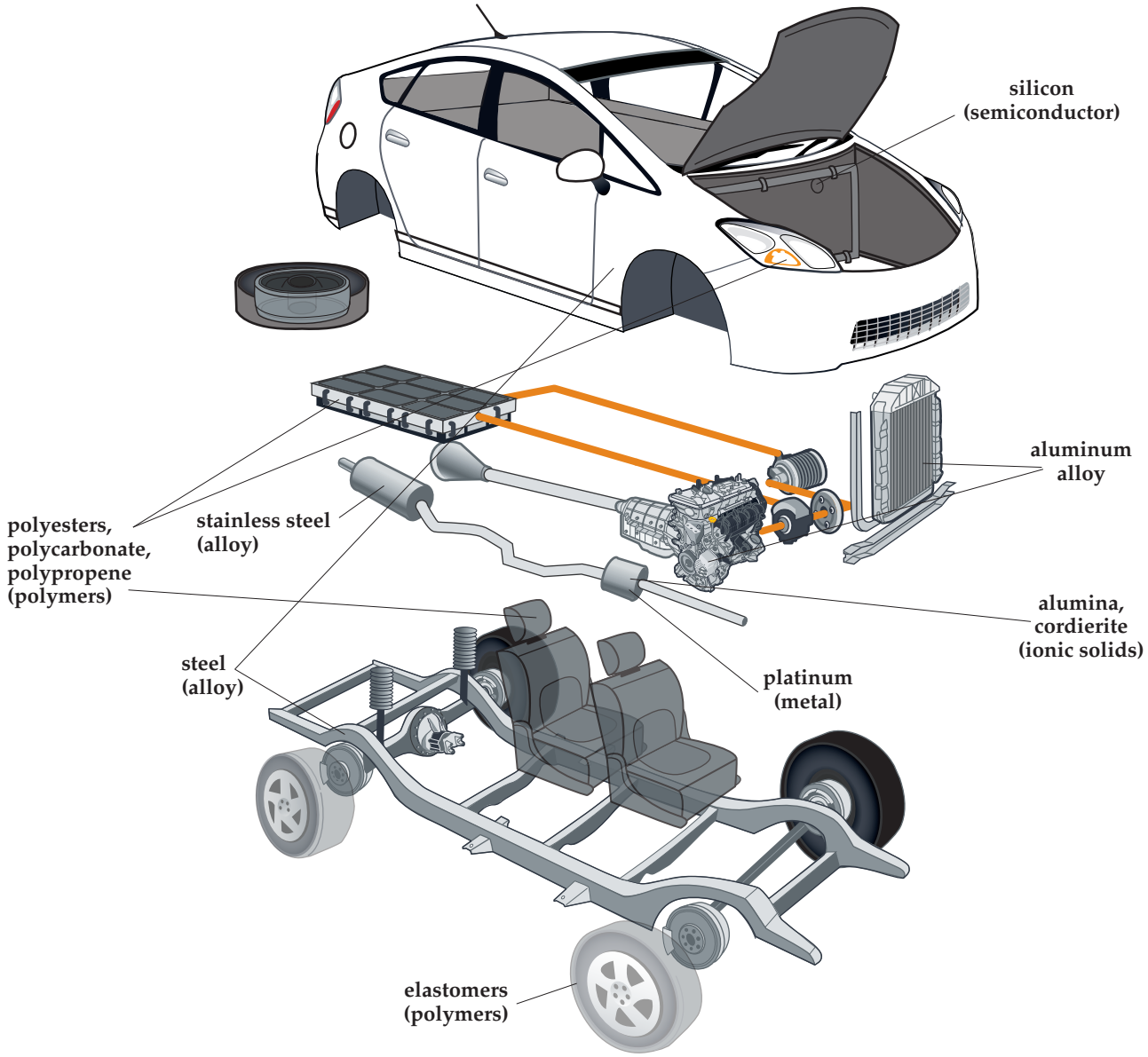


◀ **Figure 12.37** The formation of the copolymer nylon 6,6.

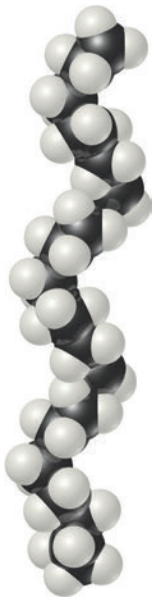
CHEMISTRY PUT TO WORK Modern Materials in the Automobile

There are over a billion motor vehicles in the world. Improvement in the fundamental understanding of the structure and properties of materials has enabled the development of motor vehicles that are safer, more powerful, more comfortable, and more fuel efficient. Let's take a look at some of these modern materials (**Figure 12.38**).

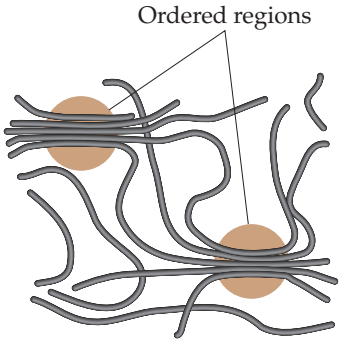
Metals and metal alloys are incorporated into many parts of an automobile. For example, aluminum is the primary component of the radiator, intake manifold, and engine block. Steel is typically the material used for the frame and body. Stainless steel is utilized in mufflers, exhaust silencers, and catalytic converters. The inside of the catalytic converter contains small particles of platinum group metals that are deposited onto a honeycomb-shaped structural ceramic. The ceramic is composed of the ionic solids alumina (Al_2O_3) coated onto cordierite ($Mg_2Al_4Si_5O_{18}$). Semiconducting oxides are used for the oxygen sensor to monitor the air/fuel ratio in the exhaust gases, which is controlled by the engine control computer that is based on silicon, a covalent network solid. Polymers are found in a motor vehicle too, with polyesters in seat covers and carpets, polycarbonate optical reflectors, and polypropene in bumpers and car batteries.



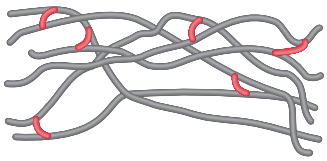
▲ **Figure 12.38** Selected modern material components of an automobile.



▲ **Figure 12.39 A segment of a polyethene chain.** This segment consists of 28 carbon atoms. In commercial polyethenes, the chain lengths range from about 10^3 to 10^5 CH_2 units.



▲ **Figure 12.40 Interactions between polymer chains.** In the circled regions, the forces that operate between adjacent segments of the chains lead to ordering analogous to the ordering in crystals, though less regular.



▲ **Figure 12.41 Cross-linking of polymer chains.** The cross-linking groups (red) constrain the relative motions of the polymer chains, making the material harder and less flexible than when the cross-links are not present.

Structure and Physical Properties of Polymers

The simple structural formulas given for polyethene and other polymers are deceptive. Because four bonds surround each carbon atom in polyethene, the atoms are arranged in a tetrahedral fashion, so that the chain is not straight as we have depicted it. Furthermore, the atoms are relatively free to rotate around the C—C single bonds. Rather than being straight and rigid, therefore, the chains are flexible, folding readily (**Figure 12.39**). The flexibility in the molecular chains causes any material made of this polymer to be very flexible.

Both synthetic and natural polymers commonly consist of a collection of *macromolecules* (large molecules) of different molecular weights. Depending on the conditions of formation, the molecular weights may be distributed over a wide range or may be closely clustered around an average value. In part because of this distribution in molecular weights, polymers are largely amorphous (noncrystalline) materials. Rather than exhibiting a well-defined crystalline phase with a sharp melting point, polymers soften over a range of temperatures. They may, however, possess short-range order in some regions of the solid, with chains lined up in regular arrays as shown in **Figure 12.40**. The extent of such ordering is indicated by the degree of **crystallinity** of the polymer. Mechanical stretching or pulling to align the chains as the molten polymer is drawn through small holes can frequently enhance the crystallinity of a polymer. Intermolecular forces between the polymer chains hold the chains together in the ordered crystalline regions, making the polymer denser, harder, less soluble, and more resistant to heat. **Table 12.7** shows how the properties of polyethene change as the degree of crystallinity increases.

The degree of crystallinity in polyethene strongly depends on the average molecular weight. Polymerization results in a mixture of macromolecules with varying values of n (numbers of monomer molecules) and, hence, varying molecular weights. Low-density polyethene (LDPE), used in forming films and sheets, has an average molecular weight in the range of 10^4 u, has a density of less than 0.94 g/cm^3, and has substantial chain branching. That is, there are side chains off the main chain of the polymer. These side chains inhibit the formation of crystalline regions, reducing the density of the material. High-density polyethene (HDPE), used to form bottles, drums, and pipes, has an average molecular weight in the range of 10^6 u and has a density of 0.94 g/cm^3 or higher. This form has fewer side chains and thus a higher degree of crystallinity.

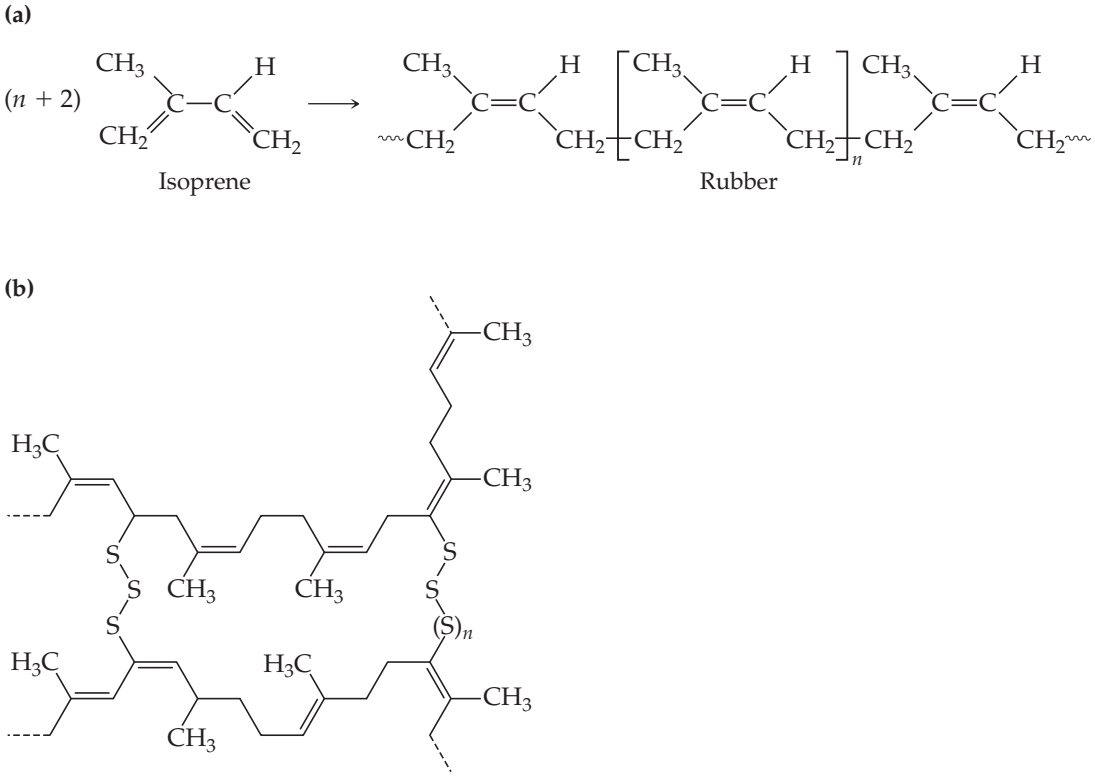
Polymers can be made stiffer by introducing chemical bonds between chains. Forming bonds between chains is called **cross-linking** (**Figure 12.41**). The greater the number of cross-links, the more rigid the polymer. Whereas thermoplastic materials consist of independent polymer chains, thermosetting plastics become cross-linked when heated; the cross-links allow them to hold their shapes.

An important example of cross-linking is the **vulcanization** of natural rubber, a process discovered by Charles Goodyear in 1839. Natural rubber is formed from a liquid resin derived from the inner bark of the *Hevea brasiliensis* tree. Chemically, it is a polymer of isoprene, C_5H_8 (**Figure 12.42**). Because rotation about the carbon–carbon double bond does not readily occur, the orientation of the groups bound to the carbons is rigid.

TABLE 12.7 Properties of Polyethene as a Function of Crystallinity

Properties	Crystallinity				
	55%	62%	70%	77%	85%
Melting point (°C)	109	116	125	130	133
Density (g/cm^3)	0.92	0.93	0.94	0.95	0.96
Stiffness*	170	325	520	820	1140
Yield stress*	11.72	17.24	22.75	28.96	35.16

*These test results show that the mechanical strength of the polymer increases with increased crystallinity. The physical units for the stiffness test are pascals; those for the yield stress test are megapascals. Discussion of the exact meaning and significance of these tests is beyond the scope of this text.

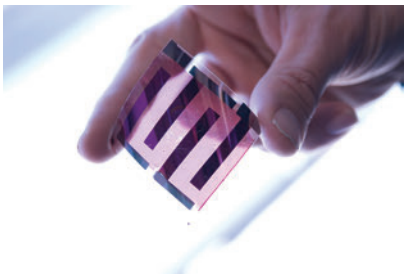


▲ **Figure 12.42 Vulcanization of natural rubber.** (**a**) Formation of polymeric natural rubber from the monomer isoprene. (**b**) Adding sulfur to rubber creates carbon–sulfur bonds and sulfur–sulfur links between chains.

In natural rubber, the chain extensions are on the same side of the double bond, as shown in Figure 12.42(**a**).

Natural rubber is not a useful polymer because it is too soft and too chemically reactive. Goodyear accidentally discovered that adding sulfur and then heating the mixture make the rubber harder and reduce its susceptibility to oxidation and other chemical degradation reactions. The sulfur changes rubber into a thermosetting polymer by cross-linking the polymer chains through reactions at some of the double bonds, as shown schematically in Figure 12.42(**b**). Cross-linking of about 5% of the double bonds creates a flexible, resilient rubber. When the rubber is stretched, the cross-links help prevent the chains from slipping, so that the rubber retains its elasticity. Because heating was an important step in his process, Goodyear named it after Vulcan, the Roman god of fire.

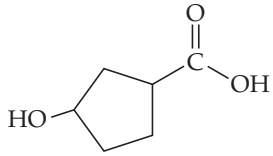
Most polymers contain sp^3-hybridized carbon atoms lacking delocalized π electrons, so they are usually electrical insulators and are colorless (which implies a large band gap). However, if the backbone of the polymer has resonance, the electrons can become delocalized over long distances, which can lead to semiconducting behavior in the polymer. Such "plastic electronics" are of great current interest for lightweight and flexible organic solar cells, organic transistors, organic light-emitting diodes, and other devices that are based on carbon rather than inorganic semiconductors like silicon (**Figure 12.43**).



▲ **Figure 12.43 Plastic electronics.** Flexible organic solar cells are made from conducting polymers.

Self-Assessment Exercises

12.35 Is this molecule a better starting material for an addition polymer or a condensation polymer?



(a) Addition polymer

(b) Condensation polymer

12.36 Bakelite is a thermosetting polymer used as an insulator in early electrical appliances. The rigid structure is due to:

(a) The high molecular weight of the polymer

(b) Formation from a rigid monomer molecule

(c) Extensive cross-linking between polymer chains

Exercises

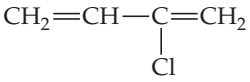
12.37 The molecular formula of *n*-decane is $CH_3(CH_2)_8CH_3$. Decane is not considered a polymer, whereas polyethene is. What is the distinction?

12.38 Indicate whether the following statement is true or false: For an addition polymerization, there are no by-products of the reaction (assuming 100% yield).

12.39 Write a balanced chemical equation for the formation of a polymer via a condensation reaction from the monomers 1,4-phenylenediamine ($H_2NC_6H_4NH_2$) and terephthalic acid ($HOOCC_6H_4COOH$).

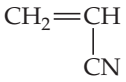
12.40 Write the chemical equation that represents the formation of

(**a**) polychloroprene from chloroprene (polychloroprene is used in highway-pavement seals, expansion joints, conveyor belts, and wire and cable jackets)



Chloroprene

(**b**) polyacrylonitrile from acrylonitrile (polyacrylonitrile is used in home furnishings, craft yarns, clothing, and many other items).



Acrylonitrile

12.41 What molecular structural features cause high-density polyethene to be denser than low-density polyethene?

12.42 Indicate whether each statement is true or false:

(**a**) Elastomers are rubbery solids.

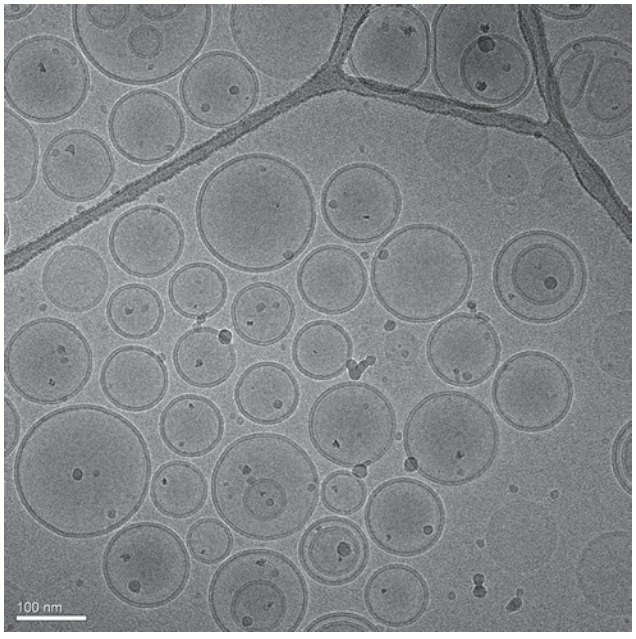
(**b**) Thermosets cannot be reshaped.

(**c**) Thermoplastic polymers can be recycled.

Answers to Self-Assessment Exercises

12.35 (b) 12.36 (c)

12.6 | Nanomaterials



The prefix *nano* means 10^{-9}. When people speak of "nanotechnology," they usually mean making devices that are on the 1–100 nm scale. It turns out that the properties of semiconductors and metals change in this size range. **Nanomaterials**—materials that have dimensions on the 1–100 nm scale—are under intense investigation in research laboratories around the world, and chemistry plays a central role in this investigation. Nanoparticles are between 10 and 1000 times larger than an atom.

By the end of this section, you should be able to

- Recognize that very small particles may have different properties to a bulk material.

Semiconductors on the Nanoscale

Figure 12.22 shows that, in small molecules, electrons occupy discrete molecular orbitals, whereas in macroscale solids the electrons occupy delocalized bands. At what point does a molecule get so large that it starts behaving as though it has delocalized bands rather than localized molecular orbitals? For semiconductors, both theory and experiment tell us that the answer is roughly at 1 to 10 nm (about 10–100 atoms across). The exact number depends on the specific semiconductor material. The equations of quantum mechanics that were used for electrons in atoms can be applied to electrons (and holes) in semiconductors to estimate the size where materials undergo a crossover from molecular orbitals to bands. Because these effects become important at 1 to 10 nm, semiconductor particles with diameters in this size range are called *quantum dots*.

One of the most spectacular effects of reducing the size of a semiconductor crystal is that the band gap changes substantially with size in the 1–10 nm range. As the particle gets smaller, the band gap gets larger, an effect observable by the naked eye. On the macro level, the semiconductor cadmium phosphide looks black because its band gap is small ($E_g = 0.5$ eV), and it absorbs all wavelengths of visible light. As the crystals are made smaller, the material progressively changes color until it looks white! It looks white because now no visible light is absorbed. The band gap is so large that only high-energy ultraviolet light can excite electrons into the conduction band ($E_g > 3.0$ eV).

Making quantum dots is most easily accomplished using chemical reactions in solution. For example, to make CdS, you can mix $Cd(NO_3)_2$ and Na_2S in water. If you do not do anything else, you will precipitate large crystals of CdS. However, if you first add a negatively charged polymer to the water (such as polyphosphate, $—(OPO_2^-)_n—$), the Cd^{2+} associates with the polymer, like tiny "meatballs" in the polymer "spaghetti." When sulfide is added, CdS particles grow, but the polymer keeps them from forming large crystals. A great deal of fine-tuning of reaction conditions is necessary to produce nanocrystals that are of uniform size and shape.

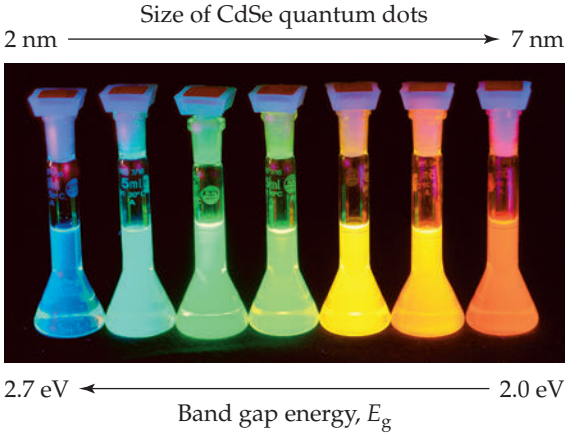
As we learned in Section 12.7, some semiconductor devices can emit light when a voltage is applied. Another way to make semiconductors emit light is to illuminate them with light whose photons have energies larger than the energy of the band gap of the semiconductor, a process called *photoluminescence*. A valence-band electron absorbs a photon and is promoted to the conduction band. If the excited electron then falls back down into the hole it left in the valence band, it emits a photon having energy equal to the band gap energy. In the case of quantum dots, the band gap is tunable with the crystal size, and thus all the colors of the rainbow can be obtained from just one material, as shown for CdSe in **Figure 12.44**.

Quantum dots are being explored for applications ranging from electronics to lasers to medical imaging because they are very bright, very stable, and small enough to be taken up by living cells even after being coated with a biocompatible surface layer.

Semiconductors do not have to be shrunk to the nanoscale in all three dimensions to show new properties. They can be laid down in relatively large two-dimensional areas on a substrate but be only a few nanometers thick to make *quantum wells*. *Quantum wires*, in which the semiconductor wire diameter is only a few nanometers but its length is very long, have also been made by various chemical routes. In both quantum wells and quantum wires, measurements along the nanoscale dimension(s) show quantum behavior, but in the long dimension, the properties seem to be just like those of the bulk material.

Go Figure

As the size of the quantum dots decreases, does the wavelength of the emitted light increase or decrease?



▲ Figure 12.44 Photoluminescence depends on particle size at the nanoscale. When illuminated with ultraviolet light, these solutions, each containing nanoparticles of the semiconductor CdSe, emit light that corresponds to their respective band gap energies. The wavelength of the light emitted depends on the size of the CdSe nanoparticles.

Metals on the Nanoscale

Metals also have unusual properties on the 1–100 nm length scale. Fundamentally, this is because the mean free path of an electron in a metal at room temperature is typically about 1–100 nm. So when the particle size of a metal is 100 nm or less, one might expect unusual effects because the "sea of electrons" encounters a "shore" (the surface of the particle).

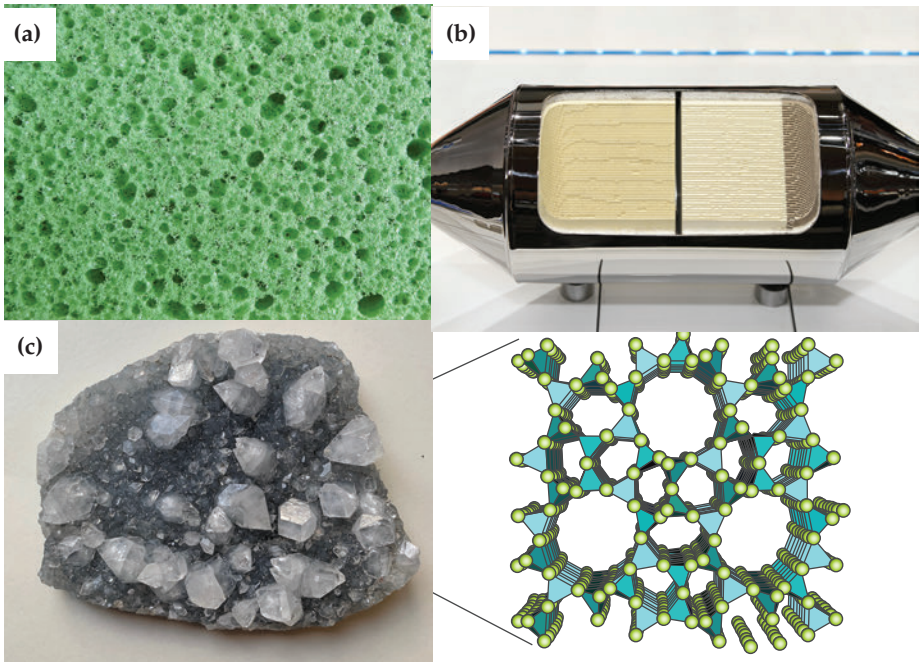
CHEMISTRY PUT TO WORK Microporous and Mesoporous Materials

Macroporous materials have pores that are visible to the naked eye. Examples include the everyday synthetic sponge [Figure 12.45(**a**)] and the honeycomb-like cordierite core of an automobile catalytic converter [Figure 12.45(**b**)], with pore sizes in the mm size range and the tens of μm size range, respectively. *Microporous* and *mesoporous* materials have much smaller pores that are not visible to the naked eye. **Microporous** solids have pores up to 2 nm in size, whereas **mesoporous** solids have pore sizes in the range 2 to 50 nm.

Microporous and mesoporous materials have a large surface area relative to their volume because of their numerous pores and cavities. **Nanomaterials**, on the other hand, have a large surface area relative to their volume because of their small particle size. The size-dependent properties of these materials has led researchers to investigate their fundamental science and application.

Zeolites, which occur naturally and can also be synthesized, are a class of aluminosilicates that have been known since 1756. There are several hundred types of microporous and mesoporous zeolites. These substances adopt a variety of structures with polyhedral cavities connected by tunnels that often resemble a honeycomb [Figure 12.45(**c**)]. The interior surfaces attract ions and molecules that weakly interact with the rigid framework of aluminum, silicon, and oxygen atoms. Various pore and cavity sizes can be prepared by varying the chemical composition and synthesis method.

Zeolites may be synthesized with weakly interacting ions occupying the cavities. Upon exposure to ions that interact more strongly with the interior surfaces, there is a preferential exchange of weakly interacting ions for more strongly interacting ions. This effectively creates what we might think of as an ionic sponge. An example that illustrates this behavior is the use of a sodium zeolite to remove radioactive cesium (^{134}Cs and ^{137}Cs) from contaminated areas around the Fukushima Daiichi nuclear power plants in Japan, which were damaged by an earthquake and tsunami in 2011. The cesium ions are attracted into the cavities of the zeolite where an ion exchange occurs (Cs^+ for Na^+). Another example is treatment of water from wells that contain relatively high concentrations of calcium, magnesium, and iron ions—so-called hard water. Heated hard water can cause problems by forming deposits inside of pipes, reducing flow over time. Hard water can be "softened" by passing it through zeolites containing sodium ions that are replaced or exchanged for calcium ions in the hard water. Periodic flushing of the zeolite with an aqueous solution containing a high concentration of sodium ions removes the calcium ions and renews the zeolite for further use.



▲ **Figure 12.45 Porous materials.** Sponges (**a**) and the core of an automobile catalytic converter (**b**) are macroporous. Zeolite ZSM-5 (**c**) is a microporous material with pore sizes near 0.5 nm.

Although it was not fully understood, people have known for hundreds of years that metals are different when they are very finely divided. Dating back to the Middle Ages, the makers of stained-glass windows knew that gold dispersed in molten glass made the glass a beautiful deep red (**Figure 12.46**). Much later, in 1857, Michael Faraday reported that dispersions of small gold particles could be made stable and were deeply colored—some of the original colloidal solutions that he made are still in the Royal Institution of Great Britain's Faraday Museum in London (**Figure 12.47**).

Other physical and chemical properties of metallic nanoparticles are also different from the properties of the bulk materials. Gold particles less than 20 nm in diameter



▲ **Figure 12.46 Stained glass window from the Chartres Cathedral in France.** Gold nanoparticles are responsible for the red color in this window, which dates back to the twelfth century.



▲ **Figure 12.47 The solution of colloidal gold nanoparticles made by Michael Faraday in the 1850s.** This is on display in the Royal Institution, London.

melt at a far lower temperature than bulk gold, for instance, and when the particles are between 2 and 3 nm in diameter, gold is no longer a "noble," unreactive metal; in this size range it becomes chemically reactive.

At nanoscale dimensions, silver has properties analogous to those of gold in its beautiful colors, although it is more reactive than gold. Currently, research laboratories around the world are showing great interest in taking advantage of the unusual optical properties of metal nanoparticles for applications in biomedical imaging and chemical detection.

Carbon on the Nanoscale

We have seen that elemental carbon is quite versatile. In its bulk sp^3 hybridized solid-state form, it is diamond; in its bulk sp^2 hybridized solid-state form, it is graphite. Over the past three decades, scientists have discovered that sp^2 hybridized carbon can also form discrete molecules, one-dimensional nanoscale tubes, and two-dimensional nanoscale sheets. Each of these forms of carbon shows very interesting properties.

Until the mid-1980s, pure solid carbon was thought to exist in only two forms: the covalent-network solids diamond and graphite. In 1985, however, a group of researchers led by Richard Smalley and Robert Curl of Rice University and Harry Kroto of the University of Sussex, England, vaporized a sample of graphite with an intense pulse of laser light and used a stream of helium gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peaks corresponding to clusters of carbon atoms, with a particularly strong peak corresponding to molecules composed of 60 carbon atoms, C_{60}.

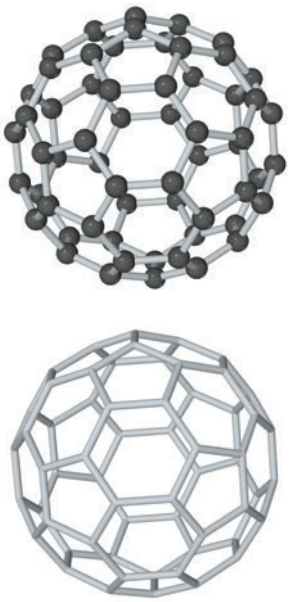
Because C_{60} clusters were so preferentially formed, the group proposed a radically different form of carbon, namely, nearly spherical C_{60} *molecules*. They proposed that the carbon atoms of C_{60} form a "ball" with 32 faces, 12 of them pentagons and 20 hexagons (**Figure 12.48**), exactly like a soccer ball. The shape of this molecule is reminiscent of the geodesic dome invented by the U.S. engineer and philosopher R. Buckminster Fuller, so C_{60} was whimsically named "buckminsterfullerene," or "buckyball" for short. Since the discovery of C_{60}, other related molecules made of pure carbon have been discovered. These molecules are now known as fullerenes.

Appreciable amounts of buckyball can be prepared by electrically evaporating graphite in an atmosphere of helium gas. About 14% of the resulting soot consists of C_{60} and a related molecule, C_{70}, which has a more elongated structure. The carbon-rich gases from which C_{60} and C_{70} condense also contain other fullerenes, mostly containing more carbon atoms, such as C_{76} and C_{84}. The smallest possible fullerene, C_{20}, was first detected in 2000. This small, ball-shaped molecule is much more reactive than the larger fullerenes. Because fullerenes are molecules, they dissolve in various organic solvents, whereas diamond and graphite do not. This solubility permits fullerenes to be separated from the other components of soot and even from one another. It also allows the study of their reactions in solution.

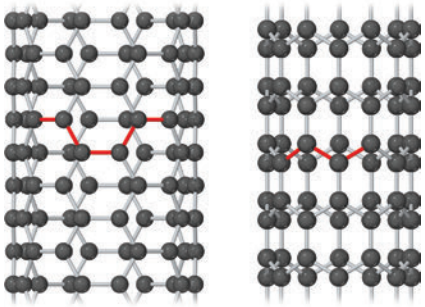
Soon after the discovery of C_{60}, chemists discovered carbon nanotubes (**Figure 12.49**). You can think of these as sheets of graphite rolled up and capped at one or both ends by half of a C_{60} molecule. Carbon nanotubes are made in a manner similar to that used to

Go Figure

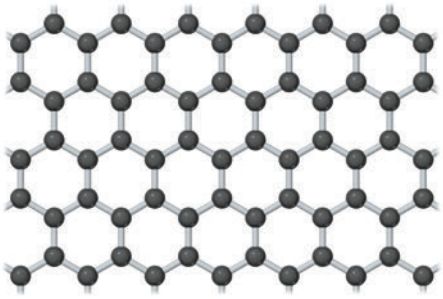
How many bonds does each carbon atom in C_{60} make? Based on this observation, would you expect the bonding in C_{60} to be more like that in diamond or that in graphite?



▲ **Figure 12.48 Buckminsterfullerene, C_{60}.** The molecule has a highly symmetric structure in which the 60 carbon atoms sit at the vertices of a truncated icosahedron. The bottom view shows only the bonds between carbon atoms.



▲ **Figure 12.49 Atomic models of carbon nanotubes.** Left: "Armchair" nanotube, which shows metallic behavior. Right: "Zigzag" nanotube, which can be either semiconducting or metallic, depending on tube diameter.



▲ **Figure 12.50 A portion of a two-dimensional graphene sheet.**

make C_{60}. They can be made in either *multiwall* or *single-walled* forms. Multiwall carbon nanotubes consist of tubes within tubes, nested together, whereas single-walled carbon nanotubes consist of single tubes. Single-walled carbon nanotubes can be 1000 nm long or even longer but are only about 1 nm in diameter. Depending on the diameter of the graphite sheet and how it is rolled up, carbon nanotubes can behave as either semiconductors or metals.

The fact that carbon nanotubes can be made either semiconducting or metallic without any doping is unique among solid-state materials, and laboratories worldwide are making and testing carbon-based electronic devices. Carbon nanotubes are also being explored for their mechanical properties. The carbon–carbon bonded framework of the nanotubes means that the imperfections that might appear in a metal nanowire of similar dimensions are nearly absent. Experiments on individual carbon nanotubes suggest that they are stronger than steel, if steel were the dimensions of a carbon nanotube. Carbon nanotubes have been spun into fibers with polymers, adding great strength and toughness to the composite material.

The two-dimensional form of carbon, graphene, is the most recent low-dimensional form of carbon to be experimentally isolated and studied. Although its properties had been the subject of theoretical predictions for over 60 years, it was not until 2004 that researchers at the University of Manchester in England isolated and identified individual sheets of carbon atoms with the honeycomb structure shown in **Figure 12.50**. Amazingly, the technique they used to isolate single-layer graphene was to successively peel away thin layers of graphite using adhesive tape. Individual layers of graphene were then transferred to a silicon wafer having a precisely defined overcoat of SiO_2. When a single layer of graphene is left on the wafer, an interference-like contrast pattern results that can be seen with an optical microscope. If not for this simple yet effective way to scan for individual graphene crystals, they would probably still remain undiscovered. Subsequently, it has been shown that graphene can be deposited on clean surfaces of other types of crystals. The scientists who led the effort at the University of Manchester, Andre Geim and Konstantin Novoselov, were awarded the 2010 Nobel Prize in Physics for their work.

The properties of graphene are remarkable. It is very strong and has a record thermal conductivity, topping carbon nanotubes in both categories. Graphene is a semimetal, which means its electronic structure is like that of a semiconductor in which the energy gap is exactly zero. The combination of graphene's two-dimensional character and the fact that it is a semimetal allows the electrons to travel very long distances, up to 0.3 μm, without scattering from another electron, atom, or impurity. Graphene can sustain electrical current densities six orders of magnitude higher than those sustainable in copper. Even though it is only one atom thick, graphene can absorb 2.3% of sunlight that strikes it. Scientists are currently exploring ways to incorporate graphene in various technologies, including electronics, sensors, batteries, and solar cells.

Sample Integrative Exercise

Putting Concepts Together

Polymers that can conduct electricity are called *conducting polymers*. Some polymers can be made semiconducting; others can be nearly metallic. Polyacetylene is an example of a polymer that is a semiconductor. It can also be doped to increase its conductivity.

Polyacetylene is made from acetylene in a reaction that looks simple but is actually tricky to do:

$$\underset{\text{Acetylene}}{H-C\equiv C-H} \qquad \underset{\text{Polyacetylene}}{+CH=CH+_n}$$

(**a**) What is the hybridization of the carbon atoms, and the geometry around those atoms, in acetylene and in polyacetylene?
(**b**) Write a balanced equation to make polyacetylene from acetylene.
(**c**) Acetylene is a gas at room temperature and pressure (298 K, 101.3 kPa). How many grams of polyacetylene can you make from a 5.00-L vessel of acetylene gas at room temperature and room pressure? Assume that acetylene behaves ideally and that the polymerization reaction occurs with 100% yield.
(**d**) Using the average bond enthalpies in Table 8.4, predict whether the formation of polyacetylene from acetylene is endothermic or exothermic.
(**e**) A sample of polyacetylene absorbs light from 300 nm down to 650 nm. What is its band gap, in electron volts?

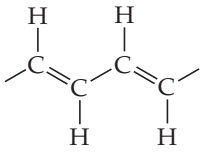
SOLUTION

Analyze For part (a), we need to recall what we have learned about *sp*, sp^2, and sp^3 hybridization and geometry. For part (b), we need to write a balanced equation. For part (c), we need to use the ideal-gas equation. For part (d), we need to recall the definitions of endothermic and exothermic and how bond enthalpies can be used to predict overall reaction enthalpies. For part (e), we need to relate the absorption of light to the differences in energy levels between filled and empty states in a material.

Plan For part (a), we should draw out the chemical structures of the reactant and product. For part (b), we need to make sure the equation is properly balanced. For part (c), we need to convert from liters of gas to moles of gas, using the ideal-gas equation ($PV = nRT$); then we need to convert from moles of acetylene gas to moles of polyacetylene using the answer from part (b); finally, we can convert to grams of polyacetylene. For part (d), we need to recall that $\Delta H_{rxn} = \Sigma(\text{bond enthalpies of bonds broken}) - \Sigma(\text{bond enthalpies of bonds formed})$. For part (e), we need to realize that the lowest energy absorbed by a material will tell us its band gap E_g (for a semiconductor or insulator) and combine $E = h\nu$ and $c = \lambda\nu$ together ($E = hc/\lambda$) to solve for E_g.

Solve

(a) Carbon usually forms four bonds. Thus, each C atom must have a single bond to H and a triple bond to the other C atom in acetylene. As a result, each C atom has two electron domains and must be *sp* hybridized. This *sp* hybridization also means that the H—C—C angles in acetylene are 180° and the molecule is linear. We can write out the partial structure of polyacetylene as follows:



Each carbon is identical but now has three bonding electron domains that surround it. Therefore, the hybridization of each carbon atom is sp^2, and each carbon has local trigonal planar geometry with 120° angles.

(b) We can write:

$$n\,C_2H_2(g) \longrightarrow +CH{=}CH+_n$$

Note that all atoms originally present in acetylene end up in the polyacetylene product.

(c) We can use the ideal-gas equation as follows:

$$PV = nRT$$
$$(101.3\text{ kPa})(5.00 \times 10^{-3}\,\text{m}^3) = n(8.314\,\text{m}^3\text{-Pa}/\text{K-mol})(298\text{ K})$$
$$n = 0.204\text{ mol}$$

Acetylene has a molar mass of 26.0 g/mol; therefore, the mass of 0.204 mol is:

$$(0.204\text{ mol})(26.0\text{ g/mol}) = 5.32\text{ g acetylene}$$

Note that from the answer to part (b), all the atoms in acetylene go into polyacetylene. Due to conservation of mass, then, the mass of polyacetylene produced must also be 5.32 g, if we assume 100% yield.

(d) Let's consider the case for $n = 1$. We note that the reactant side of the equation in part (b) has one C≡C triple bond and two C—H single bonds. The product side of the equation in part (b) has one C=C double bond, one C—C single bond (to link to the adjacent monomer), and two C—H single bonds. Therefore, we are breaking one C≡C triple bond and are forming one C=C double bond and one C—C single bond. Accordingly, the enthalpy change for polyacetylene formation is:

$$\Delta H_{rxn} = (\text{C}{\equiv}\text{C enthalpy}) - (\text{C}{=}\text{C enthalpy}) - (\text{C}{-}\text{C enthalpy})$$
$$= (839\text{ kJ/mol}) - (614\text{ kJ/mol}) - (348\text{ kJ/mol})$$
$$= -123\text{ kJ/mol}$$

Because ΔH is a negative number, the reaction releases heat and is exothermic.

(e) The sample of polyacetylene absorbs many wavelengths of light, but the one we care about is the longest one, which corresponds to the lowest energy.

$$E = hc/\lambda$$
$$= (6.626 \times 10^{-34}\,\text{J-s})(3.00 \times 10^{8}\,\text{m-s}^{-1})/(650 \times 10^{-9}\,\text{m})$$
$$= 3.06 \times 10^{-19}\,\text{J}$$

We recognize that this energy corresponds to the energy difference between the bottom of the conduction band and the top of the valence band, and so is equivalent to the band gap E_g. Now we have to convert the number to electron volts. Since $1.602 \times 10^{-19}\,\text{J} = 1\text{ eV}$, we find that:

$$E_g = 1.91\text{ eV}$$

Self-Assessment Exercise

12.43 Large crystals of ZnS can show photoluminescence, emitting ultraviolet photons with energies equal to the band gap energy and a wavelength of 340 nm. Is it possible to shift the luminescence so that the emitted photons are in the visible region of the spectrum by making appropriately sized nanocrystals?

(a) Yes

(b) No

Exercises

12.44 GaP has a band gap of 2.26 eV. If GaP is illuminated with ultraviolet light, it emits light equal to the band gap energy. (**a**) What color is the emitted light? (**b**) Would appropriately sized GaP quantum dots be able to emit blue light? (**c**) What about red light?

12.45 Indicate whether this statement is true or false:

If you want a semiconductor that emits blue light, you could either use a material that has a band gap corresponding to the energy of a blue photon or you could use a material that has a smaller band gap but make an appropriately sized nanoparticle of the same material.

12.46 Gold adopts a face-centered cubic structure with a unit cell edge of 408 pm (Figure 12.11). How many gold atoms are there in a sphere that is 20 nm in diameter? Recall that the volume of a sphere is $\frac{4}{3}\pi r^3$.

12.47 What evidence supports the notion that buckyballs are actual molecules and not extended materials?

(**a**) Buckyballs are made of carbon.

(**b**) Buckyballs have a well-defined atomic structure and molecular weight.

(**c**) Buckyballs have a well-defined melting point.

(**d**) Buckyballs are semiconductors.

(**e**) More than one of the previous choices.

Answers to Self-Assessment Exercise

12.43 (b)

Chapter Summary and Key Terms

CLASSIFICATION OF SOLIDS (SECTION 12.1) The structures and properties of solids can be classified according to the forces that hold the atoms together. **Metallic solids** are held together by a delocalized sea of collectively shared valence electrons. **Ionic solids** are held together by the mutual attraction between cations and anions. **Covalent-network solids** are held together by an extended network of covalent bonds. **Molecular solids** are held together by weak intermolecular forces. **Polymers** contain very long chains of atoms held together by covalent bonds. These chains are usually held to one another by weaker intermolecular forces. **Nanomaterials** are solids where the dimensions of individual crystals are on the order of 1–100 nm.

In **crystalline solids**, particles are arranged in a regularly repeating pattern. In **amorphous solids**, however, particles show no long-range order. In a crystalline solid the smallest repeating unit is called a **unit cell**. All unit cells in a crystal contain an identical arrangement of atoms. The geometrical pattern of points on which the unit cells are arranged is called a **crystal lattice**. To generate a crystal structure a **motif**, which is an atom or group of atoms, is associated with each and every **lattice point**.

In two dimensions, the unit cell is a parallelogram whose size and shape are defined by two **lattice vectors** (a and b). There are five **primitive lattices**, lattices in which the lattice points are located only at the corners of the unit cell: square, hexagonal, rectangular, rhombic, and oblique. In three dimensions the unit cell is a parallelepiped whose size and shape are defined by three lattice vectors (a, b, and c), and there are seven primitive lattices: cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, and triclinic. Placing an additional lattice point at the center of a cubic unit cell leads to a **body-centered cubic lattice**, while placing an additional point at the center of each face of the unit cell leads to a **face-centered cubic lattice**.

METALLIC SOLIDS (SECTION 12.2) **Metallic solids** are typically good conductors of electricity and heat, *malleable*, which means that they can be hammered into thin sheets, and *ductile*, which means that they can be drawn into wires. Metals tend to form structures where the atoms are closely packed. Two related forms of close packing, **cubic close packing** and **hexagonal close packing**, are possible. In both, each atom has a **coordination number** of 12.

Alloys are materials that possess characteristic metallic properties and are composed of more than one element. The elements in an alloy can be distributed either homogeneously or heterogeneously. Alloys which contain homogeneous mixtures of elements can either be substitutional or interstitial alloys. In a **substitutional alloy** the atoms of the minority element(s) occupy positions normally occupied by atoms of the majority element. In an **interstitial alloy** atoms of the minority element(s), often smaller nonmetallic atoms, occupy interstitial positions that lie in the "holes" between atoms of the majority element. In a **heterogeneous alloy** the elements are not distributed uniformly; instead, two or more distinct phases with characteristic compositions are present. **Intermetallic compounds** are alloys that have a fixed composition and definite properties.

The properties of metals can be accounted for in a qualitative way by the **electron-sea model**, in which the electrons are visualized as being free to move throughout the metal. In the molecular orbital model the valence atomic orbitals of the metal atoms interact to form energy **bands** that are incompletely filled by valence electrons. Consequently, the electronic structure of a bulk solid is referred to as a **band structure**. The orbitals that constitute the energy band are delocalized over the atoms of the metal, and their energies are closely spaced. In a metal the valence shell s, p, and d orbitals form bands, and these bands overlap, resulting in one or more partially filled bands. Because the energy differences between orbitals *within a band* are extremely small, promoting electrons to higher-energy orbitals requires very little energy. This gives rise to high electrical and thermal conductivity, as well as other characteristic metallic properties.

IONIC SOLIDS (SECTION 12.3) **Ionic solids** consist of cations and anions held together by electrostatic attractions. Because these interactions are quite strong, ionic compounds tend to have high melting points. The attractions become stronger as the charges of the ions increase and/or the sizes of the ions decrease. The presence of both attractive (cation–anion) and repulsive (cation–cation and anion–anion) interactions helps to explain why ionic compounds are brittle. Like metals, the structures of ionic compounds tend to be symmetric, but to minimize direct contact between ions of like charge, the coordination numbers (typically 4 to 8) are necessarily smaller than those seen in close-packed metals. The exact structure depends on the relative sizes of the ions and the cation-to-anion ratio in the empirical formula.

COVALENT SOLIDS (SECTION 12.4) **Molecular solids** consist of atoms or molecules held together by intermolecular forces. Because these forces are relatively weak, molecular solids tend to be soft and possess low melting points. The melting point depends on the strength of the intermolecular forces, as well as the efficiency with which the molecules can pack together.

Covalent-network solids consist of atoms held together in large networks by covalent bonds. These solids are much harder and have higher melting points than molecular solids. Important examples include diamond, where the carbons are tetrahedrally coordinated to each other, and graphite, where the sp^2-hybridized carbon atoms form hexagonal layers. **Semiconductors** are solids that do conduct electricity, but to a far lesser extent than metals. **Insulators** do not conduct electricity at all.

Elemental semiconductors, like Si and Ge, as well as compound semiconductors, like GaAs, InP, and CdTe, are important examples of covalent-network solids. In a semiconductor the filled bonding molecular orbitals make up the **valence band**, while the empty antibonding molecular orbitals make up the **conduction band**. The valence and conduction bands are separated by an energy that is referred to as the **band gap**, E_g. The size of the band gap increases as the bond length decreases and as the difference in electronegativity between the two elements increases.

Doping semiconductors changes their ability to conduct electricity by orders of magnitude. An n-type semiconductor is one that is doped so that there are excess electrons in the conduction band; a p-type semiconductor is one that is doped so that there are missing electrons, which are called **holes**, in the valence band.

POLYMERS (SECTION 12.5) **Polymers** are molecules of high molecular weight formed by joining large numbers of small molecules called **monomers**. **Plastics** are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastic** polymers can be reshaped, typically through heating, in contrast to **thermosetting plastics**, which are formed into objects through an irreversible chemical process and cannot readily be reshaped. An **elastomer** is a material that exhibits elastic behavior; that is, it returns to its original shape following stretching or bending.

In an **addition polymerization** reaction, the molecules form new linkages by opening existing π bonds. Polyethene forms, for example, when the carbon–carbon double bonds of ethene open up. In a **condensation polymerization** reaction, the monomers are joined by eliminating a small molecule between them. The various kinds of nylon are formed, for example, by removing a water molecule between an amine and a carboxylic acid. A polymer formed from two different monomers is called a **copolymer**.

Polymers are largely amorphous, but some materials possess a degree of **crystallinity**. For a given chemical composition, the crystallinity depends on the molecular weight and the degree of branching along the main polymer chain. Polymer properties are also strongly affected by **cross-linking**, in which short chains of atoms connect the long polymer chains. Rubber is cross-linked by short chains of sulfur atoms in a process called **vulcanization**.

NANOMATERIALS (SECTION 12.6) When one or more dimensions of a material become sufficiently small, generally smaller than 100 nm, the properties of the material change. Materials with dimensions on this length scale are called **nanomaterials**. Quantum dots are semiconductor particles with diameters of 1–10 nm. In this size range the material's band gap energy becomes size-dependent. Metal nanoparticles have different chemical and physical properties in the 1–100-nm size range. Nanoparticles of gold, for example, are more reactive than bulk gold and no longer have a golden color. Nanoscience has produced a number of previously unknown forms of sp^2-hybridized carbon. Fullerenes, like C_{60}, are large molecules containing only carbon atoms. Carbon nanotubes are sheets of graphite rolled up. They can behave as either semiconductors or metals depending on how the sheet was rolled. Graphene, which is an isolated layer from graphite, is a two-dimensional form of carbon. These nanomaterials are being developed now for many applications in electronics, batteries, solar cells, and medicine.

Learning Outcomes After studying this chapter, you should be able to:

- Classify solids based on their bonding/intermolecular forces and understand how differences in bonding relate to physical properties. (Section 12.1) *Related Exercises: 12.4, 12.5, 12.58, 12.59, 12.60*
- Describe the difference between crystalline and amorphous solids. (Section 12.1) *Related Exercises: 12.62, 12.63*
- Define and describe the relationships between unit cells, crystal lattice, lattice vectors, and lattice points. (Section 12.1) *Related Exercises: 12.7, 12.64*
- Explain why there are a limited number of lattices. Recognize the five two-dimensional and the seven three-dimensional primitive lattices. Describe the locations of lattice points for body-centered and face-centered lattices. (Section 12.1) *Related Exercises: 12.7, 12.9, 12.10, 12.64, 12.66, 12.67*
- State the characteristics and properties of metals. (Section 12.2) *Related Exercises: 12.14, 12.50, 12.69, 12.70*
- Calculate the empirical formula and density of ionic and metallic solids from a picture of the unit cell. Estimate the length of a cubic unit cell from the radii of the atoms/ions present. (Sections 12.2 and 12.3) *Related Exercises: 2.15, 12.71–12.73, 12.75, 12.76*
- Explain how homogeneous and heterogeneous alloys differ. Describe the differences between substitutional alloys, interstitial alloys, and intermetallic compounds. (Section 12.2) *Related Exercises: 12.16–12.18, 12.77–12.79*
- Explain the electron-sea model of metallic bonding. (Section 12.2) *Related Exercise: 12.82*
- Use the molecular orbital model of metallic bonding to generate the electronic band structures of metals and qualitatively predict the trends in melting point, boiling point, and hardness of metals. (Section 12.2) *Related Exercises: 12.20, 12.84, 12.85*
- Predict the structures of ionic solids from their ionic radii and empirical formula. (Section 12.3) *Related Exercises: 12.26, 12.89*
- Predict the empirical formula from the structure of an ionic solid. (Section 12.3) *Related Exercises: 12.23, 12.86*
- Interpret melting point and boiling point data of molecular solids in terms of intermolecular forces and crystalline packing. (Section 12.4) *Related Exercise: 12.26*
- Identify the valence band, conduction band, and band gap, for semiconductors and insulators. (Section 12.4) *Related Exercise: 12.55*
- Account for the relative band gap energies of semiconductors in terms of periodic trends. Calculate the wavelength of a photon emitted from an LED given its band gap. (Section 12.4) *Related Exercises: 12.32–12.34, 12.93, 12.95–12.98*
- Predict how n-type and p-type doping can be used to control the conductivity of semiconductors. (Section 12.4) *Related Exercises: 12.29, 12.94*
- Define the terms monomer, plastic, thermoplastic, thermosetting plastic, elastomer, copolymers, and cross-linking. (Section 12.5) *Related Exercise: 12.99*
- Describe how polymers are formed from monomers and recognize the features of a molecule that allow it to react to form a polymer. Explain the differences between addition polymerization and condensation polymerization. (Section 12.5) *Related Exercises: 12.39, 12.101*
- Explain how the interactions between polymer chains impact the physical properties of polymers. (Section 12.5) *Related Exercises: 12.41, 12.42, 12.104, 12.105*

- Describe how the properties of bulk semiconductors and metals change as the size of the crystals decreases to the nanometer-length scale. (Section 12.6) *Related Exercises: 12.44, 12.107, 12.108*
- Describe the structures and unique properties of fullerenes, carbon nanotubes, and graphene. (Section 12.6) *Related Exercises: 12.47, 12.109*

Key Equations

- $\dfrac{\text{Number of cations per formula unit}}{\text{Number of anions per formula unit}} = \dfrac{\text{anion coordination number}}{\text{cation coordination number}}$ [12.1] Relationship between cation and anion coordination numbers and the empirical formula of an ionic compound

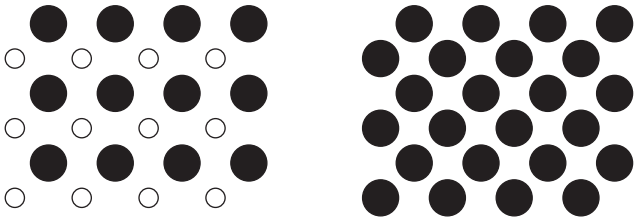
Exercises

Visualizing Concepts

12.48 Two solids are shown here. One is a semiconductor and one is an insulator. Which one is which? Explain your reasoning. [Sections 12.1, 12.4]



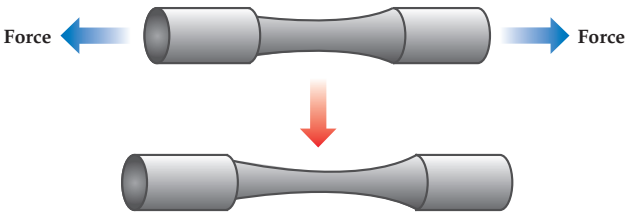
12.49 For each of the two-dimensional structures shown here (**a**) draw the unit cell, (**b**) determine the type of two-dimensional lattice (from Figure 12.4), and (**c**) determine how many of each type of circle (white or black) there are per unit cell. [Section 12.1]



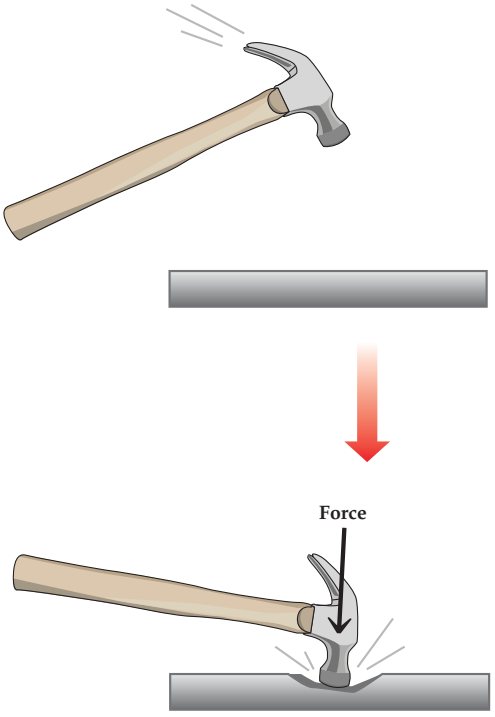
(i) **(ii)**

12.50 Shown here are sketches of two processes. Which of the processes refers to the ductility of metals and which refers to malleability of metals? [Section 12.2]

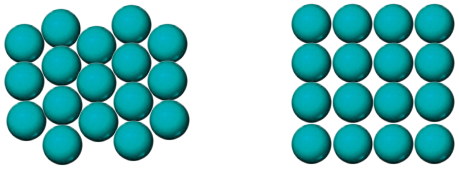
(a)



(b)



12.51 Which arrangement of atoms in a lattice represents close-packing? (Section 12.2)

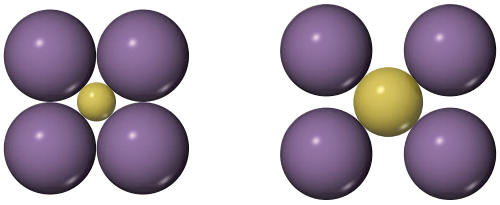


(i) **(ii)**

12.52 (**a**) What kind of packing arrangement is seen in the following photo? (**b**) What is the coordination number of each cannonball in the interior of the stack? (**c**) What are the coordination numbers for the numbered cannonballs on the visible side of the stack? [Section 12.2]

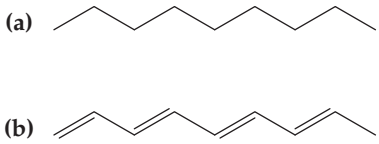


12.53 Which arrangement of cations (yellow) and anions (blue) in a lattice is the more stable? Explain your reasoning. [Section 12.3]

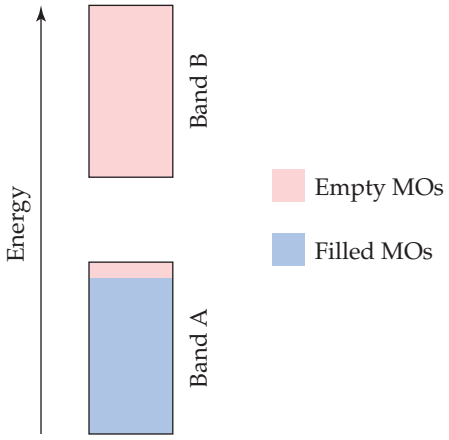


(a) (b)

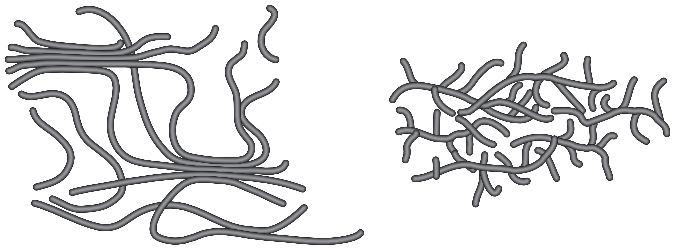
12.54 Which of these molecular fragments would you expect to be more likely to give rise to electrical conductivity? Explain your reasoning. [Sections 12.4, 12.5]



12.55 The electronic structure of a doped semiconductor is shown here. (**a**) Which band, A or B, is the valence band? (**b**) Which band is the conduction band? (**c**) Which region of the diagram represents the band gap? (**d**) Which band consists of bonding molecular orbitals? (**e**) Is this an example of an n-type or p-type semiconductor? (**f**) If the semiconductor is germanium, which of the following elements could be the dopant: Ga, Si, or P? [Section 12.4]



12.56 Shown here are cartoons of two different polymers. Which of these polymers would you expect to be more crystalline? Which one would have the higher melting point? [Section 12.5]



(a) (b)

Classification of Solids (Section 12.1)

12.57 Covalent bonding occurs in both molecular and covalent-network solids. Which of the following statements best explains why these two kinds of solids differ so greatly in their hardness and melting points?

(**a**) The molecules in molecular solids have stronger covalent bonding than covalent-network solids do.

(**b**) The molecules in molecular solids are held together by weak intermolecular interactions.

(**c**) The atoms in covalent-network solids are more polarizable than those in molecular solids.

(**d**) Molecular solids are denser than covalent-network solids.

12.58 What kinds of attractive forces exist between particles (atoms, molecules, or ions) in (**a**) molecular crystals, (**b**) covalent-network crystals, (**c**) ionic crystals, (**d**) and metallic crystals?

12.59 Indicate the type of solid (molecular, metallic, ionic, or covalent-network) for each compound: (**a**) B, (**b**) Li, (**c**) LiCl, (**d**) diethylether ($C_4H_{10}O$), (**e**) chloroform ($CHCl_3$), (**f**) Li_2O.

12.60 Indicate the type of solid (molecular, metallic, ionic, or covalent-network) for each compound: (**a**) SiC, (**b**) Ni, (**c**) $CaCl_2$, (**d**) camphor ($C_{10}H_{16}O$), (**e**) SiO_2.

12.61 You are given a gray substance that melts at 700 °C; the solid is a conductor of electricity and is insoluble in water. Which type of solid (molecular, metallic, covalent-network, or ionic) might this substance be?

12.62 (**a**) Draw a picture that represents a crystalline solid at the atomic level. (**b**) Now draw a picture that represents an amorphous solid at the atomic level.

12.63 Amorphous silica, SiO_2, has a density of about 2.2 g/cm^3, whereas the density of crystalline quartz, another form of SiO_2, is 2.65 g/cm^3. Which of the following statements is the best explanation for the difference in density?

(**a**) Amorphous silica is a network-covalent solid, but quartz is metallic.

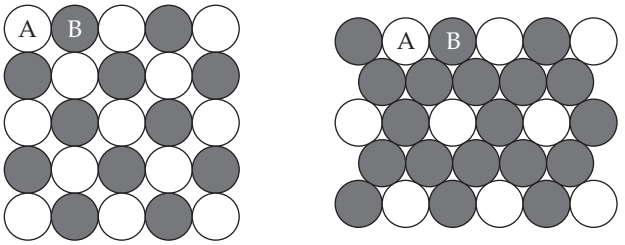
(**b**) Amorphous silica crystallizes in a primitive cubic lattice.

(**c**) Quartz is harder than amorphous silica.

(**d**) Quartz must have a larger unit cell than amorphous silica.

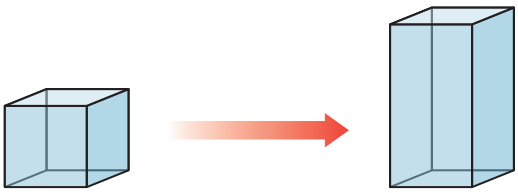
(**e**) The atoms in amorphous silica do not pack as efficiently in three dimensions as compared to the atoms in quartz.

12.64 Two patterns of packing for two different circles of the same size are shown here. For each structure (**a**) draw the two-dimensional unit cell; (**b**) determine the angle between the lattice vectors, γ, and determine whether the lattice vectors are of the same length or of different lengths; and (**c**) determine the type of two-dimensional lattice (from Figure 12.4).



(i) (ii)

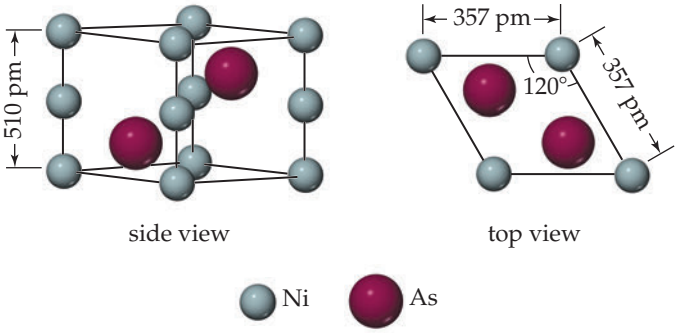
12.65 Imagine the primitive cubic lattice. Now imagine grabbing the top of it and stretching it straight up. All angles remain 90°. What kind of primitive lattice have you made?



12.66 Which of the three-dimensional primitive lattices has a unit cell where none of the internal angles is 90°? (**a**) Orthorhombic, (**b**) hexagonal, (**c**) rhombohedral, (**d**) triclinic, (**e**) both rhombohedral and triclinic.

12.67 What is the minimum number of atoms that could be contained in the unit cell of an element with a body-centered cubic lattice? (**a**) 1, (**b**) 2, (**c**) 3, (**d**) 4, (**e**) 5.

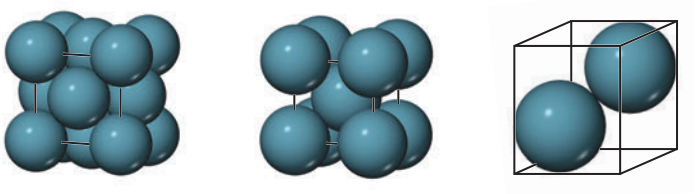
12.68 The unit cell of nickel arsenide is shown here. (**a**) What type of lattice does this crystal possess? (**b**) What is the empirical formula?



Metallic Solids (Section 12.2)

12.69 For each of these solids, state whether you would expect it to possess metallic properties: (**a**) $TiCl_4$, (**b**) NiCo alloy, (**c**) W, (**d**) Ge, (**e**) ScN.

12.70 Consider the unit cells shown here for three different structures that are commonly observed for metallic elements. (**a**) Which structure(s) corresponds to the densest packing of atoms? (**b**) Which structure(s) corresponds to the least dense packing of atoms?



Structure type A Structure type B Structure type C

12.71 Potassium metal (atomic weight 39.10 g/mol) adopts a body-centered cubic structure with a density of 0.856 g/cm^3. (**a**) Use this information and Avogadro's number (6.022×10^{23}) to estimate the atomic radius of potassium. (**b**) If potassium didn't react so vigorously, it could float on water. Use the answer from part (a) to estimate the density of K if its structure were that of a cubic close-packed metal. Would it still float on water?

12.72 Rhodium crystallizes in a face-centered cubic unit cell that has an edge length of 0.381 nm. (**a**) Calculate the atomic radius of a rhodium atom. (**b**) Calculate the density of rhodium metal.

12.73 Calcium crystallizes in a face-centered cubic unit cell at room temperature that has an edge length of 558.8 pm. (**a**) Calculate the atomic radius of a calcium atom. (**b**) Calculate the density of Ca metal at this temperature.

12.74 Calculate the volume in Å^3 of each of the following types of cubic unit cells if it is composed of atoms with an atomic radius of 182 pm. (**a**) primitive (**b**) face-centered cubic. Note $1\ \text{Å} = 1 \times 10^{-10}$ m

12.75 Aluminum metal crystallizes in a face-centered cubic unit cell. (**a**) How many aluminum atoms are in a unit cell? (**b**) What is the coordination number of each aluminum atom? (**c**) Estimate the length of the unit cell edge, *a*, from the atomic radius of aluminum (143 pm). (**d**) Calculate the density of aluminum metal.

12.76 An element crystallizes in a face-centered cubic lattice. The edge of the unit cell is 0.408 nm, and the density of the crystal is 10.49 g/cm^3. Calculate the atomic weight of the element and identify the element.

12.77 Which of these statements about alloys and intermetallic compounds is false? (**a**) Bronze is an example of an alloy. (**b**) "Alloy" is just another word for "a chemical compound of fixed composition that is made of two or more metals." (**c**) Intermetallics are compounds of two or more metals that have a definite composition and are not considered alloys. (**d**) If you mix two metals together and, at the atomic level, they separate into two or more different compositional phases, you have created a heterogeneous alloy. (**e**) Alloys can be formed even if the atoms that comprise them are rather different in size.

12.78 For each of the following alloy compositions, indicate whether you would expect it to be a substitutional alloy, an interstitial alloy, or an intermetallic compound:

(**a**) $Fe_{0.97}Si_{0.03}$, (**b**) $Fe_{0.60}Ni_{0.40}$, (**c**) $SmCo_5$.

12.79 Indicate whether each statement is true or false:

(**a**) Substitutional alloys tend to be more ductile than interstitial alloys.
(**b**) Interstitial alloys tend to form between elements with similar ionic radii.
(**c**) Nonmetallic elements are never found in alloys.

12.80 Which element or elements are alloyed with gold to make the following types of "colored gold" used in the jewelry industry? For each type, also indicate what type of alloy is formed: (**a**) white gold, (**b**) rose gold, (**c**) green gold.

12.81 An increase in temperature causes most metals to undergo *thermal expansion*, which means the volume of the metal increases upon heating. How does thermal expansion affect the unit cell length? What is the effect of an increase in temperature on the density of a metal?

12.82 State whether each sentence is true or false:

(**a**) Metals have high electrical conductivities because the electrons in the metal are delocalized.
(**b**) Metals have high electrical conductivities because they are denser than other solids.

(**c**) Metals have large thermal conductivities because they expand when heated.

(**d**) Metals have small thermal conductivities because the delocalized electrons cannot easily transfer the kinetic energy imparted to the metal from heat.

12.83 Which of the following statements does not follow from the fact that the alkali metals have relatively weak metal–metal bonding?

(**a**) The alkali metals are less dense than other metals.

(**b**) The alkali metals are soft enough to be cut with a knife.

(**c**) The alkali metals are more reactive than other metals.

(**d**) The alkali metals have higher melting points than other metals.

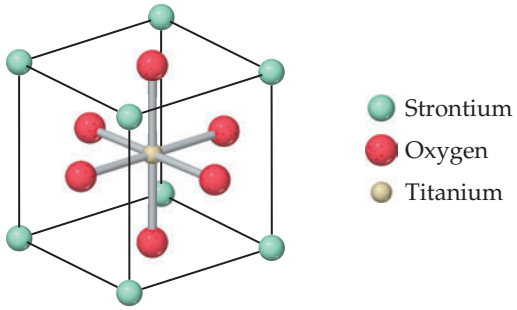
(**e**) The alkali metals have low ionization energies.

12.84 Arrange the following metals in increasing order of expected melting point: La, W, Ta, Hf. Explain this trend in melting points.

12.85 For each of the following groups, which metal would you expect to have the highest melting point: (**a**) gold, rhenium, or cesium; (**b**) rubidium, molybdenum, or indium; (**c**) ruthenium, strontium, or cadmium?

Ionic Solids (Sections 12.3)

12.86 Tausonite, a mineral composed of Sr, O, and Ti, has the cubic unit cell shown in the drawing. (**a**) What is the empirical formula of this mineral? (**b**) How many oxygens are coordinated to titanium? (**c**) To see the full coordination environment of the other ions, we have to consider neighboring unit cells. How many oxygens are coordinated to strontium?



12.87 Galena, also called lead glance, is a mineral composed of lead(II) sulfide(PbS). The mineral adopts the rock salt structure. The length of an edge of the PbS unit cell is 0.593 nm at 25 °C. Determine the density of PbS in g/cm^3.

12.88 Boron phosphide (BP) adopts the zinc blende structure. The length of the unit cell edge is 0.457 nm. (**a**) Calculate the density of BP in this form. (**b**) Boron arsenide (BAs) also forms a solid phase with the zinc blende structure. The length of the unit cell edge in this compound is 0.478 nm. What accounts for the larger unit cell length? (**c**) Which of the two substances has the higher density? How do you account for the difference in densities?

12.89 CuI, CsI, and NaI each adopt a different type of structure. The three different structures are those shown in Figure 12.26. (**a**) Use ionic radii, Cs^+ (r = 181 pm), Na^+ (r = 116 pm), Cu^+ (r = 74 pm), and, I^- (r = 206 pm), to predict which compound will crystallize with which structure. (**b**) What is the coordination number of iodide in each of these structures?

12.90 The coordination number for Mg^{2+} ion is usually six. Assuming this assumption holds, determine the anion coordination number in the following compounds: (**a**) MgS, (**b**) MgF_2, (**c**) MgO.

Covalent Solids (Section 12.4)

12.91 Classify each of the following statements as true or false:

(**a**) Although both molecular solids and covalent-network solids have covalent bonds, the melting points of molecular solids are much lower because their covalent bonds are much weaker.

(**b**) Other factors being equal, highly symmetric molecules tend to form solids with higher melting points than asymmetrically shaped molecules.

12.92 Both covalent-network solids and ionic solids can have melting points well in excess of room temperature, and both can be poor conductors of electricity in their pure form. However, in other ways their properties are quite different.

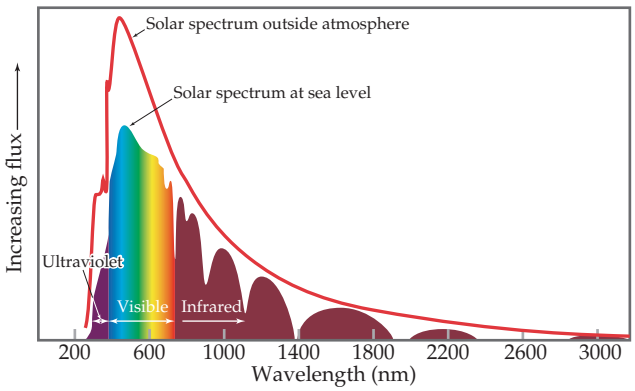
(**a**) Which type of solid is more likely to dissolve in water?

(**b**) Which type of solid can become a considerably better conductor of electricity via chemical substitution?

12.93 For each of the following pairs of semiconductors, which one will have the larger band gap: (**a**) CdS or CdTe, (**b**) GaN or InP, (**c**) GaAs or InAs?

12.94 If you want to dope GaAs to make an n-type semiconductor with an element to replace Ga, which element(s) would you pick?

12.95 Silicon has a band gap of 1.1 eV at room temperature. (**a**) What wavelength of light would a photon of this energy correspond to? (**b**) Draw a vertical line at this wavelength in the figure shown, which shows the light output of the Sun as a function of wavelength. Does silicon absorb all, none, or a portion of the visible light that comes from the Sun? (**c**) You can estimate the portion of the overall solar spectrum that silicon absorbs by considering the area under the curve. If you call the area under the entire curve "100%," what approximate percentage of the area under the curve is absorbed by silicon?



12.96 The semiconductor gallium nitride (GaN) has a band gap of 3.4 eV. What wavelength of light would be emitted from an LED made from GaN? What region of the electromagnetic spectrum is this?

12.97 GaAs and GaP make solid solutions that have the same crystal structure as the parent materials, with As and P randomly distributed throughout the crystal. GaP_xAs_{1-x} exists for any value of x. If we assume that the band gap varies linearly with composition between x = 0 and x = 1, estimate the band gap for $GaP_{0.8}As_{0.2}$. (GaAs and GaP band gaps are 1.43 eV and 2.26 eV, respectively.) What wavelength of light does this correspond to?

12.98 Orange light-emitting diodes are made from GaAs and GaP solid solutions, GaP_xAs_{1-x} (see Exercise 12.97). The original orange LEDs emitted light with a wavelength of 590 nm. If

we assume that the band gap varies linearly with composition between $x = 0$ and $x = 1$, estimate the composition (the value of x) that is used in these LEDs.

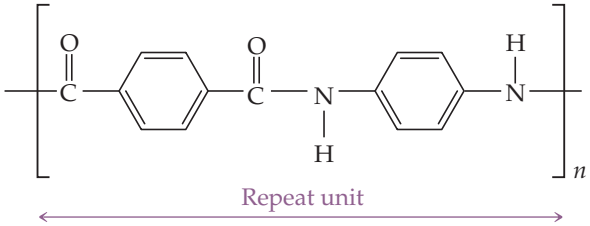
Polymers (Section 12.5)

12.99 (**a**) What is a monomer? (**b**) Which of these molecules can be used as a monomer: ethanol, ethene, methane?

12.100 State whether each of these numbers is a reasonable value for a polymer's molecular weight: 100 u, 10,000 u, 100,000 u, 1,000,000 u?

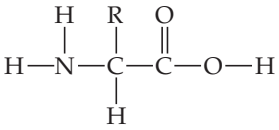
12.101 An addition polymerization forms the polymer originally used as Saran™ wrap. It has the following structure $+CCl_2-CH_2+_n$. Draw the structure of the monomer.

12.102 The polymer Kevlar, a condensation polymer, is used as reinforcement in car tires, strings of archery bows, and as a component of bulletproof vests.



Draw the structures of the two monomers that yield Kevlar.

12.103 Proteins are naturally occurring polymers formed by condensation reactions of amino acids, which have the general structure



In this structure, —R represents —H, $-CH_3$, or another group of atoms; there are 20 different natural amino acids, and each has one of 20 different R groups. (**a**) Draw the general structure of a protein formed by condensation polymerization of the generic amino acid shown here. (**b**) When only a few amino acids react to make a chain, the product is called a "peptide" rather than a protein; only when there are 50 amino acids or more in the chain would the molecule be called a protein. For three amino acids (distinguished by having three different R groups, R1, R2, and R3), draw the peptide that results from their condensation reactions. (**c**) The order in which the R groups exist in a peptide or protein has a huge influence on its biological activity. To distinguish different peptides and proteins, chemists call the first amino acid the one at the "N terminus" and the last one the one at the "C terminus." From your drawing in part (b) you should be able to figure out what "N terminus" and "C terminus" mean. How many different peptides can be made from your three different amino acids?

12.104 (**a**) What molecular features make a polymer flexible? (**b**) If you cross-link a polymer, is it more flexible or less flexible than it was before?

12.105 If you want to make a polymer for plastic wrap, should you strive to make a polymer that has a high or low degree of crystallinity?

Nanomaterials (Section 12.6)

12.106 Explain why "bands" may not be the most accurate description of bonding in a solid when the solid has nanoscale dimensions.

12.107 Indicate whether each statement is true or false:

(**a**) The band gap of a semiconductor decreases as the particle size decreases in the 1–10-nm range.

(**b**) The light that is emitted from a semiconductor, upon external stimulation, becomes longer in wavelength as the particle size of the semiconductor decreases.

12.108 An ideal quantum dot for use in TVs does not contain any cadmium due to concerns about disposal. One potential material for this purpose is InP, which adopts the zinc blende (ZnS) structure (face-centered cubic). The unit cell edge length is 586.9 pm. (**a**) If the quantum dot is shaped like a cube, how many of each type of atom are there in a cubic crystal with an edge length of 3.00 nm? 5.00 nm? (**b**) If one of the nanoparticles in part (a) emits blue light and the other emits orange light, which color is emitted by the crystal with the 3.00-nm edge length? With the 5.00-nm edge length?

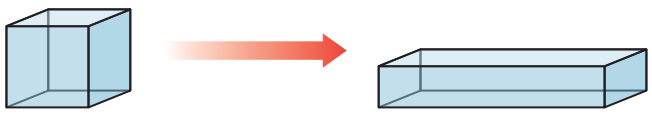
12.109 Which statement correctly describes a difference between graphene and graphite?
(**a**) Graphene is a molecule but graphite is not. (**b**) Graphene is a single sheet of carbon atoms and graphite contains many, and larger, sheets of carbon atoms. (**c**) Graphene is an insulator but graphite is a metal. (**d**) Graphite is pure carbon but graphene is not. (**e**) The carbons are sp^2 hybridized in graphene but sp^3 hybridized in graphite.

Additional Exercises

12.110 Selected chlorides have the following melting points: NaCl (801 °C), $MgCl_2$ (714 °C), PCl_3 (−94 °C), SCl_2 (−121 °C) (**a**) For each compound, indicate what type its solid form is (molecular, metallic, ionic, or covalent-network). (**b**) Predict which of the following compounds has a higher melting point: $CaCl_2$ or $SiCl_4$.

12.111 A face-centered tetragonal lattice is not one of the 14 three-dimensional lattices. Show that a face-centered tetragonal unit cell can be redefined as a body-centered tetragonal lattice with a smaller unit cell.

12.112 Imagine the primitive cubic lattice. Now imagine pushing on top of it, straight down. Next, stretch another face by pulling it to the right. All angles remain 90°. What kind of primitive lattice have you made?



12.113 Pure iron crystallizes in a body-centered cubic structure, but small amounts of impurities can stabilize a face-centered cubic structure. Which form of iron has a higher density?

12.114 Introduction of carbon into a metallic lattice generally results in a harder, less ductile substance with lower electrical and thermal conductivities. Explain why this might be so.

12.115 Ni_3Al is used in the turbines of aircraft engines because of its strength and low density. Nickel metal has a cubic

close-packed structure with a face-centered cubic unit cell, while Ni_3Al has the ordered cubic structure shown in Figure 12.17. The length of the cubic unit cell edge is 353 pm for nickel and 356 pm for Ni_3Al. Use these data to calculate and compare the densities of these two materials.

12.116 For each of the intermetallic compounds shown in Figure 12.17 determine the number of each type of atom in the unit cell. Do your answers correspond to the ratios expected from the empirical formulas: Ni_3Al, Nb_3Sn, and $SmCo_5$?

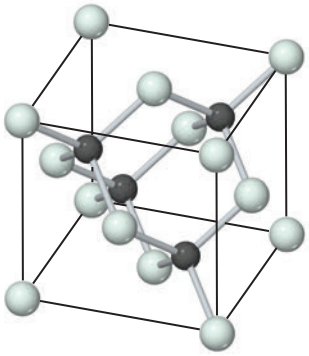
12.117 What type of lattice—primitive cubic, body-centered cubic, or face-centered cubic—does each of the following structure types possess: (**a**) NaF, (**b**) Ag, (**c**) Fe, (**d**) CsCl, (**e**) ScF_3?

12.118 Greenockite (CdS) was utilized as a pigment known as vermillion. It has a band gap of 2.6 eV near room temperature for the bulk solid. What wavelength of light (in nm) would a photon of this energy correspond to?

12.119 The electrical conductivity of aluminum is approximately 10^9 times greater than that of its neighbor in the periodic table, silicon. Aluminum has a face-centered cubic structure, and silicon has the diamond structure. A classmate of yours tells you that density is the reason aluminum is a metal but silicon is not; therefore, if you were to put silicon under high pressure, it too would act like a metal. Discuss this idea with your classmates, looking up data about Al and Si as needed.

12.120 Silicon carbide, SiC, has the three-dimensional structure shown in the figure.

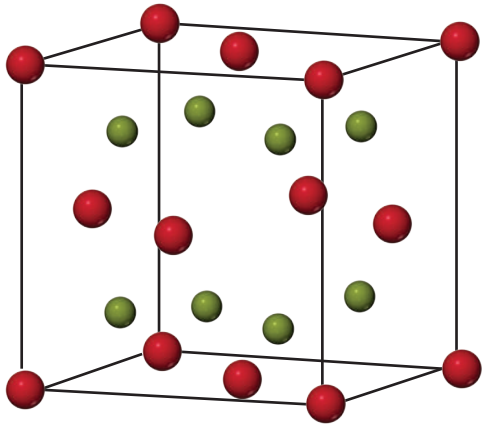
(**a**) Name another compound that has the same structure. (**b**) Would you expect the bonding in SiC to be predominantly ionic, metallic, or covalent? (**c**) How do the bonding and structure of SiC lead to its high thermal stability (to 2700 °C) and exceptional hardness?



12.121 Energy bands are considered continuous due to the large number of closely spaced energy levels. The range of energy levels in a crystal of copper is approximately 1×10^{-19} J. Assuming equal spacing between levels, the spacing between energy levels may be approximated by dividing the range of energies by the number of atoms in the crystal. (**a**) How many copper atoms are in a piece of copper metal in the shape of a cube with edge length 0.5 mm? The density of copper is 8.96 g/cm^3. (**b**) Determine the average spacing in J between energy levels in the copper metal in part (a). (**c**) Is this spacing larger, substantially smaller, or about the same as the 1×10^{-18} J separation between energy levels in a hydrogen atom?

12.122 Unlike metals, semiconductors increase their conductivity as you heat them (up to a point). Suggest an explanation.

12.123 Sodium oxide (Na_2O) adopts a cubic structure with Na atoms represented by green spheres and O atoms by red spheres.



(**a**) How many atoms of each type are there in the unit cell?

(**b**) Determine the coordination number and describe the shape of the coordination environment for the sodium ion.

(**c**) The unit cell edge length is 555 pm. Determine the density of Na_2O.

12.124 Teflon is a polymer formed by the polymerization of $F_2C{=}CF_2$. (**a**) Draw the structure of a section of this polymer. (**b**) What type of polymerization reaction is required to form Teflon?

12.125 Hydrogen bonding between polyamide chains plays an important role in determining the properties of a nylon such as nylon 6,6 (Table 12.6). Draw the structural formulas for two adjacent chains of nylon 6,6 and show where hydrogen-bonding interactions could occur between them.

12.126 Explain why X rays can be used to measure atomic distances in crystals but visible light cannot be used for this purpose.

12.127 In their study of X-ray diffraction, William and Lawrence Bragg determined that the relationship among the wavelength of the radiation (λ), the angle at which the radiation is diffracted (θ), and the distance between planes of atoms in the crystal that cause the diffraction (d) is given by $n\lambda = 2d \sin\theta$. X rays from a copper X-ray tube that have a wavelength of 154 pm are diffracted at an angle of 14.22 degrees by crystalline silicon. Using the Bragg equation, calculate the distance between the planes of atoms responsible for diffraction in this crystal, assuming $n = 1$ (first-order diffraction).

12.128 Germanium has the same structure as silicon, but the unit cell size is different because Ge and Si atoms are not the same size. If you were to repeat the experiment described in the previous problem but replace the Si crystal with a Ge crystal, would you expect the X rays to be diffracted at a larger or smaller angle θ?

12.129 (**a**) The density of diamond is 3.5 g/cm^3, and that of graphite is 2.3 g/cm^3. Based on the structure of buckminsterfullerene, what would you expect its density to be relative to these other forms of carbon? (**b**) X-ray diffraction studies of buckminsterfullerene show that it has a face-centered cubic lattice of C_{60} molecules. The length of an edge of the unit cell is 142 pm. Calculate the density of buckminsterfullerene.

12.130 When you shine light of band gap energy or higher on a semiconductor and promote electrons from the valence band to the conduction band, do you expect the conductivity of the semiconductor to (**a**) remain unchanged, (**b**) increase, or (**c**) decrease?

Integrative Exercises

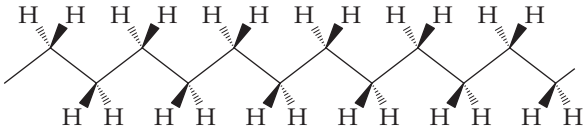
12.131 The carat scale used to describe gold alloys is based on mass percentages. (**a**) If an alloy is formed that is 75 mol% silver and 25 mol% gold, what is the carat number of the alloy? Use Figure 12.18 to estimate the color of this alloy. (**b**) If an alloy is formed that is 75 mol% copper and 25 mol% gold, what is the carat number of the alloy? What is the color of this alloy?

12.132 Spinel is a mineral that contains 37.9% Al, 17.1% Mg, and 45.0% O, by mass, and has a density of 3.57 g/cm^3. The unit cell is cubic with an edge length of 809 pm. How many atoms of each type are in the unit cell?

12.133 (**a**) What are the C—C—C bond angles in diamond? (**b**) What are they in graphite (in one sheet)? (**c**) What atomic orbitals are involved in the stacking of graphite sheets with each other?

12.134 Employing the bond enthalpy values listed in Table 8.4, estimate the molar enthalpy change occurring upon (**a**) polymerization of ethene, (**b**) formation of nylon 6,6, (**c**) formation of polyethene terephthalate (PET).

12.135 Although polyethene can twist and turn in random ways, the most stable form is a linear one with the carbon backbone oriented as shown in the following figure:



The carbon atoms of the backbone are not shown for clarity. The solid wedges in the figure indicate bonds from carbon that come out of the plane of the page; the dashed wedges indicate bonds that lie behind the plane of the page.

(**a**) What is the hybridization of orbitals at each carbon atom? What angles do you expect between the bonds?

(**b**) Now imagine that the polymer is polypropene rather than polyethene. Draw structures for polypropene in which (i) the CH_3 groups all lie on the same side of the plane of the paper (this form is called isotactic polypropene), (ii) the CH_3 groups lie on alternating sides of the plane (syndiotactic polypropene), or (iii) the CH_3 groups are randomly distributed on either side (atactic polypropene). Which of these forms would you expect to have the highest crystallinity and melting point, and which the lowest? Explain in terms of intermolecular interactions and molecular shapes.

(c) Polypropene fibers have been employed in athletic wear. The product is said to be superior to cotton or polyester clothing in wicking moisture away from the body through the fabric to the outside. Explain the difference between polypropene and polyester or cotton (which has many —OH groups along the molecular chain) in terms of intermolecular interactions with water.

12.136 (**a**) In polyvinyl chloride shown in Table 12.6, which bonds have the lowest average bond enthalpy? (**b**) When subjected to high pressure and heated, polyvinyl chloride converts to diamond. During this transformation which bonds are most likely to break first? (**c**) Employing the values of average bond enthalpy in Table 8.3, estimate the overall enthalpy change for converting PVC to diamond.

12.137 Silicon has the diamond structure with a unit cell edge length of 543 pm and eight atoms per unit cell. (**a**) How many silicon atoms are there in 1 cm^3 of material? (**b**) Suppose you dope that 1 cm^3 sample of silicon with 1 ppm of phosphorus that will increase the conductivity by a factor of a million. How many milligrams of phosphorus are required?

12.138 One method to synthesize ionic solids is by the heating of two reactants at high temperatures. Consider the reaction of MgO with TiO_2 to form $MgTiO_3$. Determine the amount of each of the two reactants to prepare 3.250 g $MgTiO_3$, assuming the reaction goes to completion.

(**a**) Write a balanced chemical reaction.

(**b**) Calculate the formula weight of $MgTiO_3$.

(**c**) Determine the moles of $MgTiO_3$.

(**d**) Determine moles and mass (g) of MgO required.

(**e**) Determine moles and mass (g) of TiO_2 required.

12.139 Look up the diameter of a silicon atom, in pm. The latest semiconductor chips have fabricated lines as small as 14 nm. How many silicon atoms does this correspond to?

Design an Experiment

Polymers were commercially made by the DuPont Company starting in the late 1920s. At that time, some chemists still could not believe that polymers were molecules; they thought covalent bonding would not "last" for millions of atoms, and that polymers were really clumps of molecules held together by weak intermolecular forces. Design an experiment to demonstrate that polymers really are large molecules and not little clumps of small molecules that are held together by weak intermolecular forces.

13

PROPERTIES OF SOLUTIONS

WHAT'S AHEAD

13.1 The Solution Process

13.2 Saturated Solutions and Solubility

13.3 Factors Affecting Solubility

13.4 Expressing Solution Concentration

13.5 Colligative Properties

13.6 Colloids

13.1 The Solution Process



In Chapters 10, 11, and 12, we explored the properties of pure gases, liquids, and solids. However, the examples of matter that we encounter in our daily lives, such as carbonated drinks, air, and glass, are frequently mixtures. In this chapter, we examine homogeneous mixtures.

As we noted in the earlier chapters, homogeneous mixtures are called *solutions*. (Sections 1.2 and 4.1) When we think of solutions, we usually think of liquids. Solutions, however, can also be solids or gases. For example, sterling silver is a homogeneous mixture of about 7% copper in silver and so is a solid solution. The air we breathe is a homogeneous mixture of several gases, making air a gaseous solution. However, because liquid solutions are the most common, we focus our attention on them in this chapter. We will be particularly concerned with aqueous solutions, which contain water as the solvent and either a gas, liquid, or solid as a solute.

By the end of this section, you should be able to

- Describe how enthalpy and entropy changes affect solution formation.

Each substance in a solution is a *component* of the solution. As we saw in Chapter 4, the *solvent* is normally the component present in the greatest amount, and all the other components are called *solutes*. *A solution is formed when one component disperses uniformly throughout another.* The ability of substances to form solutions depends on two factors: (1) the natural tendency of substances to mix and spread into larger volumes when not restrained in some way and (2) the types of intermolecular interactions involved in the solution process.

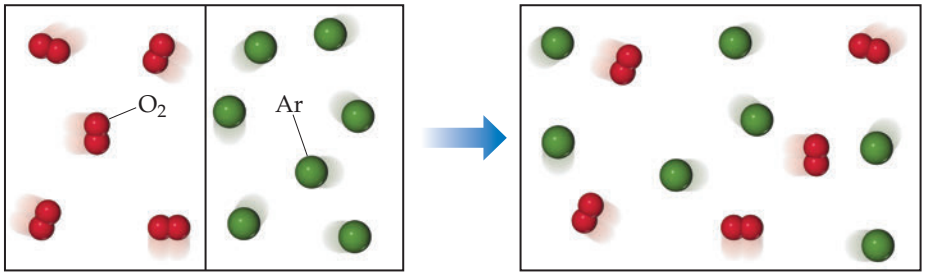
The Natural Tendency toward Mixing

Suppose we have $O_2(g)$ and Ar(g) separated by a barrier, as in **Figure 13.1**. If the barrier is removed, the gases mix to form a solution. The molecules experience very little intermolecular interactions and behave like ideal gas particles. As a result, their molecular motion causes them to spread through the larger volume, and a gaseous solution is formed.

The mixing of gases is a *spontaneous* process, meaning it occurs of its own accord without any input of energy from outside the system. When the molecules mix and become more randomly distributed, there is an increase in a thermodynamic quantity called *entropy*. Entropy will be defined more rigorously in Chapter 19; but for now, we can consider that the entropy of a system increases if its degree of disorder increases, or if its energy becomes dispersed over a greater number of particles. Therefore, the mixing of gases we just described increases the entropy of the system. The enthalpy of the system, however, changes little upon gas mixing because there are few intermolecular interactions between the gas particles. All of the intermolecular forces (dispersion forces, dipole–dipole interactions, hydrogen bonding) and their corresponding energies are part of the enthalpy of the system. Decreasing the enthalpy of the system would correspond to increasing favorable intermolecular interactions between gas particles. Furthermore, the balance between increasing the entropy and decreasing the enthalpy of a system is what determines whether a process is spontaneous. Thus, the *formation of solutions is favored by the increase in entropy that accompanies mixing*.

When molecules of different types are brought together, mixing occurs spontaneously unless the molecules are restrained either by sufficiently strong intermolecular

Go Figure What aspect of the kinetic theory of gases tells us that the gases will mix?



▲ **Figure 13.1** **Spontaneous mixing of two gases to form a homogeneous mixture (a solution).**

forces or by physical barriers. Thus, gases spontaneously mix unless restrained by their containers because with gases intermolecular forces are too weak to restrain the molecules. However, when the solvent or solute is a solid or liquid, intermolecular forces become important in determining whether a solution forms. For example, although ionic bonds hold sodium and chloride ions together in solid sodium chloride, the solid dissolves in water because of the compensating strength of the attractive forces between the ions and water molecules. Sodium chloride does not dissolve in petrol, however, because the intermolecular forces between the ions and the petrol molecules are too weak.

The Effect of Intermolecular Forces on Solution Formation

Any of the intermolecular forces discussed in Chapter 11 can operate between solute and solvent particles in a solution. These forces are summarized in **Figure 13.2**. Dispersion forces, for example, dominate when one nonpolar substance, such as C_7H_{16}, dissolves in another, such as C_5H_{12}, and ion–dipole forces dominate in solutions of ionic substances in water.

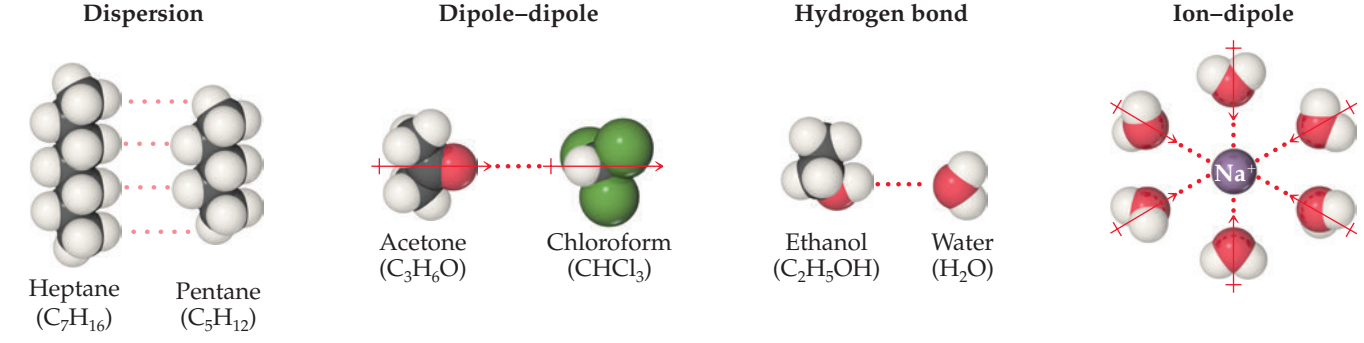
Three kinds of intermolecular interactions are involved in solution formation:

1. *Solute–solute* interactions between solute particles must be overcome to disperse the solute particles through the solvent.
2. *Solvent–solvent* interactions between solvent particles must be overcome to make room for the solute particles in the solvent.
3. *Solvent–solute* interactions between the solvent and solute particles occur as the particles mix.

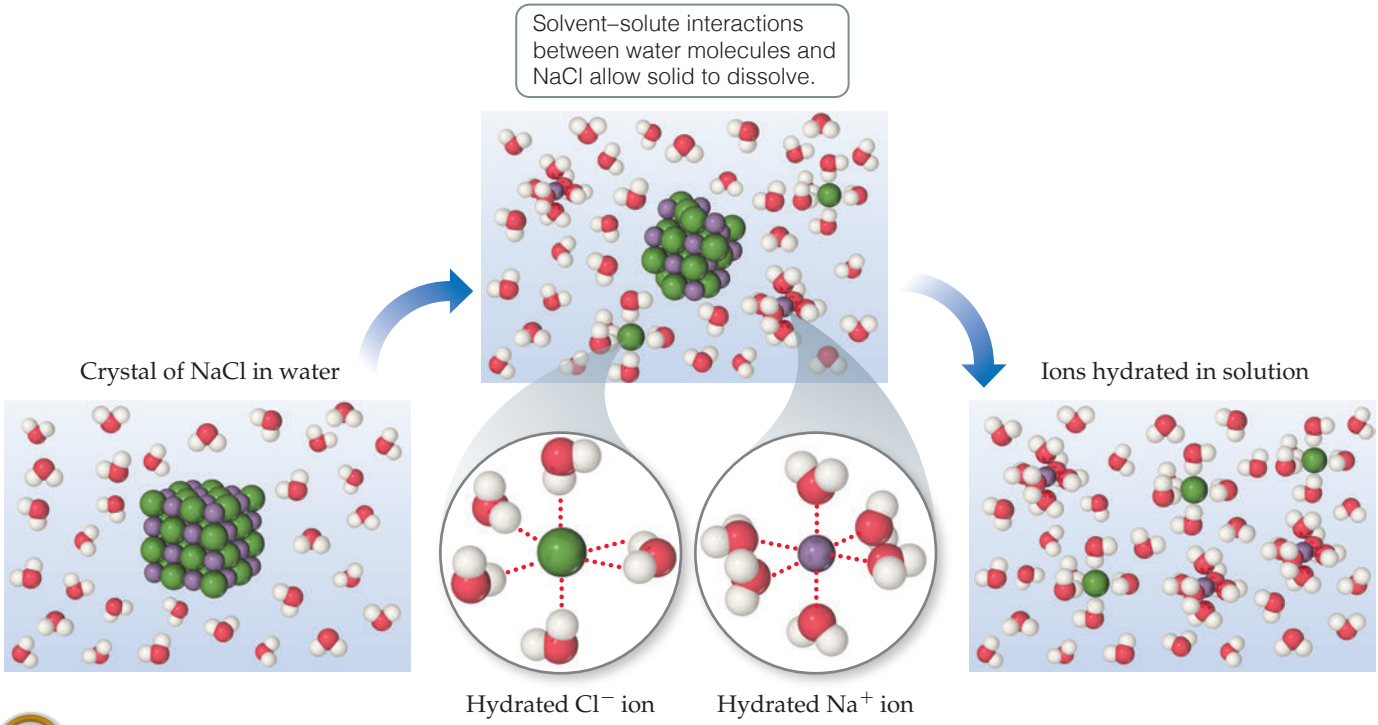
The extent to which one substance is able to dissolve in another depends on the relative magnitudes of these three types of interactions. Solutions form when the magnitudes of the solvent–solute interactions are either comparable to or greater than the solute–solute and solvent–solvent interactions. For example, heptane (C_7H_{16}) and pentane (C_5H_{12}) dissolve in each other in all proportions. For this discussion, we can arbitrarily call heptane the solvent and pentane the solute. Both substances are nonpolar, and the magnitudes of the solvent–solute interactions (attractive dispersion forces) are comparable to the solute–solute and the solvent–solvent interactions. Thus, no forces impede mixing, and the tendency to mix (increase entropy) causes the solution to form spontaneously.

An everyday example of solution formation occurs when you dissolve salt in water. Solid NaCl dissolves readily in water because the attractive solvent–solute interactions between the polar H_2O molecules and the ions are strong enough to overcome the attractive solute–solute interactions between ions in the NaCl(*s*) and the attractive solvent–solvent interactions between H_2O molecules. When NaCl is added to water

Go Figure Which atom in water points toward Na^+ in the ion–dipole interaction? Why?



▲ **Figure 13.2** Intermolecular interactions involved in solutions.



▲ **Figure 13.3** **Dissolution of the ionic solid NaCl in water.**

(**Figure 13.3**), the water molecules orient themselves on the surface of the NaCl crystals with the positive end of the water dipole oriented toward Cl^- ions and the negative end oriented toward Na^+ ions. These ion–dipole attractions are strong enough to pull the surface ions away from the solid, thus overcoming the solute–solute interactions. For the solid to dissolve, some solvent–solvent interactions must also be overcome to create room for the ions to "fit" among all the water molecules.

Once separated from the solid, the Na^+ and Cl^- ions are surrounded by water molecules. Interactions such as this between solute and solvent molecules are known as **solvation**. When the solvent is water, the interactions are referred to as **hydration**.

Energetics of Solution Formation

Solution processes are typically accompanied by changes in enthalpy. For example, when NaCl dissolves in water, the process is slightly endothermic, $\Delta H_{soln} = 3.9$ kJ/mol. We can use Hess's law to analyze how the solute–solute, solvent–solvent, and solute–solvent interactions influence the enthalpy of solution.

We can imagine the solution process as having three components, each with an associated enthalpy change: A cluster of n solute particles must separate from one another (ΔH_{solute}), a cluster of m solvent particles separate from one another ($\Delta H_{solvent}$), and these solute and solvent particles mix (ΔH_{mix}).

1. $(\text{solute})_n \rightleftharpoons n\ \text{solute}$ $\quad \Delta H_{solute}$

2. $(\text{solvent})_m \rightleftharpoons m\ \text{solvent}$ $\quad \Delta H_{solvent}$

3. $n\ \text{solute} + m\ \text{solvent} \rightleftharpoons \text{solution}$ $\quad \Delta H_{mix}$

4. $(\text{solute})_n + (\text{solvent})_m \rightleftharpoons \text{solution}$ $\quad \Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$

As seen earlier, the overall enthalpy change, ΔH_{soln}, is the sum of the three steps:

$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix} \qquad [13.1]$$

Separation of the solute particles from one another always requires an input of energy to overcome their attractive interactions. The process is therefore endothermic ($\Delta H_{solute} > 0$). Likewise, separation of solvent molecules to accommodate the solute always requires energy ($\Delta H_{solvent} > 0$). The third component, which arises from the

attractive interactions between solute particles and solvent particles, is always exothermic ($\Delta H_{mix} < 0$).

The three enthalpy terms in Equation 13.1 can be added together to give either a negative or a positive sum, depending on the actual numbers for the system being considered (**Figure 13.4**). Thus, the formation of a solution can be either exothermic or endothermic. For example, when magnesium sulfate ($MgSO_4$) is added to water, the solution process is exothermic: $\Delta H_{soln} = -91.2$ kJ/mol. In contrast, the dissolution of ammonium nitrate (NH_4NO_3) is endothermic: $\Delta H_{soln} = 26.4$ kJ/mol. These particular salts are the main components in the instant heat packs and ice packs used to treat athletic injuries.

The enthalpy change for a process can provide insight into the extent to which the process occurs. Exothermic processes tend to proceed spontaneously. On the other hand, if ΔH_{soln} is too endothermic, the solute might not dissolve to any significant extent in the chosen solvent. Thus, for solutions to form, the solvent–solute interaction must be strong enough to make ΔH_{mix} comparable in magnitude to $\Delta H_{solute} + \Delta H_{solvent}$. This fact further explains why ionic solutes do not dissolve in nonpolar solvents. The nonpolar solvent molecules experience only weak attractive interactions with the ions, and these interactions do not compensate for the energies required to separate the ions from one another.

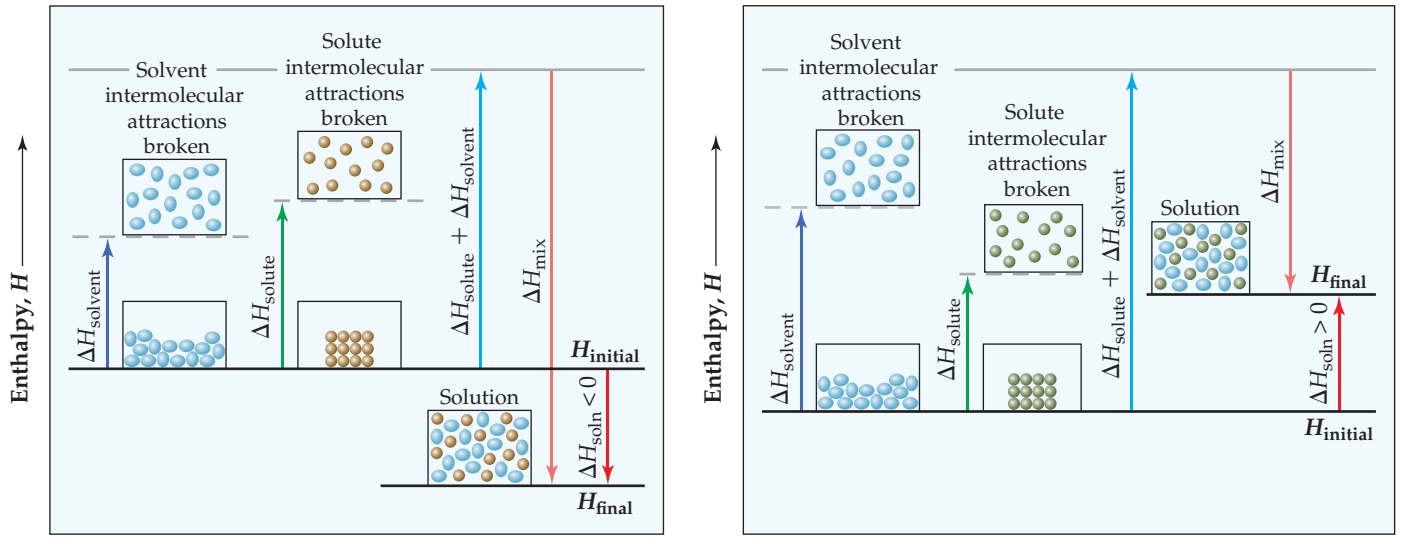
By similar reasoning, a polar liquid solute, such as water, does not dissolve in a nonpolar liquid solvent, such as octane (C_8H_{18}). The water molecules experience strong hydrogen-bonding interactions with one another—attractive forces that must be overcome if the water molecules are to be dispersed throughout the octane solvent. The energy required to separate the H_2O molecules from one another is not recovered in the form of attractive interactions between the H_2O and C_8H_{18} molecules.

Solution Formation and Chemical Reactions

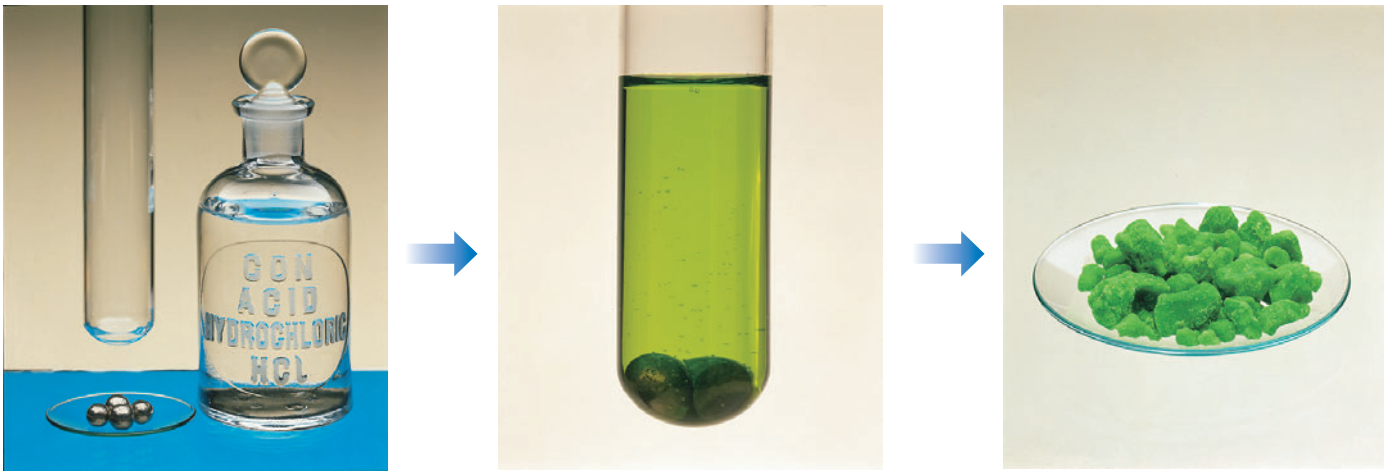
In discussing solutions, we must be careful to distinguish the physical process of solution formation from chemical reactions that lead to a solution. For example, nickel metal dissolves on contact with an aqueous hydrochloric acid solution because the following reaction occurs:

$$Ni(s) + 2\,HCl(aq) \longrightarrow NiCl_2(aq) + H_2(g) \qquad [13.2]$$

Go Figure How does the magnitude of ΔH_{mix} compare with the magnitude of $\Delta H_{solvent} + \Delta H_{solute}$ for exothermic solution processes?



▲ **Figure 13.4** Enthalpy changes accompanying the solution process.



Nickel metal and hydrochloric acid

Nickel reacts with hydrochloric acid, forming $NiCl_2(aq)$ and $H_2(g)$. The solution is of $NiCl_2$, not Ni metal

$NiCl_2{\cdot}6\,H_2O(s)$ remains when solvent evaporated

▲ **Figure 13.5** **The reaction between nickel metal and hydrochloric acid is *not* a simple dissolution.** The product is $NiCl_2 \cdot 6\,H_2O(s)$, nickel(II) chloride hexahydrate, which has exactly 6 waters of hydration in the crystal lattice for every nickel ion.

In this instance, one of the resulting solutes is not Ni metal but rather its salt $NiCl_2$. If the solution is evaporated to dryness, $NiCl_2 \cdot 6\,H_2O(s)$ is recovered (**Figure 13.5**). Compounds such as $NiCl_2 \cdot 6\,H_2O(s)$ that have a defined number of water molecules in the crystal lattice are known as *hydrates*. When NaCl(*s*) is dissolved in water, on the other hand, no chemical reaction occurs. If the solution is evaporated to dryness, NaCl is recovered. Our focus throughout this chapter is on solutions from which the solute can be recovered unchanged from the solution.

Self-Assessment Exercise

13.1 What do you predict to be the enthalpy change when samples of HCl(*g*) and $CO_2(g)$ are mixed?

(a) $\Delta H < 0$
(b) $\Delta H > 0$
(c) $\Delta H \simeq 0$

Exercises

13.2 Indicate whether each statement is true or false: (**a**) NaCl dissolves in water but not in benzene (C_6H_6) because benzene is denser than water. (**b**) NaCl dissolves in water but not in benzene because water has a large dipole moment and benzene has zero dipole moment. (**c**) NaCl dissolves in water but not in benzene because the water–ion interactions are stronger than benzene–ion interactions.

13.3 Indicate the principal type of solute–solvent interaction in each of the following solutions and rank the solutions from weakest to strongest solute–solvent interaction: (**a**) KCl in water, (**b**) CH_2Cl_2 in benzene (C_6H_6), (**c**) methanol (CH_3OH) in water.

13.4 An ionic compound has a very negative ΔH_{soln} in water. (**a**) Would you expect it to be very soluble or nearly insoluble in water? (**b**) Which term would you expect to be the largest negative number: $\Delta H_{solvent}$, ΔH_{solute}, or ΔH_{mix}?

13.5 For the dissolution of NaCl in water, $\Delta H_{soln} = +3$ kJ/mol. Which term would you expect to be the largest negative number: ΔH_{solute}, $\Delta H_{solvent}$, or ΔH_{mix}?

13.6 Two nonpolar organic liquids, benzene (C_6H_6) and toluene (C_7H_8), are mixed. (**a**) Do you expect ΔH_{soln} to be a large positive number, a large negative number, or close to zero? Explain. (**b**) Benzene and toluene are miscible with each other in all proportions. In making a solution of them, is the entropy of the system increased, decreased, or close to zero, compared to the separate pure liquids?

Answers to Self-Assessment Exercises

13.1 (c)

13.2 | Saturated Solutions and Solubility



Sodium chloride, salt, is an essential part of our diet. One commercial way to obtain salt is to harvest it from the ocean. Sea water is allowed to evaporate in shallow ponds and as it does the solution becomes more and more concentrated in the dissolved salts. A point comes when the solution is saturated and further evaporation results in the precipitation of salt, which may be harvested.

By the end of this section, you should be able to

- Describe the role of equilibrium in the solution process and its relationship to the solubility of a solute.

As a solid solute begins to dissolve in a solvent, the concentration of solute particles in solution increases, increasing the chances that some solute particles will collide with the surface of the solid and reattach. This process, which is the opposite of the solution process, is called **crystallization**. Thus, two opposing processes occur in a solution in contact with undissolved solute. This situation is represented in this chemical equation:

$$\text{Solute} + \text{solvent} \underset{\text{crystallize}}{\overset{\text{dissolve}}{\rightleftharpoons}} \text{solution} \qquad [13.3]$$

When the rates of these opposing processes become equal, a *dynamic equilibrium* is established, and there is no further increase in the amount of solute in solution.

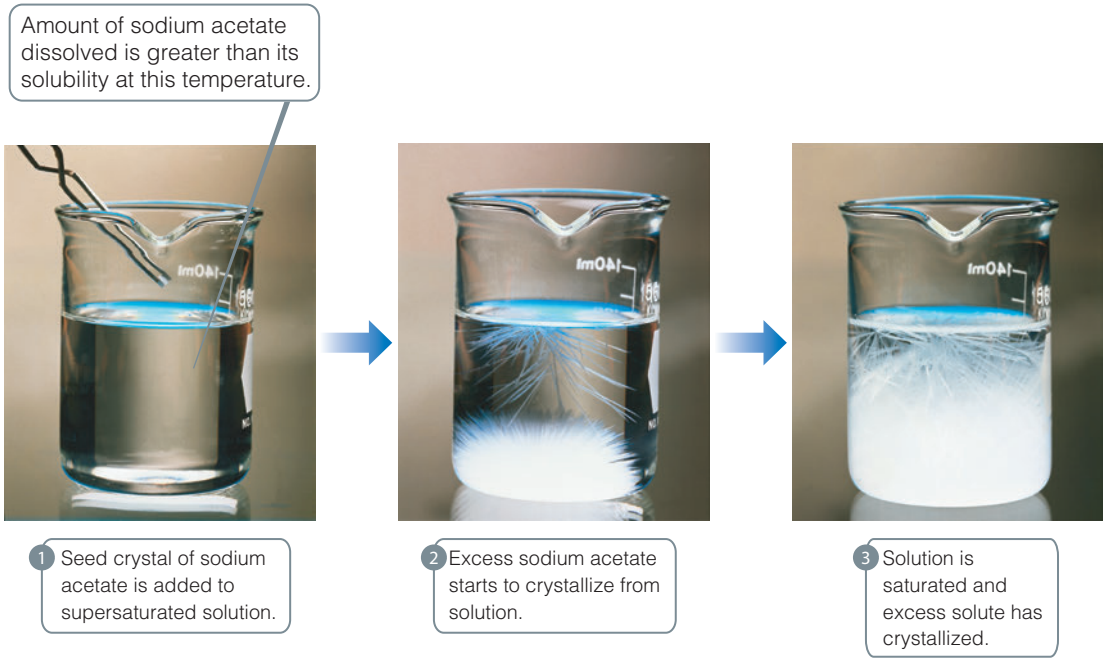
A solution that is in equilibrium with undissolved solute is **saturated**. Additional solute will not dissolve if added to a saturated solution. The amount of solute needed to form a saturated solution in a given quantity of solvent is known as the **solubility** of that solute. That is,

> *the solubility of a particular solute in a particular solvent is the maximum amount of the solute that can dissolve in a given amount of the solvent at a specified temperature, assuming that excess solute is present.*

For example, the solubility of NaCl in water at 0 °C is 35.7 g per 100 mL of water. This is the maximum amount of NaCl that can be dissolved in water to give a stable equilibrium solution at that temperature.

If we dissolve less solute than the amount needed to form a saturated solution, the solution is **unsaturated**. Thus, a solution containing 10.0 g of NaCl per 100 mL of water at 0 °C is unsaturated because it has the capacity to dissolve more solute.

Go Figure How many grams of sodium acetate are in solution in the third beaker?



▲ **Figure 13.6 Precipitation from a supersaturated sodium acetate solution.** The solution on the left was formed by dissolving about 170 g of the salt in 100 mL of water at 100 °C and then slowly cooling it to 20 °C. Because the solubility of sodium acetate in water at 20 °C is 46 g per 100 mL of water, the solution is supersaturated. Addition of a sodium acetate crystal causes the excess solute to crystallize from solution.

Under suitable conditions, it is possible to form solutions that contain a greater amount of solute than needed to form a saturated solution. Such solutions are **supersaturated**. For example, when a saturated solution of sodium acetate is made at a high temperature and then slowly cooled, all of the solute may remain dissolved even though its solubility decreases as the temperature decreases. Because the solute in a supersaturated solution is present in a concentration higher than the equilibrium concentration, supersaturated solutions are unstable with respect to crystallization of the solute. For crystallization to occur, however, the solute particles must arrange themselves properly to form crystals. The addition of a small crystal of the solute (a seed crystal) provides a template for crystallization of the excess solute, leading to a saturated solution in contact with excess solid (Figure 13.6).

Self-Assessment Exercise

13.7 If a magnesium chloride is added to a saturated solution of magnesium chloride, will it dissolve?

(a) No
(b) Yes

Exercises

13.8 The solubility of copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) in water at 30 °C is 50 g per 100 mL of water. (**a**) Is a 1.30 *M* solution of $CuSO_4 \cdot 12\ H_2O$ in water at 30 °C saturated, supersaturated, or unsaturated? (**b**) Given a solution of $CuSO_4 \cdot 12\ H_2O$ of unknown concentration, what experiment could you perform to determine whether the new solution is saturated, supersaturated, or unsaturated?

Answers to Self-Assessment Exercises

13.7 (a)

13.3 | Factors Affecting Solubility



Have you noticed how ice cubes you make at home usually have bubbles in their center? This results from the solubility of air in water decreasing as the temperature drops. The water in your ice tray usually freezes from the outer edges. This concentrates the dissolved gases towards the center, the water becomes saturated, and further freezing results in the air bubbling out of the water and becoming trapped by the surrounding ice. So, how do you make clear ice cubes? If you boil the water before freezing it, the heat drives out most of the dissolved gases and results in clear ice.

By the end of this section, you should be able to

- Understand what factors affect solubility

The extent to which one substance dissolves in another depends on the nature of both substances. It also depends on temperature and, at least for gases, on pressure.

TABLE 13.1 Solubilities of Gases in Water at 20 °C, at 101.3 kPa Gas Pressure

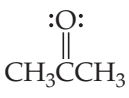
Gas	Molar Mass (g/mol)	Solubility (*M*)
N_2	28.0	0.69×10^{-3}
O_2	32.0	1.38×10^{-3}
Ar	39.9	1.50×10^{-3}
Kr	83.8	2.79×10^{-3}

Solute–Solvent Interactions

The natural tendency of substances to mix and the various interactions among solute and solvent particles are all involved in determining solubilities. Nevertheless, insight into variations in solubility can often be gained by focusing on the interaction between the solute and solvent. The data in **Table 13.1** show that the solubilities of various gases in water increase with increasing molar mass. The attractive forces between the gas molecules and solvent molecules are mainly dispersion forces, which increase with increasing size and molar mass. Thus, the data indicate that the solubilities of gases in water increase as the attraction between solute (gas) and solvent (water) increases. In general, when other factors are comparable, *the stronger the attractions between solute and solvent molecules, the greater the solubility of the solute in that solvent.*

Because of favorable dipole–dipole attractions between polar solvent molecules and polar solute molecules, *polar liquids tend to dissolve in polar solvents*. Water is both polar and able to form hydrogen bonds. Thus, polar molecules, especially those that can form hydrogen bonds with water molecules, tend to be soluble in water. For example, acetone, a polar molecule with the structural formula shown here, mixes in all proportions with water. Acetone has a strongly polar C═O bond and pairs of nonbonding electrons on the O atom that can form hydrogen bonds with water.





Acetone



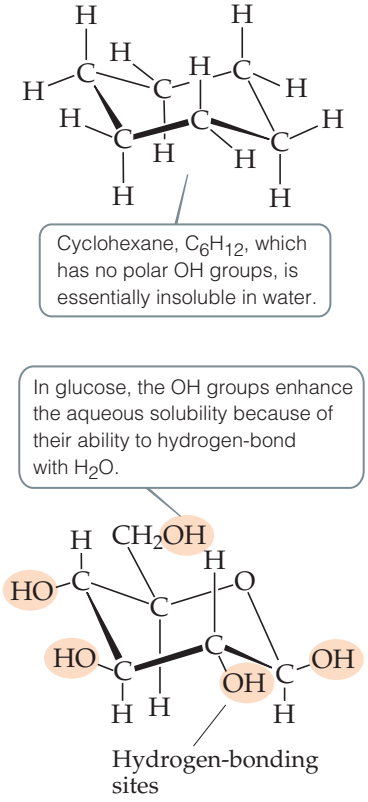
▲ **Figure 13.7 Hexane, a hydrocarbon, is immiscible with water.** Hexane is the top layer because it is less dense than water.

Liquids that mix in all proportions, such as acetone and water, are **miscible**, whereas those that do not dissolve in one another are **immiscible**. Petrol, which is a mixture of hydrocarbons, is immiscible with water. Hydrocarbons are nonpolar substances because of several factors: The C—C bonds are nonpolar, the C—H bonds are nearly nonpolar, and the molecules are symmetrical enough to cancel much of the weak C—H bond dipoles. The attraction between the polar water molecules and the nonpolar hydrocarbon molecules is not sufficiently strong to allow the formation of a solution. *Nonpolar liquids tend to be insoluble in polar liquids*, as **Figure 13.7** shows for hexane (C_6H_{14}) and water.

Many organic compounds have polar groups attached to a nonpolar framework of carbon and hydrogen atoms. For example, the series of organic compounds in **Table 13.2** all contain the polar OH group. Organic compounds with this molecular feature are called *alcohols*. The O—H bond is able to form hydrogen bonds. For example, ethanol (CH_3CH_2OH) molecules can form hydrogen bonds with water molecules as well as with each other (**Figure 13.8**). As a result, the solute–solute, solvent–solvent, and solute–solvent forces are not greatly different in a mixture of CH_3CH_2OH and H_2O. No major change occurs in the environments of the molecules as they are mixed. Therefore, the increased entropy when the components mix plays a significant role in solution formation, and ethanol is completely miscible with water.

Notice in Table 13.2 that the number of carbon atoms in an alcohol affects its solubility in water. As this number increases, the polar OH group becomes an even smaller part of the molecule, and the molecule behaves more like a hydrocarbon. The solubility of the alcohol in water decreases correspondingly. On the other hand, the solubility of alcohols in a nonpolar solvent like hexane (C_6H_{14}) increases as the nonpolar hydrocarbon chain lengthens.

One way to enhance the solubility of a substance in water is to increase the number of polar groups the substance contains. For example, increasing the number of OH groups in a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility. Glucose ($C_6H_{12}O_6$, **Figure 13.9**) has five OH groups on a six-carbon framework, which makes the molecule very soluble in

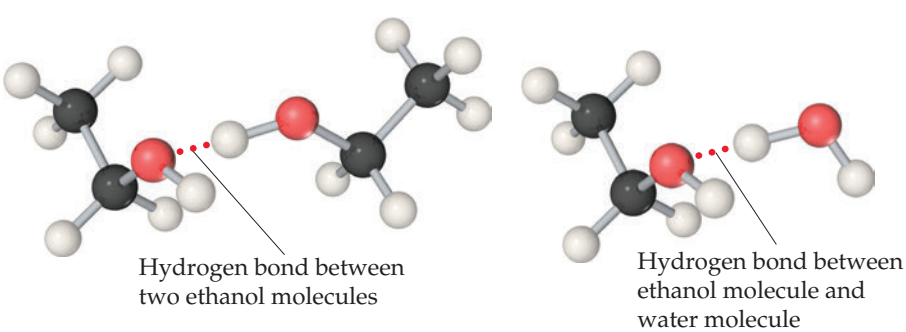


▲ **Figure 13.9 The correlation of molecular structure with solubility.**

TABLE 13.2 Solubilities of Some Alcohols in Water and in Hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propanol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butanol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentanol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexanol)	0.0058	∞

*Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol (∞) indicates that the alcohol is completely miscible with the solvent.



▲ **Figure 13.8 Hydrogen bonding involving OH groups.**

water: 830 g dissolves in 1.00 L of water at 17.5 °C. In contrast, cyclohexane (C_6H_{12}), which has a similar structure to glucose but with all of the OH groups replaced by H, is essentially insoluble in water (only 55 mg of cyclohexane can dissolve in 1.00 L of water at 25 °C).

Over years of study, examination of different solvent–solute combinations has led to an important generalization:

Substances with similar intermolecular attractive forces tend to be soluble in one another.

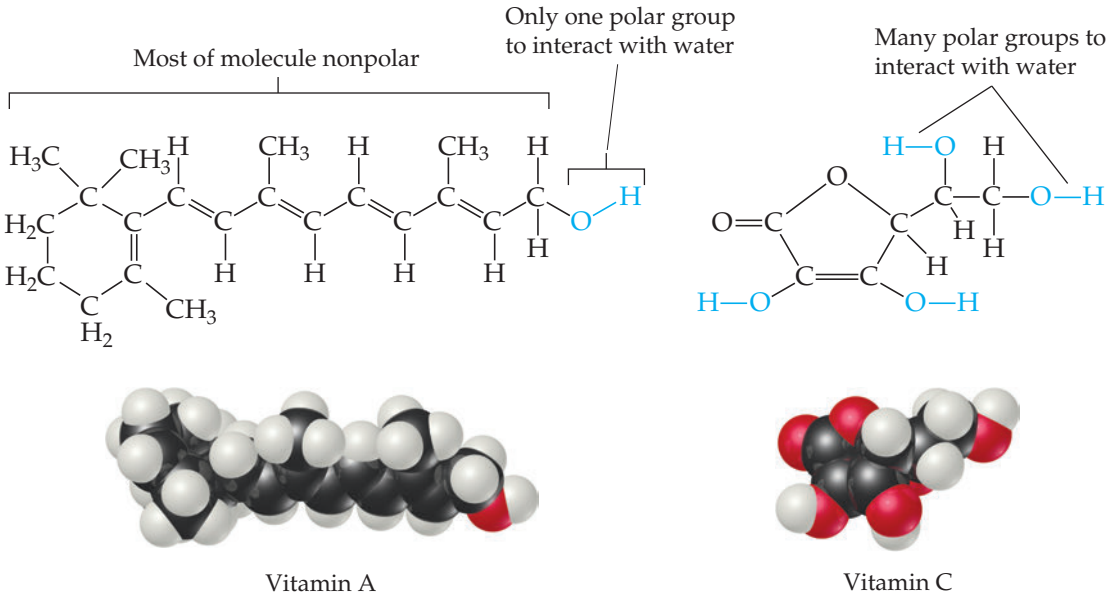
This generalization is often simply stated as "*like dissolves like*." Nonpolar substances are more likely to be soluble in nonpolar solvents; ionic and polar solutes are more likely to be soluble in polar solvents. Network solids such as diamond and quartz are not soluble in either polar or nonpolar solvents because of the strong bonding within the solid.

CHEMISTRY AND LIFE Fat-Soluble and Water-Soluble Vitamins

Vitamins have unique chemical structures that affect their solubilities in different parts of the human body. Vitamin C and the B vitamins are soluble in water, for example, whereas vitamins A, D, E, and K are soluble in nonpolar solvents and in fatty tissue (which is nonpolar). Because of their water solubility, vitamins B and C are not stored to any appreciable extent in the body, and so foods containing these vitamins should be included in the daily diet. In contrast, the fat-soluble vitamins are stored in sufficient quantities to keep vitamin-deficiency diseases from appearing even after a person has subsisted for a long period on a vitamin-deficient diet.

That some vitamins are soluble in water and others are not can be explained in terms of their structures. Notice in **Figure 13.10** that vitamin A (retinol) is an alcohol with a very long carbon chain. Because the OH group is such a small part of the molecule, the molecule resembles the long-chain alcohols listed in Table 13.2. This vitamin is nearly nonpolar. In contrast, the vitamin C molecule is smaller and has several OH groups that can form hydrogen bonds with water, somewhat like glucose.

Related Exercises: 13.22, 13.46

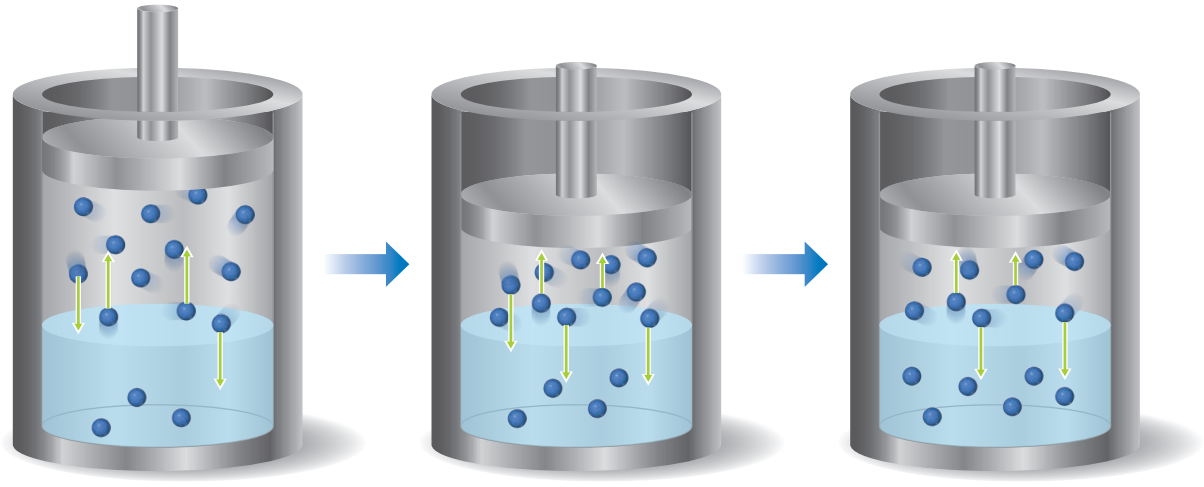


▲ **Figure 13.10** **The molecular structures of vitamins A and C.**

Pressure Effects

The solubilities of solids and liquids are not appreciably affected by pressure, whereas *the solubility of a gas in any solvent is increased as the partial pressure of the gas above the solvent increases*. We can understand the effect of pressure on gas solubility by considering **Figure 13.11**, which shows carbon dioxide gas distributed between the gas and solution phases. When equilibrium is established, the rate at which gas molecules enter the solution equals the rate at which solute molecules escape from the solution to enter the gas phase. The equal number of up and down arrows in the left container in Figure 13.11 represent these opposing processes.

Go Figure If the partial pressure of a gas over a solution is doubled, how has the concentration of gas in the solution changed after equilibrium is restored?



▲ **Figure 13.11** **Effect of pressure on gas solubility.**

Sample Exercise 13.1

Predicting Solubility Patterns

Predict whether each of the following substances is more likely to dissolve in the nonpolar solvent tetrachloromethane (CCl_4) or in water: C_7H_{16}, Na_2SO_4, HCl, and I_2.

SOLUTION

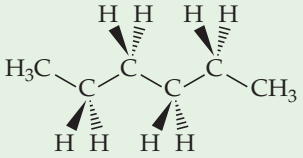
Analyze We are given two solvents, one that is nonpolar (CCl_4) and the other that is polar (H_2O), and asked to determine which will be the better solvent for each solute listed.

Plan By examining the formulas of the solutes, we can predict whether they are ionic or molecular. For those that are molecular, we can predict whether they are polar or nonpolar. We can then apply the idea that the nonpolar solvent will be better for the nonpolar solutes, whereas the polar solvent will be better for the ionic and polar solutes.

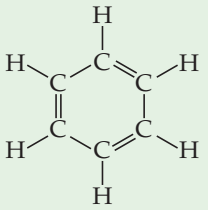
Solve C_7H_{16} is a hydrocarbon, so it is molecular and nonpolar. Na_2SO_4, a compound containing a metal and nonmetals, is ionic. HCl, a diatomic molecule containing two nonmetals that differ in electronegativity, is polar. I_2, a diatomic molecule with atoms of equal electronegativity, is nonpolar. We would therefore predict that C_7H_{16} and I_2 (the nonpolar solutes) would be more soluble in the nonpolar CCl_4 than in polar H_2O, whereas water would be the better solvent for Na_2SO_4 and HCl (the ionic and polar covalent solutes).

Practice Exercise

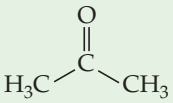
Which of the following solvents will best dissolve wax, which is a complex mixture of compounds that mostly are $CH_3-CH_2-CH_2-CH_2-CH_2-$?



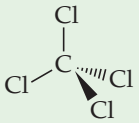
(**a**) Hexane



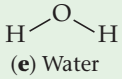
(**b**) Benzene



(**c**) Acetone



(**d**) Carbon tetrachloride



(**e**) Water

Now suppose we exert greater pressure on the piston and compress the gas above the solution, as shown in the middle container in Figure 13.11. If we reduce the gas volume to half its original value, the pressure of the gas increases to about twice its original value. As a result of this pressure increase, the rate at which gas molecules strike the liquid surface and enter the solution phase increases. Thus, the solubility of the gas in the solution increases until equilibrium is again established; that is, solubility increases until the rate at which gas molecules enter the solution equals the rate at which they escape from the solution. Thus, *the solubility of a gas in a liquid solvent increases in direct proportion to the partial pressure of the gas above the solution* (**Figure 13.12**).

The relationship between pressure and gas solubility is expressed by **Henry's law**:

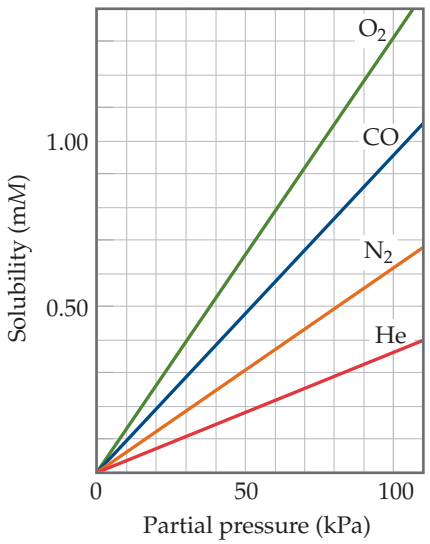
$$S_g = kP_g \qquad [13.4]$$

Here, S_g is the solubility of the gas in the solvent (usually expressed as molarity), P_g is the partial pressure of the gas over the solution, and k is a proportionality constant known as the *Henry's law constant*. The value of this constant depends on the solute, solvent, and temperature. As an example, the solubility of N_2 gas in water at 25 °C and 79.03 kPa pressure is $4.75 \times 10^{-4}\,M$. The Henry's law constant for N_2 in 25 °C water is thus $(4.75 \times 10^{-4}\,\text{mol/L})/79.03\,\text{kPa} = 6.1 \times 10^{-6}\,\text{mol/m}^3\,\text{Pa}$. If the partial pressure of N_2 is doubled, Henry's law predicts that the solubility in water at 25 °C also doubles to $9.50 \times 10^{-4}\,M$.

Bottlers use the effect of pressure on solubility in producing carbonated beverages, which are bottled under a carbon dioxide pressure greater than 101.3 kPa. When the bottles are opened to the air, the partial pressure of CO_2 above the solution decreases. Hence, the solubility of CO_2 decreases, and $CO_2(g)$ escapes from the solution as bubbles (**Figure 13.13**).

Go Figure

Does the gas with the largest molar mass have the highest or lowest solubility in water?



▲ **Figure 13.12 The solubility of a gas in water is directly proportional to the partial pressure of the gas.** The solubilities are in millimoles of gas per liter of solution.



▲ **Figure 13.13 Gas solubility decreases as pressure decreases.** CO_2 bubbles out of solution when a carbonated beverage is opened because the CO_2 partial pressure above the solution is reduced.

Sample Exercise 13.2

A Henry's Law Calculation

Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure of CO_2 of 0.41 MPa over the liquid at 25 °C. The Henry's law constant for CO_2 in water at this temperature is 3.4×10^{-4} mol/m^3 Pa.

SOLUTION

Analyze We are given the partial pressure of CO_2, P_{CO_2}, and the Henry's law constant, k, and asked to calculate the concentration of CO_2 in the solution.

Plan With the information given, we can use Henry's law, Equation 13.4, to calculate the solubility, S_{CO_2}.

Solve $S_{CO_2} = kP_{CO_2} = (3.4 \times 10^{-4}\ \text{mol/m}^3\ \text{Pa})(0.41\ \text{MPa})$

$= 0.14\ \text{mol/L} = 0.14\ M$

Check The units are correct for solubility, and the answer has two significant figures consistent with both the partial pressure of CO_2 and the value of the Henry's law constant.

Practice Exercise

You double the partial pressure of a gas over a liquid at constant temperature. Which of these statements is then true?

(**a**) The Henry's law constant is doubled.
(**b**) The Henry's law constant is decreased by half.
(**c**) There are half as many gas molecules in the liquid.
(**d**) There are twice as many gas molecules in the liquid.
(**e**) There is no change in the number of gas molecules in the liquid.

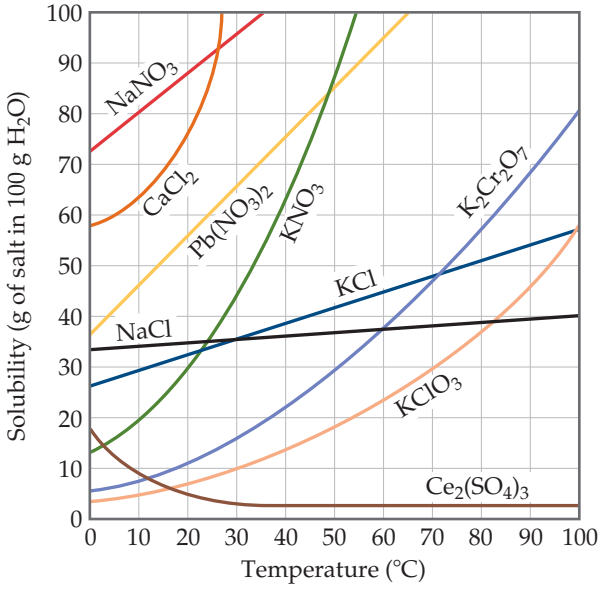
Temperature Effects

The solubility of most solid solutes in water increases as the solution temperature increases, as Figure 13.14 shows. There are exceptions to this rule, however, as seen for $Ce_2(SO_4)_3$, whose solubility curve slopes downward with increasing temperature.

In contrast to solid solutes, *the solubility of gases in water decreases with increasing temperature* (Figure 13.15). If a glass of cold tap water is warmed, you can see bubbles on the inside of the glass because some of the dissolved air comes out of solution.

Go Figure

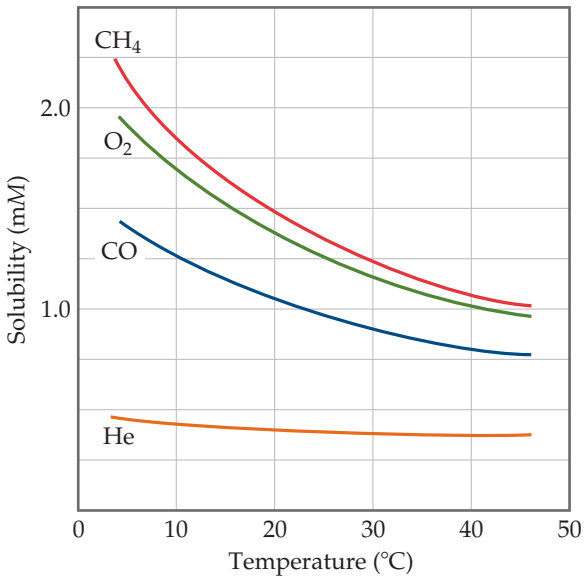
How does the solubility of KCl at 80 °C compare with that of NaCl at the same temperature?



▲ **Figure 13.14 Solubilities of some ionic compounds in water as a function of temperature.**

Go Figure

Between which two gases would you expect N_2 to fit on this graph?



▲ **Figure 13.15 Solubilities of four gases in water as a function of temperature.** The solubilities are in millimoles per liter of solution, for a constant total pressure of 1 atm in the gas phase.

Similarly, as carbonated beverages are allowed to warm, the solubility of CO_2 decreases, and $CO_2(g)$ escapes from the solution.

If you think about it, you can rationalize why the solubilities of gases and ionic solids in water respond differently to temperature. As you heat an aqueous solution that contains a gas, you give enough energy to the gas particles for them to escape from the solution and go into the gas phase. Thus, increasing temperature reduces the solubility of the gas. On the other hand, if you heat up a mixture of water and an ionic solid, you give energy to the solid so it can break into its constituent ions that are then hydrated by water. Thus, increasing temperature increases the solubility of the ionic solid.

CHEMISTRY AND LIFE Blood Gases and Deep-Sea Diving

Because gas solubility increases with increasing pressure, divers who breathe compressed air (Figure 13.16) must be concerned about the solubility of gases in their blood. Although the gases are not very soluble at sea level, their solubilities can be appreciable at deep levels where their partial pressures are greater. Thus, divers must ascend slowly to prevent dissolved gases from being released rapidly from solution and forming bubbles in the blood and other fluids in the body. These bubbles affect nerve impulses and cause decompression sickness, or "the bends," which is a painful and potentially fatal condition. Nitrogen is the main problem because it is the most abundant gas in air and because it can be removed from the body only through the respiratory system. Oxygen, in contrast, is consumed in metabolism.

Deep-sea divers sometimes substitute helium for nitrogen in the air they breathe because helium has a much lower solubility in biological fluids than N_2. For example, divers working at a depth of 30 m experience a pressure of about 405.3 kPa. At this pressure, a mixture of 95% helium and 5% oxygen gives an oxygen partial pressure of about 20.3 kPa, which is the partial pressure of oxygen in normal air at 101.3 kPa. If the oxygen partial pressure becomes too great, the urge to breathe is reduced, CO_2 is not removed from the body, and CO_2 poisoning occurs. At excessive concentrations in the body, carbon dioxide acts as a neurotoxin, interfering with nerve conduction and transmission.



▲ **Figure 13.16 Gas solubility increases as pressure increases.** Divers who use compressed gases must be concerned about the solubility of the gases in their blood.

Related Exercises: 13.25, 13.77, 13.112

Self-Assessment Exercise

13.9 Is there likely to be more gases dissolved in a mountain lake or a pond at sea level?

(a) Mountain lake

(b) Pond at sea level

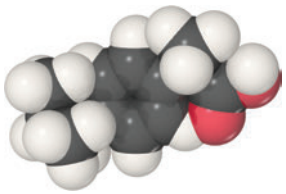
Exercises

13.10 By referring to Figure 13.14, determine the mass of each of the following salts required to form a saturated solution in 250 g of water at 20 °C: (**a**) NaCl, (**b**) $CaCl_2$, (**c**) KNO_3.

13.11 Oil and water are immiscible. Which is the most likely reason? (**a**) Oil molecules are denser than water. (**b**) Oil molecules are composed mostly of carbon and hydrogen. (**c**) Oil molecules have higher molar masses than water. (**d**) Oil molecules have higher vapor pressures than water. (**e**) Oil molecules have higher boiling points than water.

13.12 Common laboratory solvents include acetone (CH_3COCH_3), methanol (CH_3OH), toluene ($C_6H_5CH_3$), and water. Which of these is the best solvent for nonpolar solutes?

13.13 Ibuprofen, widely used as a pain reliever, has a limited solubility in water, less than 1 mg/mL. Which part of the molecule's structure (gray, white, red) contributes to its water solubility? Which part of the molecule (gray, white, red) contributes to its water insolubility?



Ibuprofen

13.14 Which of the following in each pair is likely to be more soluble in water: (**a**) cyclohexane (C_6H_{12}) or glucose ($C_6H_{12}O_6$), (**b**) propanoic acid (CH_3CH_2COOH) or sodium propanoate (CH_3CH_2COONa), (**c**) HCl or ethyl chloride (CH_3CH_2Cl)? Explain in each case.

13.15 Indicate whether each statement is true or false:

(**a**) If you compare the solubility of a gas in water at two different temperatures, you find the gas is more soluble at the lower temperature.

(**b**) The solubility of most ionic solids in water decreases as the temperature of the solution increases.

(**c**) The solubility of most gases in water decreases as the temperature increases because water is breaking its hydrogen bonding to the gas molecules as the temperature is raised.

(**d**) Some ionic solids become less soluble in water as the temperature is raised.

13.16 The Henry's law constant for hydrogen gas (H_2) in water at 25 °C is $7.7 \times 10^{-6}\ M$/kPa and the constant for argon (Ar) at 25 °C is $1.4 \times 10^{-5}\ M$/kPa. If the two gases are each present at 253 kPa pressure, calculate the solubility of each gas.

13.9 (b)

Answers to Self-Assessment Exercises

13.4 Expressing Solution Concentration



The concentration of a solution can be expressed either qualitatively or quantitatively. The terms *dilute* and *concentrated* are used to describe a solution qualitatively. A solution with a relatively small concentration of solute is said to be dilute; one with a large concentration is said to be concentrated. Chemists use various ways to express concentration quantitatively, and we examine several of these next.

By the end of this section, you should be able to convert between different concentration units.

Mass Percentage, ppm, and ppb

One of the simplest quantitative expressions of concentration is the **mass percentage** of a component in a solution, given by

$$\text{Mass \% of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 100 \qquad [13.5]$$

Because *percent* means "per hundred," a solution of hydrochloric acid that is 36% HCl by mass contains 36 g of HCl for each 100 g of solution.

We often express the concentration of very dilute solutions in **parts per million (ppm)** or **parts per billion (ppb)**. These quantities are similar to mass percentage but use 10^6 (a million) or 10^9 (a billion), respectively, in place of 100, as a multiplier for the ratio of the mass of solute to the mass of solution. Thus, parts per million is defined as

$$\text{ppm of component} = \frac{\text{mass of component in solution}}{\text{total mass of solution}} \times 10^6 \qquad [13.6]$$

A solution whose solute concentration is 1 ppm contains 1 g of solute for each million (10^6) grams of solution or, equivalently, 1 mg of solute per kilogram of solution. Because the density of water is 1 g/mL, 1 kg of a dilute aqueous solution has a volume very close to 1 L. Thus, 1 ppm also corresponds to 1 mg of solute per liter of aqueous solution.

The acceptable maximum concentrations of toxic or carcinogenic substances in the environment are often expressed in ppm or ppb. For example, the World Health Organisation recommended maximum allowable concentration of arsenic in drinking water is 0.010 ppm; that is, 0.010 mg of arsenic per liter of water. This concentration corresponds to 10 ppb.

Mole Fraction, Molarity, and Molality

Concentration expressions are often based on the number of moles of one or more components of the solution. Recall from Section 10.5 that the *mole fraction* of a component of a solution is given by

$$\text{Mole fraction of component} = \frac{\text{moles of component}}{\text{total moles of all components}} \qquad [13.7]$$

Sample Exercise 13.3

Calculation of Mass-Related Concentrations

(**a**) A solution is made by dissolving 13.5 g of glucose ($C_6H_{12}O_6$) in 0.100 kg of water. What is the mass percentage of solute in this solution?

(**b**) A 2.5 g sample of groundwater was found to contain 5.4 μg of Zn^{2+}. What is the concentration of Zn^{2+} in parts per million?

SOLUTION

(**a**) **Analyze** We are given the number of grams of solute (13.5 g) and the number of grams of solvent (0.100 kg = 100 g). From this, we must calculate the mass percentage of solute.

Plan We can calculate the mass percentage by using Equation 13.5. The mass of the solution is the sum of the mass of solute (glucose) and the mass of solvent (water).

Solve $$\text{Mass \% of glucose} = \frac{\text{mass glucose}}{\text{mass solution}} \times 100$$
$$= \frac{13.5\ \cancel{g}}{(13.5 + 100)\ \cancel{g}} \times 100 = 11.9\%$$

Comment The mass percentage of water in this solution is (100 − 11.9)% = 88.1%.

(**b**) **Analyze** In this case we are given the number of micrograms of solute. Because 1 μg is 1×10^{-6} g, 5.4 μg = 5.4×10^{-6} g.
Plan We calculate the parts per million using Equation 13.6.

Solve $$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$$
$$= \frac{5.4 \times 10^{-6}\ \cancel{g}}{2.5\ \cancel{g}} \times 10^6 = 2.2\ \text{ppm}$$

Practice Exercise

Calculate the mass percentage of NaCl in a solution containing 1.50 g of NaCl in 50.0 g of water.
(**a**) 0.0291% (**b**) 0.0300% (**c**) 0.0513% (**d**) 2.91% (**e**) 3.00%

The symbol X is commonly used for mole fraction, with a subscript to indicate the component of interest. For example, the mole fraction of HCl in a hydrochloric acid solution is represented as X_{HCl}. Thus, if a solution contains 1.00 mol of HCl (36.5 g) and 8.00 mol of water (144 g), the mole fraction of HCl is $X_{HCl} = (1.00\ \text{mol})/(1.00\ \text{mol} + 8.00\ \text{mol}) = 0.111$. Mole fractions have no units because the units in the numerator and the denominator cancel. The sum of the mole fractions of all components of a solution must equal 1. Thus, in the aqueous HCl solution, $X_{H_2O} = 1.000 - 0.111 = 0.889$. Mole fractions are very useful when dealing with gases, as we saw in Section 10.5, but have limited use when dealing with liquid solutions.

Recall from Section 4.5 that the *molarity* (M) of a solute in a solution is defined as

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \qquad [13.8]$$

For example, if you dissolve 0.500 mol of Na_2CO_3 in enough water to form 0.250 L of solution, the molarity of Na_2CO_3 in the solution is $(0.500\ \text{mol})/(0.250\ \text{L}) = 2.00\ M$. Molarity is especially useful for relating the volume of a solution to the quantity of solute contained in that volume, as we saw in our discussions of titrations.

The **molality** of a solution, denoted *m*, is a concentration unit that is also based on moles of solute. Molality equals the number of moles of solute per kilogram of solvent:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilograms of solvent}} \qquad [13.9]$$

Thus, if you form a solution by mixing 0.200 mol of NaOH (8.00 g) and 0.500 kg of water (500 g), the concentration of the solution is $(0.200\ \text{mol})/(0.500\ \text{kg}) = 0.400\ m$ (that is, 0.400 molal) in NaOH.

The definitions of molarity and molality are similar enough that they can be easily confused.

- Molarity depends on the *volume of solution*.
- Molality depends on the *mass of solvent*.

When water is the solvent, the molality and molarity of dilute solutions are numerically about the same because 1 kg of solvent is nearly the same as 1 kg of solution, and 1 kg of the solution has a volume of about 1 L.

The molality of a given solution does not vary with temperature because masses do not vary with temperature. The molarity of the solution does change with temperature, however, because the volume of the solution expands or contracts with temperature. Thus, molality is often the concentration unit of choice when a solution is to be used over a range of temperatures.

Sample Exercise 13.4

Calculation of Molality

A solution is made by dissolving 4.35 g of glucose ($C_6H_{12}O_6$) in 25.0 mL of water at 25 °C. Calculate the molality of glucose in the solution. Water has a density of 1.00 g/mL.

SOLUTION

Analyze We are asked to calculate a solution concentration in units of molality. To do this, we must determine the number of moles of solute (glucose) and the number of kilograms of solvent (water).

Plan We use the molar mass of $C_6H_{12}O_6$ to convert grams of glucose to moles. We use the density of water to convert milliliters of water to kilograms. The molality equals the number of moles of solute (glucose) divided by the number of kilograms of solvent (water).

Solve

Use the molar mass of glucose, 180.2 g/mol, to convert grams to moles:

$$\text{Mol } C_6H_{12}O_6 = (4.35\ \text{g } \cancel{C_6H_{12}O_6})\left(\frac{1\ \text{mol } C_6H_{12}O_6}{180.2\ \text{g } \cancel{C_6H_{12}O_6}}\right) = 0.0241\ \text{mol } C_6H_{12}O_6$$

Because water has a density of 1.00 g/mL, the mass of the solvent is:

$$(25.0\ \cancel{\text{mL}})(1.00\ \text{g}/\cancel{\text{mL}}) = 25.0\ \text{g} = 0.0250\ \text{kg}$$

Finally, use Equation 13.9 to obtain the molality:

$$\text{Molality of } C_6H_{12}O_6 = \frac{0.0241\ \text{mol } C_6H_{12}O_6}{0.0250\ \text{kg } H_2O} = 0.964\ m$$

Practice Exercise

Suppose you take a solution and add more solvent, so that the original mass of solvent is doubled. You take this new solution and add more solute, so that the original mass of the solute is doubled. What happens to the molality of the final solution, compared to the original molality?

(**a**) It is doubled.
(**b**) It is decreased by half.
(**c**) It is unchanged.
(**d**) It will increase or decrease depending on the molar mass of the solute.
(**e**) There is no way to tell without knowing the molar mass of the solute.

Converting Concentration Units

If you follow the dimensional analysis techniques you learned in Chapter 1, you can convert between concentration units, as shown in Sample Exercise 13.5. To convert between molality and molarity, the density of the solution will be needed, as in Sample Exercise 13.6.

Sample Exercise 13.5

Calculation of Mole Fraction and Molality

An aqueous solution of hydrochloric acid contains 36% HCl by mass. (**a**) Calculate the mole fraction of HCl in the solution. (**b**) Calculate the molality of HCl in the solution.

SOLUTION

Analyze We are asked to calculate the concentration of the solute, HCl, in two related concentration units, given only the percentage by mass of the solute in the solution.

Plan In converting concentration units based on the mass or moles of solute and solvent (mass percentage, mole fraction, and molality), it is useful to assume a certain total mass of solution. Let's assume that there is exactly 100 g of solution. Because the solution is 36% HCl, it contains 36 g of HCl and $(100 - 36)$ g $= 64$ g of H_2O. We must convert grams of solute (HCl) to moles to calculate either mole fraction or molality. We must convert grams of solvent (H_2O) to moles to calculate mole fractions and to kilograms to calculate molality.

Solve

(**a**) To calculate the mole fraction of HCl, we convert the masses of HCl and H_2O to moles and then use Equation 13.7:

$$\text{Moles HCl} = (36\ \text{g}\ \cancel{\text{HCl}})\left(\frac{1\ \text{mol HCl}}{36.5\ \text{g}\ \cancel{\text{HCl}}}\right) = 0.99\ \text{mol HCl}$$

$$\text{Moles } H_2O = (64\ \text{g}\ \cancel{H_2O})\left(\frac{1\ \text{mol } H_2O}{18\ \text{g}\ \cancel{H_2O}}\right) = 3.6\ \text{mol } H_2O$$

$$X_{HCl} = \frac{\text{moles HCl}}{\text{moles } H_2O + \text{moles HCl}} = \frac{0.99}{3.6 + 0.99} = \frac{0.99}{4.6} = 0.22$$

(**b**) To calculate the molality of HCl in the solution, we use Equation 13.9. We calculated the number of moles of HCl in part (a), and the mass of solvent is 64 g $= 0.064$ kg:

$$\text{Molality of HCl} = \frac{0.99\ \text{mol HCl}}{0.064\ \text{kg } H_2O} = 15\ m$$

Notice that we can't readily calculate the molarity of the solution because we don't know the volume of the 100 g of solution.

Practice Exercise

The solubility of oxygen gas in water at 40 °C is 1.0 mmol per liter of solution. What is this concentration in units of mole fraction?

(**a**) 1.00×10^{-6} (**b**) 1.80×10^{-5} (**c**) 1.00×10^{-2}
(**d**) 1.80×10^{-2} (**e**) 5.55×10^{-2}

Sample Exercise 13.6

Calculation of Molarity Using the Density of the Solution

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C_7H_8) and 225 g of benzene. Calculate the molarity of the solution.

SOLUTION

Analyze Our goal is to calculate the molarity of a solution, given the masses of solute (5.0 g) and solvent (225 g) and the density of the solution (0.876 g/mL).

Plan The molarity of a solution is the number of moles of solute divided by the number of liters of solution (Equation 13.8). The number of moles of solute (C_7H_8) is calculated from the number of grams of solute and its molar mass. The volume of the solution is obtained from the mass of the solution (mass of solution = mass of solute + mass of solvent = 5.0 g + 225 g = 230 g) and its density.

Solve

The number of moles of solute is:

$$\text{Moles } C_7H_8 = (5.0\ \text{g}\ \cancel{C_7H_8})\left(\frac{1\ \text{mol } C_7H_8}{92\ \text{g}\ \cancel{C_7H_8}}\right) = 0.054\ \text{mol}$$

Continued

The density of the solution is used to convert the mass of the solution to its volume:

$$\text{Milliliters soln} = (230\ \text{g})\left(\frac{1\ \text{mL}}{0.876\ \text{g}}\right) = 263\ \text{mL}$$

Molarity is moles of solute per liter of solution:

$$\text{Molarity} = \left(\frac{\text{moles } C_7H_8}{\text{liter soln}}\right) = \left(\frac{0.054\ \text{mol } C_7H_8}{263\ \text{mL soln}}\right)\left(\frac{1000\ \text{mL soln}}{1\ \text{L soln}}\right) = 0.21\ M$$

Check The magnitude of our answer is reasonable. Rounding moles to 0.05 and liters to 0.25 gives a molarity of $(0.05\ \text{mol})/(0.25\ \text{L}) = 0.2\ M$.

The units for our answer (mol/L) are correct, and the answer, 0.21, has two significant figures, corresponding to the number of significant figures in the mass of solute (2).

Comment Because the mass of the solvent (0.225 kg) and the volume of the solution (0.263) are similar in magnitude, the molarity and molality are also similar in magnitude: $(0.054\ \text{mol } C_7H_8)/(0.225\ \text{kg solvent}) = 0.24\ m$.

Practice Exercise

A solution containing equal masses of glycerol ($C_3H_8O_3$) and water has a density of 1.10 g/mL. Calculate (**a**) the molality of glycerol, (**b**) the mole fraction of glycerol, (**c**) the molarity of glycerol in the solution.

Self-Assessment Exercise

13.17 Commercial concentrated aqueous ammonia is 28% NH_3 by mass and has a density of 0.90 g/mL. What is the molarity of this solution?

(a) 15 *M*

(b) 16 *M*

(c) 252 *M*

Assume 1.00 L of solution. Calculate mass of 1 L of solution using density.

$$1.00\ \text{L solution} \times \frac{1000\ \text{mL}}{1\ \text{L}} \times \frac{0.90\ \text{g solution}}{1\ \text{mL solution}} = 9.0 \times 10^2\ \text{g solution/L}$$

Calculate mass of NH_3 using mass%, then mol NH_3 in 1.00 L.

$$\frac{900\ \text{g solution}}{1.00\ \text{L solution}} \times \frac{28\ \text{g } NH_3}{100\ \text{g solution}} \times \frac{1\ \text{mol } NH_3}{17.03\ \text{g } NH_3} = 14.80 = 15\ \text{mol } NH_3/\text{L solution} = 15\ M\ NH_3$$

Exercises

13.18 (**a**) What is the mass percentage of iodine in a solution containing 0.035 mol I_2 in 125 g of CCl_4? (**b**) Seawater contains 0.0079 g of Sr^{2+} per kilogram of water. What is the concentration of Sr^{2+} in ppm?

13.19 A solution is made containing 20.8 g of phenol (C_6H_5OH) in 425 g of ethanol (CH_3CH_2OH). Calculate (**a**) the mole fraction of phenol, (**b**) the mass percent of phenol, (**c**) the molality of phenol.

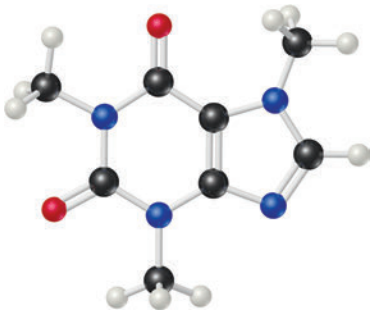
13.20 What is the molarity of each of the following solutions: (**a**) 15.0 g of $Al_2(SO_4)_3$ in 0.250 mL solution, (**b**) 5.25 g of $Mn(NO_3)_2 \cdot 2\ H_2O$ in 175 mL of solution, (**c**) 35.0 mL of 9.00 *M* H_2SO_4 diluted to 0.500 L?

13.21 (**a**) What is the molality of a solution formed by dissolving 1.12 mol of KCl in 16.0 mol of water? (**b**) How many grams of sulfur (S_8) must be dissolved in 100.0 g of naphthalene ($C_{10}H_8$) to make a 0.12 *m* solution?

13.22 Ascorbic acid (vitamin C, $C_6H_8O_6$) is a water-soluble vitamin. A solution containing 80.5 g of ascorbic acid dissolved in 210 g of water has a density of 1.22 g/mL at 55 °C. Calculate (**a**) the mass percentage, (**b**) the mole fraction, (**c**) the molality, (**d**) the molarity of ascorbic acid in this solution.

13.23 Calculate the number of moles of solute present in each of the following solutions: (**a**) 255 mL of 1.50 *M* $HNO_3(aq)$, (**b**) 50.0 mg of an aqueous solution that is 1.50 *m* NaCl, (**c**) 75.0 g of an aqueous solution that is 1.50% sucrose ($C_{12}H_{22}O_{11}$) by mass.

13.24 Caffeine ($C_8H_{10}N_4O_2$) is a stimulant found in coffee and tea. If a solution of caffeine in the solvent chloroform ($CHCl_3$) has a concentration of 0.0500 *m*, calculate (**a**) the percentage of caffeine by mass, (**b**) the mole fraction of caffeine in the solution.



Caffeine

13.25 Breathing air that contains 4.0 % by volume CO_2 over time causes rapid breathing, throbbing headache, and nausea, among other symptoms. What is the concentration of CO_2 in such air in terms of (**a**) mol percentage, (**b**) molarity, assuming 101.3 kPa pressure and a body temperature of 37 °C?

Answers to Self-Assessment Exercises

13.17 (a)

13.5 | Colligative Properties



If you scatter a small amount of icing sugar on a bowl of strawberries, they appear to become juicer. The sugar draws juice from inside the cells of the fruit to the outside. This is a process called osmosis and is one of four colligative properties that we study next. By the end of this section, you should be able to

- Identify the colligative property operating in a given situation
- Perform calculations involving colligative properties

Some physical properties of solutions differ in important ways from those of the pure solvent. For example, pure water freezes at 0 °C, but aqueous solutions freeze at lower temperatures. We apply this behavior when we add ethylene glycol antifreeze to a car's radiator to lower the freezing point of the solution. The added solute also raises the boiling point of the solution above that of pure water, making it possible to operate the engine at a higher temperature.

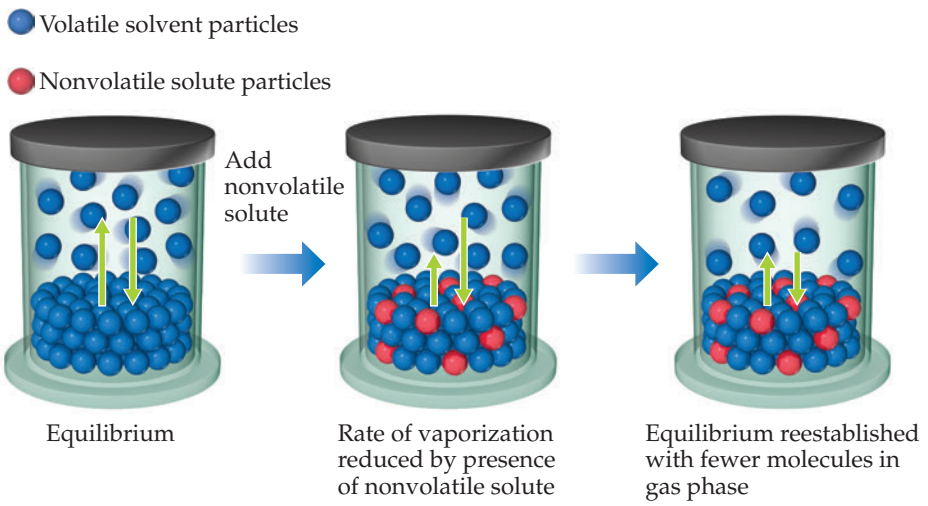
Lowering of the freezing point and raising of the boiling point are physical properties of solutions that depend on the *quantity* (concentration) but not on the *kind* or *identity* of the solute particles. Such properties are called **colligative properties**. (*Colligative* means "depending on the collection"; colligative properties depend on the collective effect of the number of solute particles.)

In addition to freezing-point lowering and boiling-point raising, two other important colligative properties are vapor–pressure lowering and osmotic pressure. As we examine each one, notice how solute concentration quantitatively affects the property.

Vapor–Pressure Lowering

A liquid in a closed container establishes equilibrium with its vapor. The *vapor pressure* is the pressure exerted by the vapor when it is at equilibrium with the liquid (that is, when the rate of vaporization equals the rate of condensation). A substance that has no measurable vapor pressure is *nonvolatile,* whereas one that exhibits a vapor pressure is *volatile*.

A solution consisting of a *volatile* liquid solvent and a *nonvolatile* solute forms spontaneously because of the increase in entropy that accompanies their mixing. In effect, the solvent molecules are stabilized in their liquid state by this process and thus have a lower tendency to escape into the vapor state. Therefore, when a *nonvolatile* solute is present, the vapor pressure of the solvent is lower than the vapor pressure of the pure solvent, as illustrated in **Figure 13.17**.



▶ **Figure 13.17 Vapor–pressure lowering.** The presence of nonvolatile solute particles in a liquid solvent results in a reduction of the vapor pressure above the liquid.

Ideally, the vapor pressure of a *volatile* solvent above a solution containing a *nonvolatile* solute is proportional to the solvent's concentration in the solution. This relationship is expressed quantitatively by **Raoult's law**, which states that the partial pressure exerted by solvent vapor above the solution, $P_{solution}$, equals the product of the mole fraction of the solvent, $X_{solvent}$, times the vapor pressure of the pure solvent, $P^\circ_{solvent}$:

$$P_{solution} = X_{solvent} P^\circ_{solvent} \qquad [13.10]$$

For example, the vapor pressure of pure water at 20 °C is $P^\circ_{H_2O} = 2.33$ kPa. Imagine holding the temperature constant while adding glucose ($C_6H_{12}O_6$) to the water so that the mole fractions in the resulting solution are $X_{H_2O} = 0.800$ and $X_{C_6H_{12}O_6} = 0.200$. According to Equation 13.10, the vapor pressure of the water above this solution is 80.0% of that of pure water:

$$P_{solution} = (0.800)(2.33\ \text{kPa}) = 1.87\ \text{kPa}$$

The presence of the *nonvolatile* solute lowers the vapor pressure of the *volatile* solvent by 2.33 kPa − 1.87 kPa = 0.46 kPa.

The vapor–pressure lowering, ΔP, is directly proportional to the mole fraction of the solute, X_{solute}:

$$\Delta P = X_{solute}\, P^\circ_{solvent} \qquad [13.11]$$

Thus, for the example of the solution of glucose in water, we have

$$\Delta P = X_{C_6H_{12}O_6} P^\circ_{H_2O} = (0.200)(2.33\ \text{kPa}) = 0.466\ \text{kPa}$$

The vapor–pressure lowering caused by adding a *nonvolatile* solute depends on the total concentration of solute particles, regardless of whether they are molecules or ions. Remember that vapor–pressure lowering is a colligative property, so its value for any solution depends on the concentration of solute particles and not on their kind or identity.

Sample Exercise 13.7

Calculation of Vapor Pressure of a Solution

Glycerin ($C_3H_8O_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25 °C. Calculate the vapor pressure at 25 °C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25 °C is 3.17 kPa (Appendix B), and its density is 1.00 g/mL.

SOLUTION

Analyze Our goal is to calculate the vapor pressure of a solution, given the volume of solute and solvent and the density of the solute.

Plan We can use Raoult's law (Equation 13.10) to calculate the vapor pressure of a solution. The mole fraction of the solvent in the solution, $X_{solvent}$, is the ratio of the number of moles of solvent (H_2O) to total moles of solution (moles $C_3H_8O_3$ + moles H_2O).

Solve

To calculate the mole fraction of water in the solution, we must determine the number of moles of $C_3H_8O_3$ and H_2O:

$$\text{Moles } C_3H_8O_3 = (50.0 \text{ mL } C_3H_8O_3)\left(\frac{1.26 \text{ g } C_3H_8O_3}{1 \text{ mL } C_3H_8O_3}\right)\left(\frac{1 \text{ mol } C_3H_8O_3}{92.1 \text{ g } C_3H_8O_3}\right) = 0.684 \text{ mol}$$

$$\text{Moles } H_2O = (500.0 \text{ mL } H_2O)\left(\frac{1.00 \text{ g } H_2O}{1 \text{ mL } H_2O}\right)\left(\frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O}\right) = 27.8 \text{ mol}$$

$$X_{H_2O} = \frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol } C_3H_8O_3} = \frac{27.8}{27.8 + 0.684} = 0.976$$

We now use Raoult's law to calculate the vapor pressure of water for the solution:

$$P_{H_2O} = X_{H_2O} P^\circ_{H_2O} = (0.976)(3.17 \text{ kPa}) = 3.09 \text{ kPa}$$

Comment The vapor pressure of the solution has been lowered by 3.17 kPa − 3.09 kPa = 0.08 kPa relative to that of pure water. The vapor–pressure lowering can be calculated directly using Equation 13.11 together with the mole fraction of the solute, $C_3H_8O_3$: $\Delta P = X_{C_3H_8O_3} P^\circ_{H_2O} = (0.024)(3.17 \text{ kPa}) = 0.076$ kPa. Notice that the use of Equation 13.11 gives one more significant figure than the number obtained by subtracting the vapor pressure of the solution from that of the pure solvent.

▶ Practice Exercise

The vapor pressure of pure water at 110 °C is 142.7 kPa. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110 °C. Assuming that Raoult's law is obeyed, what is the mole fraction of ethylene glycol in the solution?

A CLOSER LOOK Ideal Solutions with Two or More Volatile Components

Solutions sometimes have two or more volatile components. Petrol, for example, is a solution of several volatile liquids. To gain some understanding of such mixtures, consider an ideal solution of two volatile liquids, A and B. (For our purposes here, it does not matter which we call the solute and which the solvent.) The partial pressures above the solution are given by Raoult's law:

$$P_A = X_A P^\circ_A \quad \text{and} \quad P_B = X_B P^\circ_B$$

and the total vapor pressure above the solution is

$$P_{total} = P_A + P_B = X_A P^\circ_A + X_B P^\circ_B$$



▲ **Figure 13.18** The volatile components of organic mixtures can be separated on an industrial scale in these distillation towers.

Consider a mixture of 1.0 mol of benzene (C_6H_6) and 2.0 mol of toluene (C_7H_8) ($X_{ben} = 0.33$, $X_{tol} = 0.67$). At 20 °C, the vapor pressures of the pure substances are $P^\circ_{ben} = 10$ kPa and $P^\circ_{tol} = 2.9$ kPa. Thus, the partial pressures above the solution are

$$P_{ben} = (0.33)(10 \text{ kPa}) = 3.3 \text{ kPa}$$

$$P_{tol} = (0.67)(2.9 \text{ kPa}) = 1.9 \text{ kPa}$$

and the total vapor pressure above the liquid is

$$P_{total} = P_{ben} + P_{tol} = 3.3 \text{ kPa} + 1.9 \text{ kPa} = 5.2 \text{ kPa}$$

Note that the vapor is richer in benzene, the more volatile component.

The mole fraction of benzene in the vapor is given by the ratio of its vapor pressure to the total pressure (Equations 10.14 and 10.15):

$$X_{ben} \text{ in vapor} = \frac{P_{ben}}{P_{tol}} = \frac{3.3 \text{ kPa}}{5.2 \text{ kPa}} = 0.63$$

Although benzene constitutes only 33% of the molecules in the solution, it makes up 63% of the molecules in the vapor.

When an ideal liquid solution containing two volatile components is in equilibrium with its vapor, the more volatile component will be relatively richer in the vapor. This fact forms the basis of *distillation*, a technique used to separate (or partially separate) mixtures containing volatile components. Distillation is a way of purifying liquids and is the procedure by which petrochemical plants achieve the separation of crude petroleum into gasoline, diesel fuel, lubricating oil, and other products (Figure 13.18). Distillation is also used routinely on a small scale in the laboratory.

Related Exercises: 13.30, 13.82

An ideal gas is defined as one that obeys the ideal-gas equation, and an **ideal solution** is defined as one that obeys Raoult's law. Whereas ideality for a gas arises from a complete lack of intermolecular interaction, ideality for a solution implies total uniformity of interaction. The molecules in an ideal solution all influence one

another in the same way—in other words, solute–solute, solvent–solvent, and solute–solvent interactions are indistinguishable from one another. Real solutions best approximate ideal behavior when the solute concentration is low and solute and solvent have similar molecular sizes and take part in similar types of intermolecular attractions.

Many solutions do not obey Raoult's law exactly and so are not ideal. If, for instance, the solvent–solute interactions in a solution are weaker than either the solvent–solvent or solute–solute interactions, the vapor pressure tends to be greater than that predicted by Raoult's law. When the solute–solvent interactions in a solution are exceptionally strong, as might be the case when hydrogen bonding exists, the vapor pressure is lower than that predicted by Raoult's law. Although you should be aware that these departures from ideality occur, we will ignore them for the remainder of this chapter.

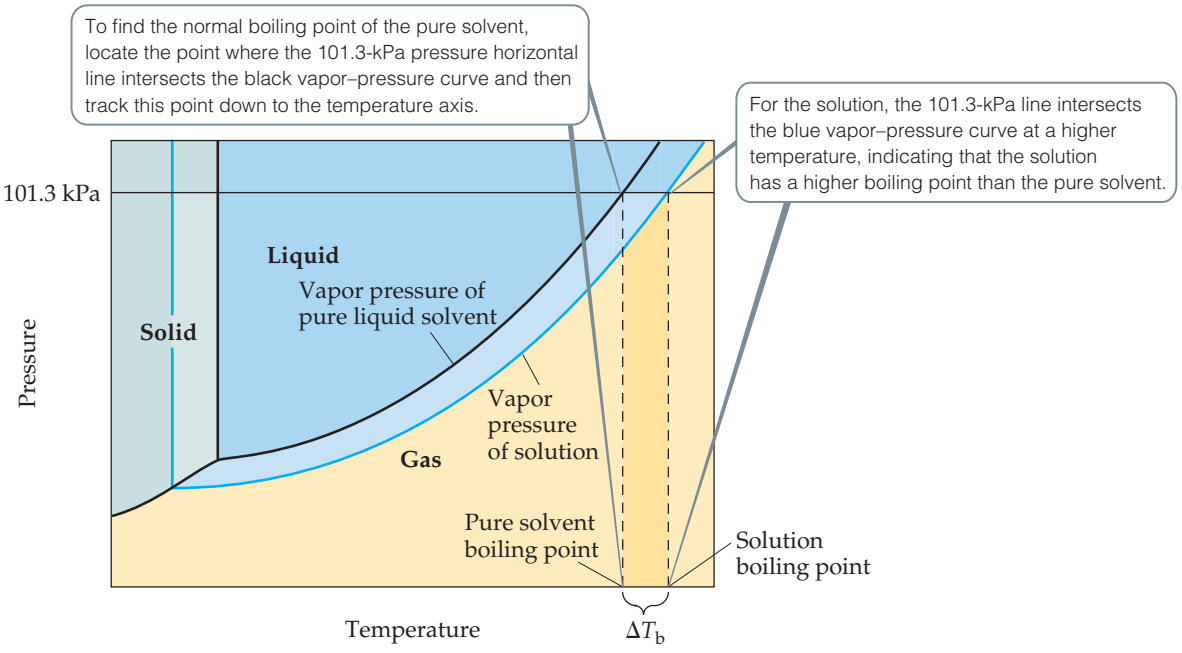
Boiling-Point Elevation

In Sections 11.5 and 11.6, we examined the vapor pressures of pure substances and how to use them to construct phase diagrams. How does the phase diagram of a solution and, hence, its boiling and freezing points differ from that of the pure solvent? The addition of a nonvolatile solute lowers the vapor pressure of the solution. Thus, in **Figure 13.19** the vapor–pressure curve of the solution is shifted downward relative to the vapor–pressure curve of the pure solvent.

Recall from Section 11.5 that the normal boiling point of a liquid is the temperature at which its vapor pressure equals 101.3 kPa. Because the solution has a lower vapor pressure than the pure solvent, a higher temperature is required for the solution to achieve a vapor pressure of 101.3 kPa. As a result, *the boiling point of the solution is higher than that of the pure solvent*. This effect is seen in Figure 13.19.

The increase in the boiling point of a solution, relative to the pure solvent, depends on the molality of the solute. But it is important to remember that boiling-point elevation is proportional to the *total* concentration of solute particles, regardless of whether the particles are molecules or ions. When NaCl dissolves in water, 2 mol of solute particles (1 mol of Na^+ and 1 mol of Cl^-) are formed for each mole of NaCl that dissolves. We take this into account by defining i, the **van't Hoff factor**, as the number of fragments that a solute breaks up into for a particular solvent. The change in boiling point for a solution compared to the pure solvent is:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = iK_b m \qquad [13.12]$$



▲ **Figure 13.19 Phase diagram illustrating boiling-point elevation.** The black lines show the pure solvent's phase equilibria curves, and the blue lines show the solution's phase equilibria curves.

In this equation, T_b(solution) is the boiling point of the solution, T_b(solvent) is the boiling point of the pure solvent, m is the molality of the solute, K_b is the **molal boiling-point-elevation constant** for the solvent (which is a proportionality constant that is experimentally determined for each solvent), and i is the van't Hoff factor. For a nonelectrolyte, we can always assume $i = 1$; for an electrolyte, i will depend on how the substance ionizes in that solvent. For instance, $i = 2$ for NaCl in water, assuming complete dissociation of ions. As a result, we expect the boiling-point elevation of a 1 m aqueous solution of NaCl to be twice as large as the boiling-point elevation of a 1 m solution of a nonelectrolyte such as sucrose. Thus, to properly predict the effect of a particular solute on boiling-point elevation (or any other colligative property), it is important to know whether the solute is an electrolyte or a nonelectrolyte.

Freezing-Point Depression

The vapor–pressure curves for the liquid and solid phases meet at the triple point. In **Figure 13.20** we see that the triple-point temperature of the solution is lower than the triple-point temperature of pure liquid because the solution has a lower vapor pressure than the pure liquid.

The freezing point of a solution is the temperature at which the first crystals of pure solvent form in equilibrium with the solution. Recall from Section 11.6 that the line representing the solid–liquid equilibrium rises nearly vertically from the triple point. It is easy to see in Figure 13.20 that the triple-point temperature of the solution is lower than that of the pure liquid, but it is also true for all points along the solid–liquid equilibrium curve: *the freezing point of the solution is lower than that of the pure liquid.*

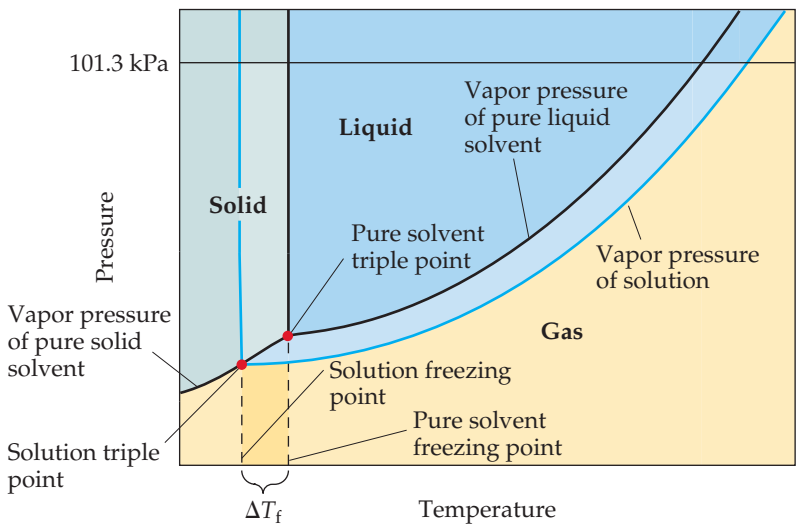
Like the boiling-point elevation, the change in freezing point ΔT_f is directly proportional to solute molality, taking into account the van't Hoff factor i:

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent}) = -iK_f m \qquad [13.13]$$

The proportionality constant K_f is the **molal freezing-point-depression constant**, analogous to K_b for boiling-point elevation. Note that because the solution freezes at a *lower* temperature than does the pure solvent, the value of ΔT_f is *negative.*

Some typical values of K_b and K_f for several common solvents are given in **Table 13.3**. For water, the table shows $K_b = 0.51\ ^\circ\text{C}/m$, which means that the boiling point of any aqueous solution that is 1 m in nonvolatile solute particles is 0.51 °C higher than the boiling point of pure water. Because solutions generally do not behave ideally, the constants listed in Table 13.3 serve well only for solutions that are rather dilute.

For water, K_f is 1.86 °C/m. Therefore, any aqueous solution that is 1 m in nonvolatile solute particles (such as 1 m $C_6H_{12}O_6$ or 0.5 m NaCl) freezes at the temperature that is 1.86 °C lower than the freezing point of pure water.



◀ **Figure 13.20 Phase diagram illustrating freezing-point depression.** The black lines show the pure solvent's phase equilibria curves, and the blue lines show the solution's phase equilibria curves.

TABLE 13.3 Molal Boiling-Point-Elevation and Freezing-Point-Depression Constants

Solvent	Normal Boiling Point (°C)	K_b (°C/*m*)	Normal Freezing Point (°C)	K_f (°C/*m*)
Water, H_2O	100.0	0.51	0.0	1.86
Benzene, C_6H_6	80.1	2.53	5.5	5.12
Ethanol, C_2H_5OH	78.4	1.22	−114.6	1.99
Tetrachloromethane, CCl_4	76.8	5.02	−22.3	29.8
Trichloromethane, $CHCl_3$	61.2	3.63	−63.5	4.68

Sample Exercise 13.8

Calculation of Boiling-Point Elevation and Freezing-Point Depression

Automotive antifreeze contains ethylene glycol, $CH_2(OH)CH_2(OH)$, a nonvolatile nonelectrolyte, in water. Calculate the boiling point and freezing point of a 25.0% by mass solution of ethylene glycol in water.

SOLUTION

Analyze We are given that a solution contains 25.0% by mass of a nonvolatile, nonelectrolyte solute and asked to calculate the boiling and freezing points of the solution. To do this, we need to calculate the boiling-point elevation and freezing-point depression.

Plan To calculate the boiling-point elevation and the freezing-point depression using Equations 13.12 and 13.13, we must express the concentration of the solution as molality. Let's assume for convenience that we have 1000 g of solution. Because the solution is 25.0% by mass ethylene glycol, the masses of ethylene glycol and water in the solution are 250 and 750 g, respectively. Using these quantities, we can calculate the molality of the solution, which we use with the molal boiling-point-elevation and freezing-point-depression constants (Table 13.3) to calculate ΔT_b and ΔT_f. We add ΔT_b to the boiling point and ΔT_f to the freezing point of the solvent to obtain the boiling point and freezing point of the solution.

Solve

The molality of the solution is calculated as follows:

$$\text{Molality} = \frac{\text{moles } C_2H_6O_2}{\text{kilograms } H_2O}$$

$$= \left(\frac{250 \text{ g } C_2H_6O_2}{750 \text{ g } H_2O}\right)\left(\frac{1 \text{ mol } C_2H_6O_2}{62.1 \text{ g } C_2H_6O_2}\right)\left(\frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O}\right) = 5.37\ m$$

We can now use Equations 13.12 and 13.13 to calculate the changes in the boiling and freezing points:

$$\Delta T_b = iK_b m = (1)(0.51\ °C/m)(5.37\ m) = 2.7\ °C$$

$$\Delta T_f = -iK_f m = -(1)(1.86\ °C/m)(5.37\ m) = -10.0\ °C$$

Hence, the boiling and freezing points of the solution are readily calculated:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent})$$

$$2.7\ °C = T_b(\text{solution}) - 100.0\ °C$$

$$T_b(\text{solution}) = 102.7\ °C$$

$$\Delta T_f = T_f(\text{solution}) - T_f(\text{solvent})$$

$$-10.0\ °C = T_f(\text{solution}) - 0.0\ °C$$

$$T_f(\text{solution}) = -10.0\ °C$$

Comment Notice that the solution is a liquid over a larger temperature range than the pure solvent.

Practice Exercise

Which aqueous solution will have the lowest freezing point?
(**a**) 0.050 *m* $CaCl_2$ (**b**) 0.15 *m* NaCl (**c**) 0.10 *m* HCl
(**d**) 0.050 *m* CH_3COOH (**e**) 0.20 *m* $C_{12}H_{22}O_{11}$

The freezing-point depression caused by solutes has useful applications: it is why antifreeze works in car cooling systems and why calcium chloride ($CaCl_2$) promotes the melting of ice on roads during winter.

Osmosis

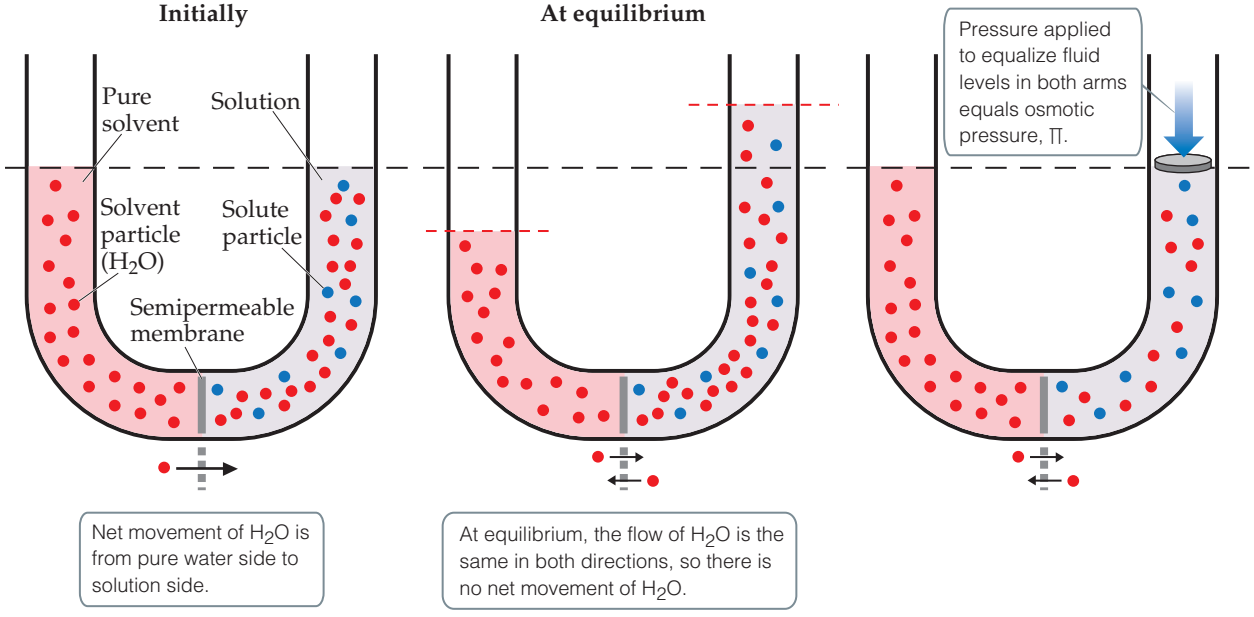
Certain materials, including many membranes in biological systems and synthetic substances such as cellophane, are *semipermeable*. When in contact with a solution, these materials allow only ions or small molecules—water molecules, for instance—to pass through their network of tiny pores.

Consider a situation in which only solvent molecules are able to pass through a semipermeable membrane placed between two solutions of different concentrations. The rate at which the solvent molecules pass from the less concentrated solution (lower solute concentration but higher solvent concentration) to the more concentrated solution (higher solute concentration but lower solvent concentration) is greater than the rate in the opposite direction. Thus, there is a net movement of solvent molecules from the solution with a lower solute concentration into the one with a higher solute concentration. In this process, called **osmosis**, *the net movement of solvent is always toward the solution with the lower solvent (higher solute) concentration*, as if the solutions were driven to attain equal concentrations.

Figure 13.21 shows the osmosis that occurs between an aqueous solution and pure water, separated by a semipermeable membrane. The U-tube contains water on the left and an aqueous solution on the right. Initially, there is a net movement of water through the membrane from left to right, leading to unequal liquid levels in the two arms of the U-tube. Eventually, at equilibrium (middle panel of Figure 13.21), the pressure difference resulting from the unequal liquid heights becomes so large that the net flow of water ceases. This pressure, which stops osmosis, is the **osmotic pressure**, Π, of the solution. If an external pressure equal to the osmotic pressure is applied to the solution, the liquid levels in the two arms can be equalized, as shown in the right panel of Figure 13.21.

The osmotic pressure obeys a law similar in form to the ideal gas law, $\Pi V = inRT$ where Π is the osmotic pressure, V is the volume of the solution, i is the van't Hoff factor,

Go Figure If the pure water in the left arm of the U-tube is replaced by a solution more concentrated than the one in the right arm, what will happen?



▲ **Figure 13.21 Osmosis is the process of a solvent moving from one compartment to another, across a semipermeable membrane, toward higher solute concentration.** Osmotic pressure is generated at equilibrium due to the different heights of liquid on either side of the membrane and is equivalent to the pressure needed to equalize the fluid levels across the membrane.

n is the number of moles of solute, R is the ideal-gas constant, and T is the absolute temperature. From this equation, we can write

$$\Pi = i\left(\frac{n}{V}\right)RT = iMRT \qquad [13.14]$$

where M is the molarity of the solution. Because the osmotic pressure for any solution depends on the solution concentration, osmotic pressure is a colligative property.

If two solutions of identical osmotic pressure are separated by a semipermeable membrane, no osmosis will occur. The two solutions are *isotonic* with respect to each other. If one solution is of lower osmotic pressure, it is *hypotonic* with respect to the more concentrated solution. The more concentrated solution is *hypertonic* with respect to the dilute solution.

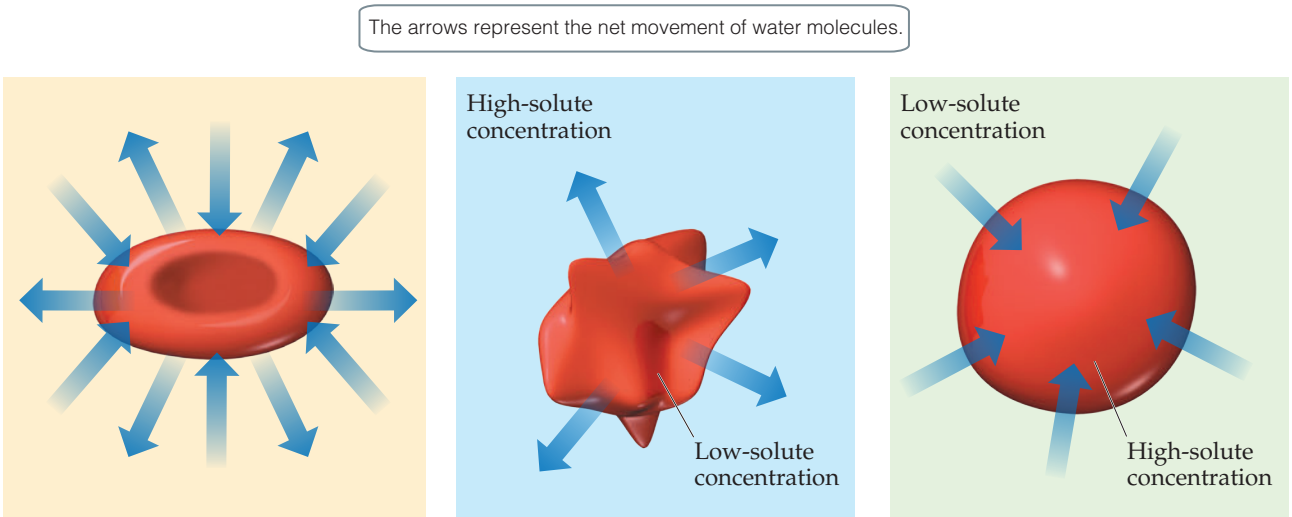
Osmosis plays an important role in living systems. The membranes of red blood cells, for example, are semipermeable. Placing a red blood cell in a solution that is *hypertonic* relative to the intracellular solution (the solution inside the cells) causes water to move out of the cell (**Figure 13.22**). This causes the cell to shrivel, a process called *crenation*. Placing the cell in a solution that is *hypo*tonic relative to the intracellular fluid causes water to move into the cell, which may cause the cell to rupture, a process called *hemolysis*. People who need body fluids or nutrients replaced but cannot be fed orally are given solutions by intravenous (IV) infusion, which feeds nutrients directly into the veins. To prevent crenation or hemolysis of red blood cells, the IV solutions must be isotonic with the intracellular fluids of the blood cells.

There are many interesting biological examples of osmosis. A cucumber placed in concentrated brine loses water via osmosis and shrivels into a pickle. People who eat a lot of salty food retain water in tissue cells and intercellular space because of osmosis. The resultant swelling or puffiness is called *edema*. Water moves from soil into plant roots partly because of osmosis. Bacteria on salted meat or candied fruit lose water through osmosis, shrivel, and die—thus preserving the food.

Determination of Molar Mass from Colligative Properties

The colligative properties of solutions provide a useful means of determining the molar mass of solutes. Any of the four colligative properties can be used, as shown in Sample Exercises 13.10 and 13.11.

Go Figure If the fluid surrounding a patient's red blood cells is depleted in electrolytes, is crenation or hemolysis more likely to occur?



Red blood cell in isotonic medium neither swells nor shrinks.

Crenation of red blood cell placed in hypertonic environment

Hemolysis of red blood cell placed in hypotonic environment

▲ **Figure 13.22 Osmosis through red blood cell walls.** If water moves out of the red blood cell, it shrivels (crenation); if water moves into the red blood cell, it will swell and may burst (hemolysis).

Sample Exercise 13.9

Osmotic Pressure Calculations

The average osmotic pressure of blood is 780 kPa at 25 °C. What molarity of glucose ($C_6H_{12}O_6$) will be isotonic with blood?

SOLUTION

Analyze We are asked to calculate the concentration of glucose in water that would be isotonic with blood, given that the osmotic pressure of blood at 25 °C is 780 kPa.

Plan Because we are given the osmotic pressure and temperature, we can solve for the concentration, using Equation 13.14. Because glucose is a nonelectrolyte, $i = 1$.

Solve

$$\Pi = iMRT$$

$$M = \frac{\Pi}{iRT} = \frac{(780\ \text{kPa})}{(1)\left(8.314\frac{\text{m}^3\ \text{Pa}}{\text{mol K}}\right)(298\ \text{K})} = 0.31\ M$$

Comment In clinical situations, the concentrations of solutions are generally expressed as mass percentages. The mass percentage of a 0.31 *M* solution of glucose is 5.3%. The concentration of NaCl that is isotonic with blood is 0.16 *M*, because $i = 2$ for NaCl in water (a 0.155 *M* solution of NaCl is 0.310 *M* in particles). A 0.16 *M* solution of NaCl is 0.9% mass in NaCl. This kind of solution is known as a physiological saline solution.

Practice Exercise

Which of the following actions will raise the osmotic pressure of a solution? (**a**) decreasing the solute concentration (**b**) decreasing the temperature (**c**) adding more solvent (**d**) increasing the temperature (**e**) none of these

Sample Exercise 13.10

Molar Mass from Freezing-Point Depression or Boiling-Point Elevation

A solution of an unknown nonvolatile nonelectrolyte was prepared by dissolving 0.250 g of the substance in 40.0 g of CCl_4. The boiling point of the resulting solution was 0.357 °C higher than that of the pure solvent. Calculate the molar mass of the solute.

SOLUTION

Analyze Our goal is to calculate the molar mass of a solute based on knowledge of the boiling-point elevation of its solution in CCl_4, $\Delta T_b = 0.357$ °C, and the masses of solute and solvent. Table 13.3 gives K_b for the solvent (CCl_4), $K_b = 5.02$ °C/*m*.

Plan We can use Equation 13.12, $\Delta T_b = iK_bm$, to calculate the molality of the solution. Because the solute is a nonelectrolyte, $i = 1$. Then we can use molality and the quantity of solvent (40.0 g CCl_4) to calculate the number of moles of solute. Finally, the molar mass of the solute equals the number of grams per mole, so we divide the number of grams of solute (0.250 g) by the number of moles we have just calculated.

Solve

From Equation 13.12, we have:

$$\text{Molality} = \frac{\Delta T_b}{iK_b} = \frac{0.357\ ^\circ\cancel{\text{C}}}{(1)5.02\ ^\circ\cancel{\text{C}}/m} = 0.0711\ m$$

Thus, the solution contains 0.0711 mol of solute per kilogram of solvent. The solution was prepared using 40.0 g = 0.0400 kg of solvent (CCl_4). The number of moles of solute in the solution is therefore:

$$(0.0400\ \text{kg}\ \cancel{CCl_4})\left(0.0711\ \frac{\text{mol solute}}{\text{kg}\ \cancel{CCl_4}}\right) = 2.84 \times 10^{-3}\ \text{mol solute}$$

The molar mass of the solute is the number of grams per mole of the substance:

$$\text{Molar mass} = \frac{0.250\ \text{g}}{2.84 \times 10^{-3}\ \text{mol}} = 88.0\ \text{g/mol}$$

Practice Exercise

A mysterious white powder could be powdered sugar ($C_{12}H_{22}O_{11}$), cocaine ($C_{17}H_{21}NO_4$), codeine ($C_{18}H_{21}NO_3$), norfenefrine ($C_8H_{11}NO_2$), or fructose ($C_6H_{12}O_6$). When 80 mg of the powder is dissolved in 1.50 mL of ethanol ($d = 0.789$ g/cm^3, normal freezing point −114.6 °C, $K_f = 1.99$ °C/*m*), the freezing point is lowered to −115.5 °C. What is the identity of the white powder? (**a**) powdered sugar (**b**) cocaine (**c**) codeine (**d**) norfenefrine (**e**) fructose

Sample Exercise 13.11

Molar Mass from Osmotic Pressure

The osmotic pressure of an aqueous solution of a certain protein was measured to determine the protein's molar mass. The solution contained 3.50 mg of protein dissolved in sufficient water to form 5.00 mL of solution. The osmotic pressure of the solution at 25 °C was found to be 205 Pa. Treating the protein as a nonelectrolyte, calculate its molar mass.

SOLUTION

Analyze Our goal is to calculate the molar mass of a high-molecular-mass protein, based on the osmotic pressure and a knowledge of the mass of protein and solution volume. Since the protein will be considered as a nonelectrolyte, $i = 1$.

Plan The temperature ($T = 25\,°C$) and osmotic pressure ($\Pi = 205$ Pa) are given, and we know the value of R so we can use Equation 13.14 to calculate the molarity of the solution, M. In doing so, we must convert temperature from °C to K. We then use the molarity and the volume of the solution (5.00 mL) to determine the number of moles of solute. Finally, we obtain the molar mass by dividing the mass of the solute (3.50 mg) by the number of moles of solute.

Solve

Solving Equation 13.14 for molarity gives:

$$\text{Molarity} = \frac{\Pi}{iRT} = \frac{205\ \text{Pa}}{(1)\left(8.314\frac{\text{m}^3\,\text{Pa}}{\text{mol K}}\right)(298\ \text{K})} = 8.28 \times 10^{-5}\,\frac{\text{mol}}{\text{L}}$$

Because the volume of the solution is $5.00\ \text{mL} = 5.00 \times 10^{-3}$ L, the number of moles of protein must be:

$$\text{Moles} = (8.28 \times 10^{-5}\ \text{mol/L})(5.00 \times 10^{-3}\ \text{L}) = 4.14 \times 10^{-7}\ \text{mol}$$

The molar mass is the number of grams per mole of the substance. Because we know the sample has a mass of $3.50\ \text{mg} = 3.50 \times 10^{-3}$ g, we can calculate the molar mass by dividing the number of grams in the sample by the number of moles we just calculated:

$$\text{Molar mass} = \frac{\text{grams}}{\text{moles}} = \frac{3.50 \times 10^{-3}\ \text{g}}{4.14 \times 10^{-7}\ \text{mol}} = 8.45 \times 10^{3}\ \text{g/mol}$$

Comment Because small pressures can be measured easily and accurately, osmotic pressure measurements provide a useful way to determine the molar masses of large molecules.

Practice Exercise

A sample of 2.05 g of polystyrene of uniform polymer chain length was dissolved in enough toluene to form 0.100 L of solution. The osmotic pressure of this solution was found to be 1.21 kPa at 25 °C. Calculate the molar mass of the polystyrene.

A CLOSER LOOK The van't Hoff Factor

The colligative properties of solutions depend on the *total* concentration of solute particles, regardless of whether the particles are ions or molecules. Thus, we expect a 0.100 *m* solution of NaCl to have a freezing-point depression of $(2)(0.100\,m)(1.86\,°C/m) = 0.372\,°C$ because it is 0.100 *m* in $Na^+(aq)$ and 0.100 *m* in $Cl^-(aq)$. The measured freezing-point depression is only 0.348 °C, however, and the situation is similar for other strong electrolytes. A 0.100 *m* solution of KCl, for example, freezes at −0.344 °C.

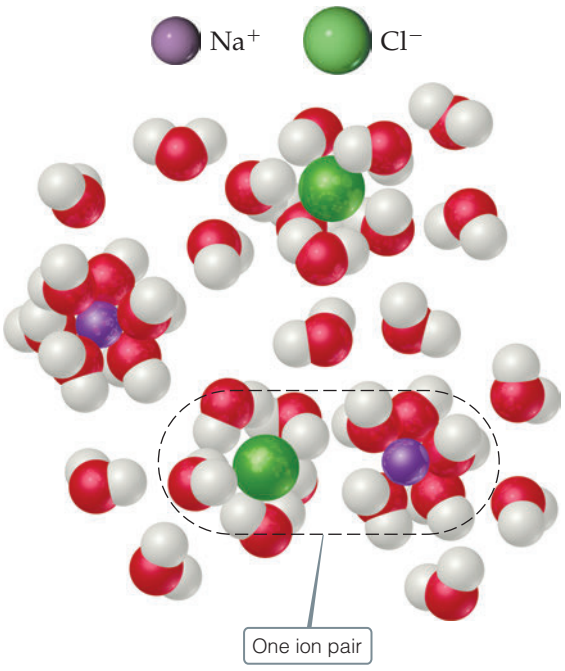
The difference between expected and observed colligative properties for strong electrolytes is due to electrostatic attractions between ions. As the ions move about in solution, ions of opposite charge collide and "stick together" for brief moments. While they are together, they behave as a single particle called an *ion pair* (Figure 13.23). The number of independent particles is thereby reduced, causing a reduction in the freezing-point depression (as well as in boiling-point elevation, vapor–pressure reduction, and osmotic pressure).

We have been assuming that the van't Hoff factor, *i*, is equal to the number of ions per formula unit of the electrolyte. The true (measured) value of this factor, however, is given by the ratio of the measured value of a colligative property to the value calculated when the substance is assumed to be a nonelectrolyte. Using the freezing-point depression, for example, we have

$$i = \frac{\Delta T_f\,(\text{measured})}{\Delta T_f\,(\text{calculated for nonelectrolyte})} \qquad [13.15]$$

The limiting value of *i* can be determined for a salt from the number of ions per formula unit. For NaCl, for example, the limiting van't Hoff factor is 2 because NaCl consists of one Na^+ and one Cl^- per formula

Continued



▲ **Figure 13.23 Ion pairing and colligative properties.** A solution of NaCl contains not only separated $Na^+(aq)$ and $Cl^-(aq)$ ions but ion pairs as well.

TABLE 13.4 Measured and Expected van't Hoff Factors for Several Substances at 25 °C

	Concentration			
Compound	0.100 *m*	0.0100 *m*	0.00100 *m*	Expected Value
Sucrose	1.00	1.00	1.00	1.00
NaCl	1.87	1.94	1.97	2.00
K_2SO_4	2.32	2.70	2.84	3.00
$MgSO_4$	1.21	1.53	1.82	2.00

unit; for K_2SO_4 it is 3 because K_2SO_4 consists of two K^+ and one SO_4^{2-} per formula unit. In the absence of any information about the actual value of *i* for a solution, we will use the limiting value in calculations.

Two trends are evident in **Table 13.4**, which gives measured van't Hoff factors for several substances at different dilutions. First, dilution affects the value of *i* for electrolytes; the more dilute the solution, the more closely *i* approaches the expected value based on the number of ions in the formula unit. Thus, we conclude that the extent of ion pairing in electrolyte solutions decreases upon dilution. Second, the lower the charges on the ions, the less *i* departs from the expected value because the extent of ion pairing decreases as the ionic charges decrease. Both trends are consistent with simple electrostatics: The force of interaction between charged particles decreases as their separation increases and as their charges decrease.

Related Exercises: 13.35, 13.93, 13.108, 13.110

Self-Assessment Exercises

13.26 A desalination plant is able to produce pure water from saltwater by a process called reverse osmosis. Which statement is true?

(a) Water freely moves through a semi-permeable membrane from the saltwater to the freshwater side.

(b) A pressure in excess of the osmotic pressure of the solution is placed on the saltwater side of the semi-permeable membrane to drive water through to the freshwater side of the membrane.

(c) The semi-permeable membrane allows ions but not water molecules to pass through.

13.27 Is the osmotic pressure of a 0.15 M solution of $NaNO_3$ greater than, less than, or equal to that of a 0.10 M solution of $Ca(NO_3)_2$?

(a) Osmotic pressure of 0.15 M $NaNO_3$ > Osmotic pressure of 0.10 M $Ca(NO_3)_2$

(b) Osmotic pressure of 0.15 M $NaNO_3$ < Osmotic pressure of 0.10 M $Ca(NO_3)_2$

(c) Osmotic pressure of 0.15 M $NaNO_3$ ≃ Osmotic pressure of 0.10 M $Ca(NO_3)_2$

Exercises

13.28 You make a solution of a nonvolatile solute with a liquid solvent. Indicate if each of the following statements is true or false. (**a**) The freezing point of the solution is unchanged by addition of the solvent. (**b**) The solid that forms as the solution freezes is nearly pure solute. (**c**) The freezing point of the solution is independent of the concentration of the solute. (**d**) The boiling point of the solution increases in proportion to the concentration of the solute. (**e**) At any temperature, the vapor pressure of the solvent over the solution is lower than what it would be for the pure solvent.

13.29 (**a**) Calculate the vapor pressure of water above a solution prepared by dissolving 28.5 g of glycerin ($C_3H_8O_3$) in 125 g of water at 343 K. (The vapor pressure of water is given in Appendix B.) (**b**) Calculate the mass of ethylene glycol ($C_2H_6O_2$) that must be added to 1.00 kg of ethanol (C_2H_5OH) to reduce its vapor pressure by 1.33 kPa at 35 °C. The vapor pressure of pure ethanol at 35 °C is 13.3 kPa.

13.30 At 63.5 °C, the vapor pressure of H_2O is 23.3 kPa, and that of ethanol (C_2H_5OH) is 53.3 kPa. A solution is made by mixing equal masses of H_2O and C_2H_5OH. (**a**) What is the mole fraction of ethanol in the solution? (**b**) Assuming ideal-solution behavior, what is the vapor pressure of the solution at 63.5 °C? (**c**) What is the mole fraction of ethanol in the vapor above the solution?

13.31 List the following aqueous solutions in order of decreasing freezing point: 0.040 *M* glycerin ($C_3H_8O_3$), 0.020 *M* KBr, 0.030 *M* phenol (C_6H_5OH).

13.32 Using data from Table 13.3, calculate the freezing and boiling points of each of the following solutions: (**a**) 0.25 *m*

glucose in ethanol; (**b**) 20.0 g of decane, $C_{10}H_{22}$, in 50.0 g $CHCl_3$; **(c)** 3.50 g NaOH in 175 g of water, (**d**) 0.45 mol ethylene glycol and 0.15 mol KBr in 150 g H_2O.

13.33 The Baltic Sea has a salinity of 1.0%, that is, its water contains 10 g of salt for every liter of solution. Assuming that the solute consists entirely of NaCl (in fact, over 90% of the salt is indeed NaCl), calculate the osmotic pressure of this seawater at 15 °C.

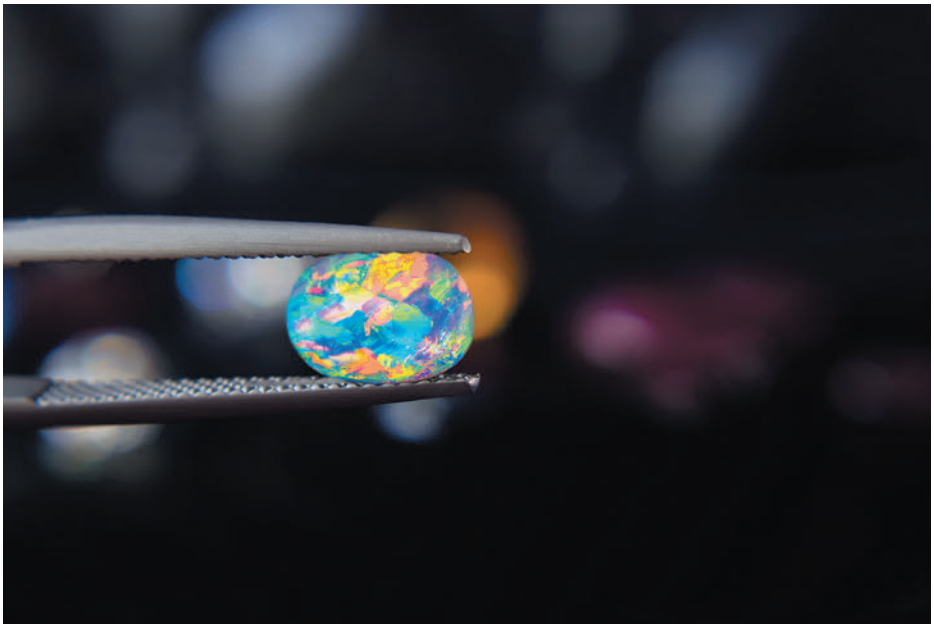
13.34 Lysozyme is an enzyme that breaks bacterial cell walls. A solution containing 0.150 g of this enzyme in 210 mL of solution has an osmotic pressure of 0.127 kPa at 25 °C. What is the molar mass of lysozyme?

13.35 Based on the data given in Table 13.4, which solution would give the larger freezing-point lowering, a 0.030 *m* solution of NaCl or a 0.020 *m* solution of K_2SO_4?

Answers to Self-Assessment Exercises

13.26 (b) **13.27** (c)

13.6 Colloids



The beautiful play of colors of the precious opal result from amorphous particles of hydrated silica that are of a similar size to the wavelength of visible light and act as a diffraction grating splitting white light into its spectral colors.

By the end of this section, you should be able to

- Articulate some of the characteristics of a colloid

Some substances appear to initially dissolve in a solvent, but over time, the substance separates from the pure solvent. For example, finely divided clay particles dispersed in water eventually settle out because of gravity. Gravity affects the clay particles because they are much larger than most molecules, consisting of thousands or even millions of atoms. In contrast, the dispersed particles in a true solution (ions in a salt solution or glucose molecules in a sugar solution) are small. Between these extremes lie dispersed particles that are larger than typical molecules but not so large that the components of the mixture separate under the influence of gravity. These intermediate types of dispersions are called either **colloidal dispersions** or simply **colloids**. Colloids form the dividing line between solutions and heterogeneous mixtures. Like solutions, colloids can be gases, liquids, or solids. Examples of each are listed in **Table 13.5**.

Particle size can be used to classify a mixture as colloid or solution. Colloid particles range in diameter from 5 to 1000 nm; solute particles are smaller than 5 nm in diameter. The nanomaterials we saw in Chapter 12, when dispersed in a liquid, are colloids. A colloid particle may even consist of a single giant molecule. The hemoglobin molecule, for example, which carries oxygen in your blood, has molecular dimensions of 6.5 × 5.5 × 5.0 nm and a molar mass of 64,500 g/mol.

TABLE 13.5 Types of Colloids

Phase of Colloid	Dispersing (solvent-like) Substance	Dispersed (solute-like) Substance	Colloid Type	Example
Gas	Gas	Gas	—	None (all are solutions)
Gas	Gas	Liquid	Aerosol	Fog
Gas	Gas	Solid	Aerosol	Smoke
Liquid	Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Liquid	Emulsion	Milk
Liquid	Liquid	Solid	Sol	Paint
Solid	Solid	Gas	Solid foam	Marshmallow
Solid	Solid	Liquid	Solid emulsion	Butter
Solid	Solid	Solid	Solid sol	Ruby glass

Although colloid particles may be so small that the dispersion appears uniform even under a microscope, they are large enough to scatter light. Consequently, most colloids appear cloudy or opaque unless they are very dilute. (For example, homogenized milk is a colloid of fat and protein molecules dispersed in water.) Furthermore, because they scatter light, a light beam can be seen as it passes through a colloidal dispersion (Figure 13.24). This scattering of light by colloidal particles, known as the **Tyndall effect**, makes it possible to see the light beam of an automobile on a dusty dirt road, or the sunlight streaming through trees or clouds. Not all wavelengths are scattered to the same extent. Colors at the blue end of the visible spectrum are scattered more than those at the red end by the molecules and small dust particles in the atmosphere. As a result, our sky appears blue. At sunset, light from the sun travels through more of the atmosphere; blue light is scattered even more, allowing the reds and yellows to pass through and be seen.

Hydrophilic and Hydrophobic Colloids

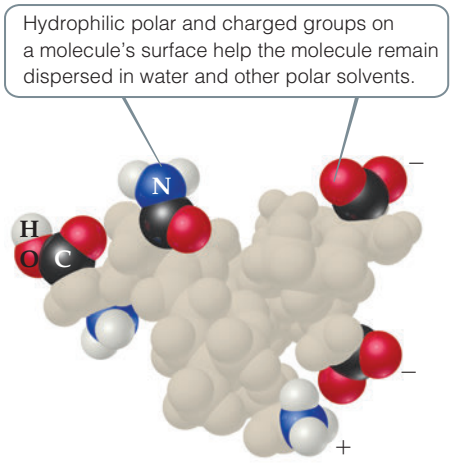
The most important colloids are those in which the dispersing medium is water. These colloids may be **hydrophilic** ("water loving") or **hydrophobic** ("water fearing"). Hydrophilic colloids are most like the solutions that we have previously examined. In the human body, the extremely large protein molecules such as enzymes and antibodies are kept in suspension by interaction with surrounding water molecules. A hydrophilic molecule folds in such a way that its hydrophobic groups are away from the water molecules, on the inside of the folded molecule, while its hydrophilic, polar groups are on



◀ **Figure 13.24 Tyndall effect in the laboratory.** The glass on the right contains a colloidal dispersion; that on the left contains a solution.

Go Figure

What is the chemical composition of the groups that carry a negative charge?

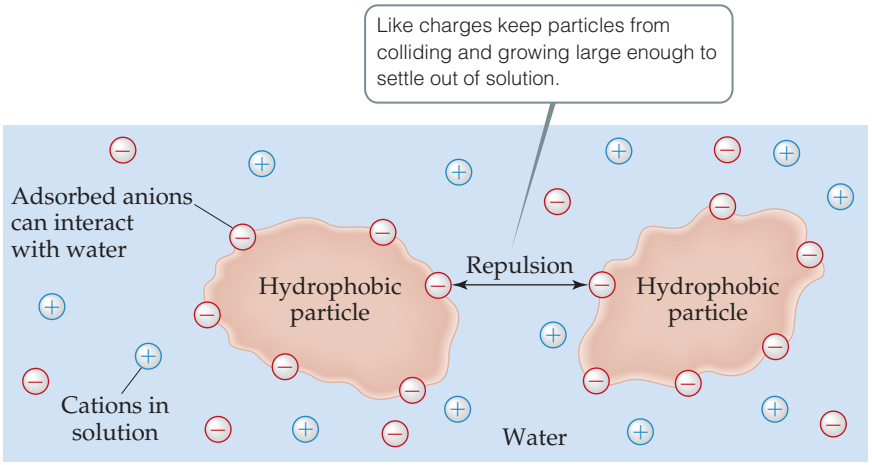


▲ **Figure 13.25 Hydrophilic colloidal particle.** Examples of the hydrophilic groups that help to keep a giant molecule (macromolecule) suspended in water.

the surface, interacting with the water molecules. The hydrophilic groups generally contain oxygen or nitrogen and often carry a charge (**Figure 13.25**).

Hydrophobic colloids can be dispersed in water only if they are stabilized in some way. Otherwise, their natural lack of affinity for water causes them to separate from the water. One method of stabilization involves adsorbing ions on the surface of the hydrophobic particles (**Figure 13.26**). (***Ad****sorption* means to adhere to a surface. It differs from ***ab****sorption*, which means to pass into the interior, as when a sponge absorbs water.) The adsorbed ions can interact with water, thereby stabilizing the colloid. At the same time, the electrostatic repulsion between adsorbed ions on neighboring colloid particles keeps the particles from sticking together rather than dispersing in the water.

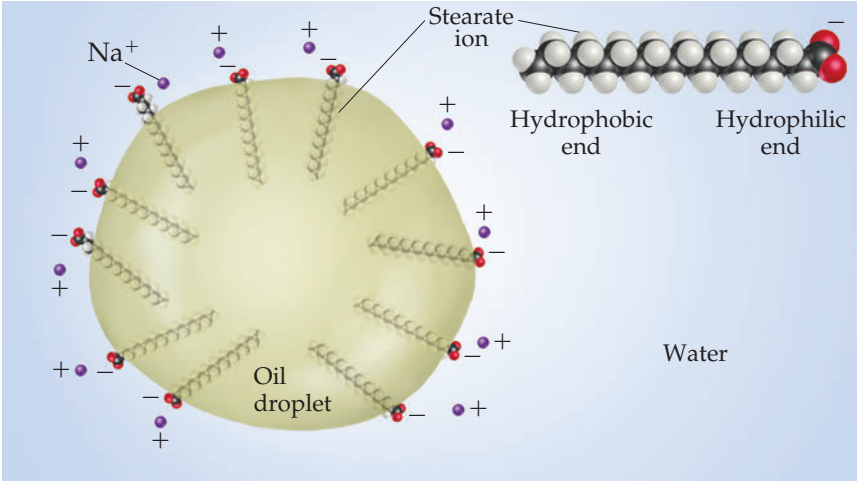
Hydrophobic colloids can also be stabilized by hydrophilic groups on their surfaces. Oil drops are hydrophobic, for example, and they do not remain suspended in water. Instead, they aggregate, forming an oil slick on the water surface. Sodium stearate (**Figure 13.27**), or any similar substance having one end that is hydrophilic (either polar or charged) and one end that is hydrophobic (nonpolar), will stabilize a suspension of oil in water. Stabilization results from the interaction of the hydrophobic ends of the stearate ions with the oil drops and the hydrophilic ends with the water.



▲ **Figure 13.26 Hydrophobic colloids stabilized in water by adsorbed anions.**

Go Figure

Which kind of intermolecular force attracts the stearate ion to the oil drop?

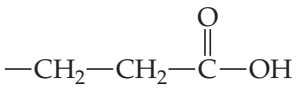


▲ **Figure 13.27 Stabilization of an emulsion of oil in water by stearate ions.**

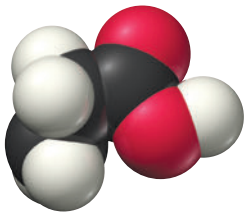
CHEMISTRY AND LIFE Sickle-Cell Anemia

Our blood contains the complex protein hemoglobin, which carries oxygen from the lungs to other parts of the body. In the genetic disease sickle-cell anemia, hemoglobin molecules are abnormal and have a lower solubility in water, especially in their unoxygenated form. Consequently, as much as 85% of the hemoglobin in red blood cells crystallizes out of solution.

The cause of the insolubility is a structural change in one part of an amino acid. Normal hemoglobin molecules contain an amino acid that has a $-CH_2CH_2COOH$ group:

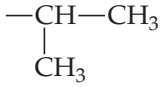


Normal

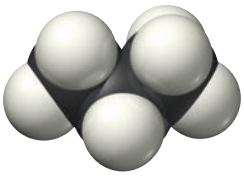


Normal

The polarity of the $-COOH$ group contributes to the solubility of the hemoglobin molecule in water. In the hemoglobin molecules of sickle-cell anemia patients, the $-CH_2CH_2COOH$ chain is absent and in its place is the nonpolar (hydrophobic) $-CH(CH_3)_2$ group:



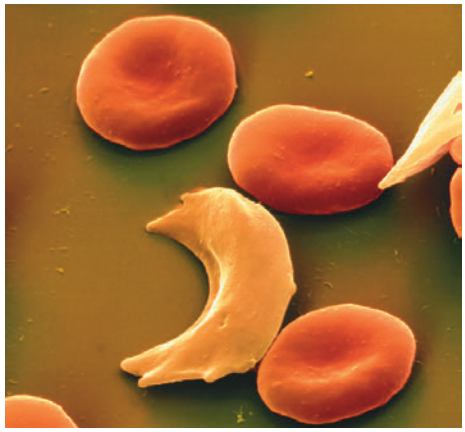
Abnormal



Abnormal

This change leads to the aggregation of the defective form of hemoglobin into particles too large to remain suspended in biological fluids. It also causes the cells to distort into the sickle shape shown in Figure 13.28. The sickled cells tend to clog capillaries, causing severe pain, weakness, and the gradual deterioration of vital organs. The disease is hereditary, and if both parents carry the defective genes, it is likely that their children will possess only abnormal hemoglobin.

You might wonder how it is that a life-threatening disease such as sickle-cell anemia has persisted in humans through evolutionary time. The answer in part is that people with the gene are far less susceptible to malaria. Thus, in tropical climates rife with malaria, those with sickle-cell genes have lower incidence of this debilitating disease.



▲ **Figure 13.28 A scanning electron micrograph of normal (round) and sickle (crescent-shaped) red blood cells.** Normal red blood cells are about 6×10^{-3} mm in diameter.

Colloid stabilization has an interesting application in the human digestive system. When fats in our diet reach the small intestine, a hormone causes the gallbladder to excrete a fluid called bile. Among the components of bile are compounds that have chemical structures similar to sodium stearate; that is, they have a hydrophilic (polar) end and a hydrophobic (nonpolar) end. These compounds emulsify the fats in the intestine and thus permit digestion and absorption of fat-soluble vitamins through the intestinal wall. The term *emulsify* means "to form an emulsion," a suspension of one liquid in another, with milk being one example (Table 13.5). A substance that aids in the formation of an emulsion is called an emulsifying agent. If you read the labels on foods and other materials, you will find that a variety of chemicals are used as emulsifying agents. These chemicals typically have a hydrophilic end and a hydrophobic end.

Colloidal Motion in Liquids

We learned in Chapter 10 that gas molecules move at some average speed that depends inversely on their molar mass, in a straight line, until they collide with something. The *mean free path* is the average distance molecules travel between collisions. Recall also that the kinetic-molecular theory of gases assumes that gas molecules are in continuous, random motion.

Colloidal particles in a solution undergo random motion as a result of collisions with solvent molecules. Because the colloidal particles are massive in comparison with solvent molecules, their movements from any one collision are very tiny. However, there are many such collisions, and they cause a random motion of the entire colloidal particle, called **Brownian motion**. In 1905, Einstein developed an equation for the average square of the displacement of a colloidal particle, a historically very important development. As you might expect, the larger the colloidal particle, the shorter its mean

free path in a given liquid (Table 13.6). Today, the understanding of Brownian motion is applied to diverse problems in everything from cheese-making to medical imaging.

TABLE 13.6 Calculated Mean Free Path, after One Hour, for Uncharged Colloidal Spheres in Water at 20 °C

Radius of sphere, nm	Mean Free Path, mm
1	1.23
10	0.390
100	0.123
1000	0.039

Self-Assessment Exercise

13.36 Potassium ions are transported into the cell through a protein channel in the cell membrane. Which type of groups would be facing the ions to help the ion transport?

(a) Hydrophilic groups
(b) Hydrophobic groups

Exercises

13.37 Choose the best answer: A colloidal dispersion of one liquid in another is called (**a**) a gel, (**b**) an emulsion, (**c**) a foam, (**d**) an aerosol.

13.38 Aerosols are important components of the atmosphere. Does the presence of aerosols in the atmosphere increase or decrease the amount of sunlight that arrives at the Earth's surface, compared to an "aerosol-free" atmosphere? Explain your reasoning.

13.39 Soaps consist of compounds such as sodium stearate, $CH_3(CH_2)_{16}COO^-Na^+$, that have both hydrophobic and hydrophilic parts. Consider the hydrocarbon part of sodium stearate to be the "tail" and the charged part to be the "head."

(**a**) Which part of sodium stearate, head or tail, is more likely to be solvated by water?

(**b**) Grease is a complex mixture of (mostly) hydrophobic compounds. Which part of sodium stearate, head or tail, is most likely to bind to grease?

(**c**) If you have large deposits of grease that you want to wash away with water, you can see that adding sodium stearate will help you produce an emulsion. What intermolecular interactions are responsible for this?

Answers to Self-Assessment Exercises

13.36 (a)

Sample Integrative Exercise

Putting Concepts Together

A 0.100 L solution is made by dissolving 0.441 g of $CaCl_2(s)$ in water. (**a**) Calculate the osmotic pressure of this solution at 27 °C, assuming that it is completely dissociated into its component ions. (**b**) The measured osmotic pressure of this solution is 259.4 kPa at 27 °C. Explain why it is less than the value calculated in (a), and calculate the van't Hoff factor, *i*, for the solute in this solution. (**c**) The enthalpy of solution for $CaCl_2$ is $\Delta H = -81.3$ kJ/mol. If the final temperature of the solution is 27 °C, what was its initial temperature? (Assume that the density of the solution is 1.00 g/mL, that its specific heat is 4.18 J/g K, and that the solution loses no heat to its surroundings.)

SOLUTION

(**a**) The osmotic pressure is given by Equation 13.14, $\Pi = iMRT$. We know the temperature, $T = 27\ ^\circ C = 300$ K, and the gas constant, $R = 8.314\ m^3\ Pa/mol\ K$. We can calculate the molarity of the solution from the mass of $CaCl_2$ and the volume of the solution:

$$\text{Molarity} = \left(\frac{0.441\ \text{g}\ CaCl_2}{0.100\ \text{L}}\right)\left(\frac{1\ \text{mol}\ CaCl_2}{110\ \text{g}\ CaCl_2}\right)$$

$$= 0.0397\ \text{mol}\ CaCl_2/\text{L}$$

Soluble ionic compounds are strong electrolytes. Thus, $CaCl_2$ consists of metal cations (Ca^{2+}) and nonmetal anions (Cl^-). When completely dissociated, each $CaCl_2$ unit forms three ions (one Ca^{2+} and two Cl^-). Hence, the calculated osmotic pressure is:

$$\Pi = iMRT = (3)(0.0397\ \text{mol/L})(8.314\ \text{m}^3\,\text{Pa/mol K})(300\ \text{K}) = 297\ \text{kPa}$$

(b) The actual values of colligative properties of electrolytes are less than those calculated because the electrostatic interactions between ions limit their independent movements. In this case, the van't Hoff factor, which measures the extent to which electrolytes actually dissociate into ions, is given by:

$$i = \frac{\Pi(\text{measured})}{\Pi(\text{calculated for nonelectrolyte})}$$

Thus, the solution behaves as if the $CaCl_2$ has dissociated into 2.62 particles instead of the ideal 3.

$$= \frac{259.4\ \text{kPa}}{(0.0397\ \text{mol/L})(8.314\ \text{m}^3\,\text{Pa/mol K})(300\ \text{K})} = 2.62$$

(c) If the solution is 0.0397 *M* in $CaCl_2$ and has a total volume of 0.100 L, the number of moles of solute is:

$$(0.100\ \text{L})(0.0397\ \text{mol/L}) = 0.00397\ \text{mol}$$

Hence, the quantity of heat generated in forming the solution is:

$$(0.00397\ \text{mol})(-81.3\ \text{kJ/mol}) = -0.323\ \text{kJ}$$

The solution absorbs this heat, causing its temperature to increase. The relationship between temperature change and heat is given by Equation 5.22:

$$q = (\text{specific heat})(\text{grams})(\Delta T)$$

The heat absorbed by the solution is $q = +0.323\ \text{kJ} = 323\ \text{J}$. The mass of the 0.100 L of solution is $(100\ \text{mL})(1.00\ \text{g/mL}) = 100\ \text{g}$ (to three significant figures). Thus, the temperature change is:

$$\Delta T = \frac{q}{(\text{specific heat of solution})(\text{grams of solution})}$$

$$= \frac{323\ \text{J}}{(4.18\ \text{J/g K})(100\ \text{g})} = 0.773\ \text{K}$$

A kelvin has the same size as a degree Celsius. Because the solution temperature increases by 0.773 °C, the initial temperature was:

$$27.0\,^\circ\text{C} - 0.773\,^\circ\text{C} = 26.2\,^\circ\text{C}$$

Chapter Summary and Key Terms

THE SOLUTION PROCESS (SECTION 13.1) Solutions form when one substance disperses uniformly throughout another. The attractive interaction of solvent molecules with solute is called **solvation**. When the solvent is water, the interaction is called **hydration**. The dissolution of ionic substances in water is promoted by hydration of the separated ions by the polar water molecules. The overall enthalpy change upon solution formation may be either positive or negative. Solution formation is favored both by a positive entropy change, corresponding to an increased dispersal of the components of the solution, and by a negative enthalpy change, indicating an exothermic process.

SATURATED SOLUTIONS AND SOLUBILITY (SECTION 13.2) The equilibrium between a saturated solution and undissolved solute is dynamic; the process of solution and the reverse process, **crystallization,** occur simultaneously. In a solution in equilibrium with undissolved solute, the two processes occur at equal rates, giving a **saturated** solution. If there is less solute present than is needed to saturate the solution, the solution is **unsaturated**. When solute concentration is greater than the equilibrium concentration value, the solution is **supersaturated**. This is an unstable condition, and separation of some solute from the solution will occur if the process is initiated with a solute seed crystal. The amount of solute needed to form a saturated solution at any particular temperature is the **solubility** of that solute at that temperature.

FACTORS AFFECTING SOLUBILITY (SECTION 13.3) The solubility of one substance in another depends on the tendency of systems to become more random, by becoming more dispersed in space, and on the relative intermolecular solute–solute and solvent–solvent energies compared with solute–solvent interactions. Polar and ionic solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents ("like dissolves like"). Liquids that mix in all proportions are **miscible**; those that do not dissolve significantly in one another are **immiscible**. Hydrogen-bonding interactions between solute and solvent often play an important role in determining solubility; for example, ethanol and water, whose molecules form hydrogen bonds with each other, are miscible. The solubilities of gases in a liquid are generally proportional to the pressure of the gas over the solution, as expressed by **Henry's law**: $S_g = kP_g$. The solubilities of most solid solutes in water increase as the temperature of the solution increases. In contrast, the solubilities of gases in water generally decrease with increasing temperature.

EXPRESSING SOLUTION CONCENTRATIONS (SECTION 13.4) Concentrations of solutions can be expressed quantitatively by several different measures, including **mass percentage** [(mass solute/mass solution) × 100] **parts per million (ppm), parts per billion (ppb),** and mole fraction. Molarity, *M,* is defined as moles of solute per liter of solution; **molality**, *m*, is defined as moles of solute per kilogram of solvent. Molarity can be converted to these other concentration units if the density of the solution is known.

COLLIGATIVE PROPERTIES (SECTION 13.5) A physical property of a solution that depends on the concentration of solute particles present, regardless of the nature of the solute, is a **colligative property**. Colligative properties include vapor–pressure lowering, freezing-point lowering, boiling-point elevation, and osmotic pressure. **Raoult's law** expresses the lowering of vapor pressure. An **ideal solution**

obeys Raoult's law. Differences in solvent–solute as compared with solvent–solvent and solute–solute intermolecular forces cause many solutions to depart from ideal behavior.

A solution containing a nonvolatile solute possesses a higher boiling point than the pure solvent. The **molal boiling-point-elevation constant**, K_b, represents the increase in boiling point for a 1 m solution of solute particles as compared with the pure solvent. Similarly, the **molal freezing-point-depression constant,** K_f, measures the lowering of the freezing point of a solution for a 1 m solution of solute particles. The temperature changes are given by the equations $\Delta T_b = iK_b m$ and $\Delta T_f = -iK_f m$ where i is the **van't Hoff factor**, which represents how many particles the solute breaks up into in the solvent. When NaCl dissolves in water, two moles of solute particles are formed for each mole of dissolved salt. The boiling point or freezing point is thus elevated or depressed, respectively, approximately twice as much as that of a nonelectrolyte solution of the same concentration. Similar considerations apply to other strong electrolytes.

Osmosis is the movement of solvent molecules through a semipermeable membrane from a less concentrated to a more concentrated solution. This net movement of solvent generates an **osmotic pressure**, Π, which can be measured in units of gas pressure, such as atm. The osmotic pressure of a solution is proportional to the solution molarity: $\Pi = iMRT$. Osmosis is a very important process in living systems, in which cell walls act as semipermeable membranes, permitting the passage of water but restricting the passage of ionic and macromolecular components.

COLLOIDS (SECTION 13.6) Particles that are large on the molecular scale but still small enough to remain suspended indefinitely in a solvent system form **colloids**, or **colloidal dispersions**. Colloids, which are intermediate between solutions and heterogeneous mixtures, have many practical applications. One useful physical property of colloids, the scattering of visible light, is referred to as the **Tyndall effect**. Aqueous colloids are classified as **hydrophilic** or **hydrophobic**. Hydrophilic colloids are common in living organisms, in which large molecular aggregates (enzymes, antibodies) remain suspended because they have many polar, or charged, atomic groups on their surfaces that interact with water. Hydrophobic colloids, such as small droplets of oil, may remain in suspension through adsorption of charged particles on their surfaces.

Colloids undergo **Brownian motion** in liquids, analogous to the random three-dimensional motion of gas molecules.

Learning Outcomes After studying this chapter, you should be able to:

- Describe how enthalpy and entropy changes affect solution formation. (Section 13.1) *Related Exercises: 13.6, 13.40, 13.56*
- Describe the relationship between intermolecular forces and solubility, including use of the "like dissolves like" rule. (Sections 13.1 and 13.3) *Related Exercises: 13.3, 13.53*
- Describe the role of equilibrium in the solution process and its relationship to the solubility of a solute. (Section 13.2) *Related Exercises: 13.8, 13.57*
- Describe the effect of temperature on the solubility of solids and gases in liquids. (Section 13.3) *Related Exercises: 13.16, 13.63*
- Describe the relationship between the partial pressure of a gas and its solubility. (Section 13.3) *Related Exercises: 13.16*
- Calculate the concentration of a solution in terms of molarity, molality, mole fraction, percent composition, and parts per million and be able to interconvert between them. (Section 13.4) *Related Exercises: 13.22, 13.69*
- Describe what a colligative property is and explain the van't Hoff factor. (Section 13.5) *Related Exercises: 13.28, 13.78, 13.83, 13.84*
- Calculate the vapor pressure of a solvent over a solution. (Section 13.5) *Related Exercises: 13.79, 13.81*
- Calculate the boiling-point elevation and freezing-point depression of a solution. (Section 13.5) *Related Exercises: 13.32, 13.86*
- Calculate the osmotic pressure of a solution. (Section 13.5) *Related Exercises: 13.33, 13.89*
- Use colligative properties of solutions to calculate molar masses of solutes. (Section 13.5) *Related Exercises: 13.34, 13.90*
- Explain the difference between a solution and a colloid. (Section 13.6) *Related Exercises: 13.37, 13.94*
- Explain how hydrophilic and hydrophobic colloids can be stabilized in water. (Section 13.6) *Related Exercises: 13.39, 13.95*

Key Equations

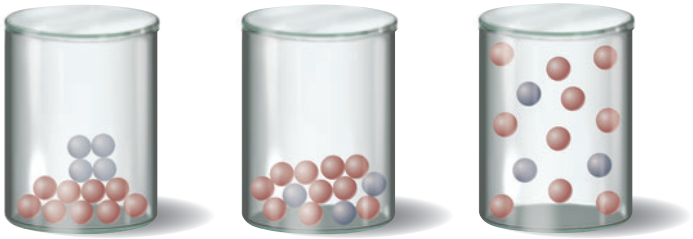
• $S_g = kP_g$	[13.4]	Henry's law, which relates gas solubility to partial pressure
• $\text{Mass \% of component} = \dfrac{\text{mass of component in soln}}{\text{total mass of soln}} \times 100$	[13.5]	Concentration in terms of mass percent
• $\text{ppm of component} = \dfrac{\text{mass of component in soln}}{\text{total mass of soln}} \times 10^6$	[13.6]	Concentration in terms of parts per million (ppm)
• $\text{Mole fraction of component} = \dfrac{\text{moles of component}}{\text{total moles of all components}}$	[13.7]	Concentration in terms of mole fraction
• $\text{Molarity} = \dfrac{\text{moles of solute}}{\text{liters of soln}}$	[13.8]	Concentration in terms of molarity
• $\text{Molality} = \dfrac{\text{moles of solute}}{\text{kilograms of solvent}}$	[13.9]	Concentration in terms of molality
• $P_{solution} = X_{solvent}P^\circ_{solvent}$	[13.10]	Raoult's law, calculating vapor pressure of solvent above a solution
• $\Delta T_b = iK_b m$	[13.12]	The boiling-point elevation of a solution

- $\Delta T_f = -iK_f m$ [13.13] The freezing-point depression of a solution
- $\Pi = i\left(\frac{n}{V}\right)RT = iMRT$ [13.14] The osmotic pressure of a solution

Exercises

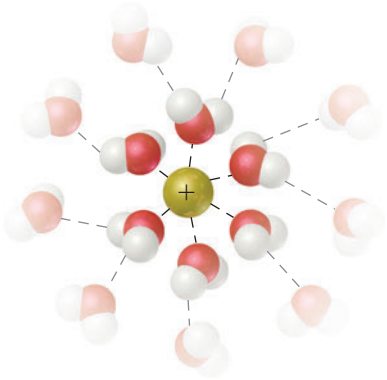
Visualizing Concepts

13.40 Rank the contents of the following containers in order of increasing entropy: [Section 13.1]



(a) (b) (c)

13.41 This figure shows the interaction of a cation with surrounding water molecules.



(**a**) Which atom of water is associated with the cation? Explain.

(**b**) Which of the following explanations accounts for the fact that the ion–solvent interaction is greater for Li^+ than for K^+?

a. Li^+ is of lower mass than K^+.
b. The ionization energy of Li is higher than that for K.
c. Li^+ has a smaller ionic radius than K^+.
d. Li has a lower density than K.
e. Li reacts with water more slowly than K. [Section 13.1]

13.42 Consider two ionic solids, both composed of singly charged ions, that have different lattice energies. (**a**) Will the solids have the same solubility in water? (**b**) If not, which solid will be more soluble in water, the one with the larger lattice energy or the one with the smaller lattice energy? Assume that solute–solvent interactions are the same for both solids. [Section 13.1]

13.43 Which *two* statements about gas mixtures are true? [Section 13.1]

(**a**) Gases always mix with other gases because the gas particles are too far apart to feel significant intermolecular attractions or repulsions.

(**b**) Just like water and oil don't mix in the liquid phase, two gases can be immiscible and not mix in the gas phase.

(**c**) If you cool a gaseous mixture, you will liquefy all the gases at the same temperature.

(**d**) Gases mix in all proportions in part because the entropy of the system increases upon doing so.

13.44 Which of the following is the best representation of a saturated solution? Explain your reasoning. [Section 13.2]



(a) (b) (c)

13.45 If you compare the solubilities of the noble gases in water, you find that solubility increases from smallest atomic weight to largest, Ar < Kr < Xe. Which of the following statements is the best explanation? [Section 13.3]

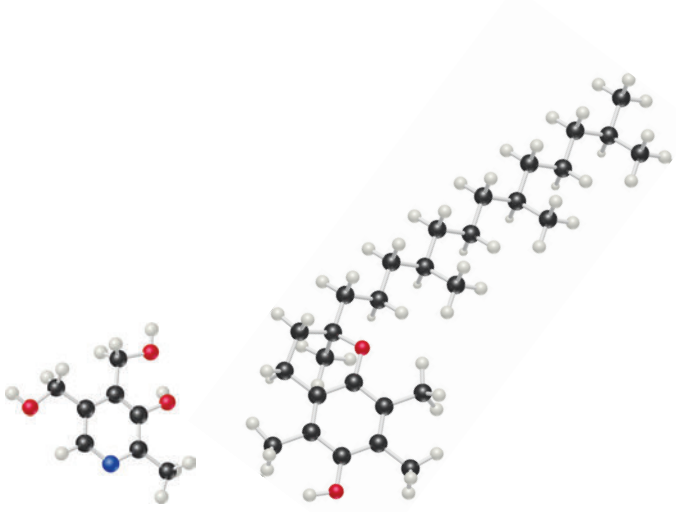
(**a**) The heavier the gas, the more it sinks to the bottom of the water and leaves room for more gas molecules at the top of the water.

(**b**) The heavier the gas, the more dispersion forces it has, and, therefore, the more attractive interactions it has with water molecules.

(**c**) The heavier the gas, the more likely it is to hydrogen-bond with water.

(**d**) The heavier the gas, the more likely it is to make a saturated solution in water.

13.46 The structures of vitamins E and B_6 are shown here. Predict which is more water soluble and which is more fat soluble. [Section 13.3]



Vitamin B_6 Vitamin E

13.47 You take a sample of water that is at room temperature and in contact with air and put it under a vacuum. Right away, you see bubbles leave the water, but after a little while, the bubbles stop. As you keep applying the vacuum, more bubbles appear. A friend tells you that the first bubbles were water vapor, and the low pressure had reduced the boiling point of water, causing the water to boil. Another friend tells you that the first bubbles were gas molecules from the air (oxygen, nitrogen, and so forth) that were dissolved in the water. Which friend is mostly likely to be correct? What, then, is responsible for the second batch of bubbles? [Section 13.4]

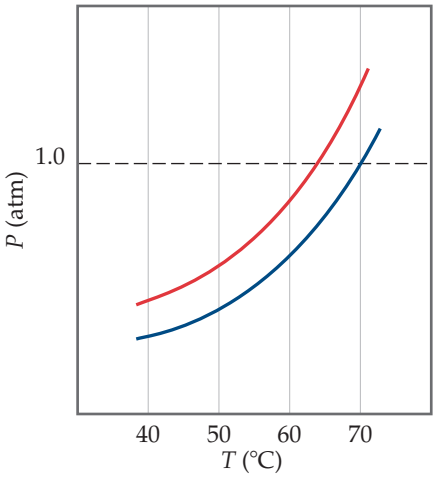
13.48 The figure shows two identical volumetric flasks containing the same solution at two temperatures.

(**a**) Does the molarity of the solution change with the change in temperature?

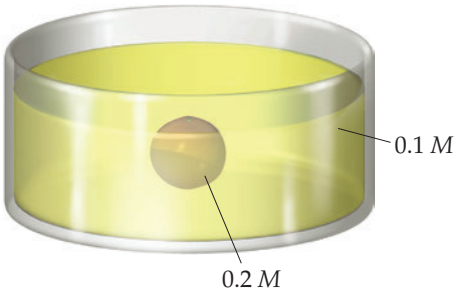
(**b**) Does the molality of the solution change with the change in temperature? [Section 13.4]



13.49 This portion of a phase diagram shows the vapor–pressure curves of a volatile solvent and of a solution of that solvent containing a nonvolatile solute. (**a**) Which line represents the solution? (**b**) What are the normal boiling points of the solvent and the solution? [Section 13.5]

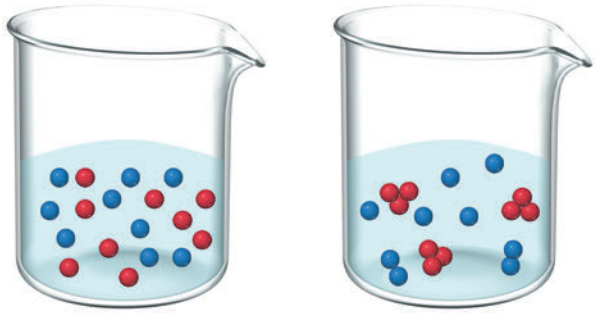


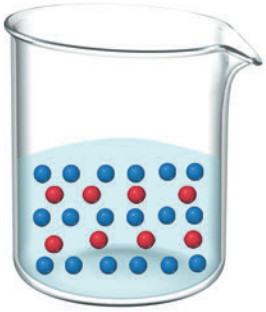
13.50 Suppose you had a balloon made of some highly flexible semipermeable membrane. The balloon is filled completely with a 0.2 *M* solution of some solute and is submerged in a 0.1 *M* solution of the same solute:



Initially, the volume of solution in the balloon is 0.25 L. Assuming the volume outside the semipermeable membrane is large, as the illustration shows, what would you expect for the solution volume inside the balloon once the system has come to equilibrium through osmosis? [Section 13.5]

13.51 Which diagram best represents a liquid–liquid emulsion such as milk? The colored balls represent different liquid molecules. [Section 13.6]





The Solution Process (Section 13.1)

13.52 Indicate whether each statement is true or false:

(**a**) A solute will dissolve in a solvent if solute–solute interactions are stronger than solute–solvent interactions.

(**b**) In making a solution, the enthalpy of mixing is always a positive number.

(**c**) An increase in entropy favors mixing.

13.53 Indicate the type of solute–solvent interaction that should be most important in each of the following solutions: (**a**) CCl_4 in benzene (C_6H_6), (**b**) methanol (CH_3OH) in water, (**c**) KBr in water, (**d**) HCl in acetonitrile (CH_3CN).

13.54 When ammonium chloride dissolves in water, the solution becomes colder. (**a**) Is the solution process exothermic or endothermic? (**b**) Why does the solution form?

13.55 (**a**) In Equation 13.1, which of the enthalpy terms for dissolving an ionic solid would correspond to the lattice energy? (**b**) Which energy term in this equation is always exothermic?

13.56 KBr is relatively soluble in water, yet its enthalpy of solution is +19.8 kJ/mol. Which of the following statements provides the best explanation for this behavior?

(**a**) Potassium salts are always soluble in water.

(**b**) The entropy of mixing must be unfavorable.

(**c**) The enthalpy of mixing must be small compared to the enthalpies for breaking up water–water interactions and K–Br ionic interactions.

(**d**) KBr has a high molar mass compared to other salts like NaCl.

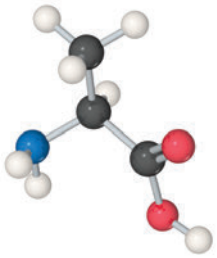
Saturated Solutions; Factors Affecting Solubility (Sections 13.2 and 13.3)

13.57 The solubility of alum, $KAl(SO_4)_2 \cdot 12\,H_2O$, in water at is 44 g per 100 g of water at 50 °C. A solution of alum in water at 80 °C is formed by dissolving 130 g in 100 g of water. When this solution is slowly cooled to 50 °C, no precipitate forms. (**a**) Is the solution that has cooled down to 50 °C unsaturated, saturated, or supersaturated? (**b**) You take a metal spatula and scratch the side of the glass vessel that contains this cooled solution, and crystals start to appear. What has just happened? (**c**) At equilibrium, what mass of crystals do you expect to form?

13.58 By referring to Figure 13.14, determine whether the addition of 50.0 g of each of the following ionic solids to 100 g of water at 20 °C will lead to a saturated solution: (**a**) NaCl, (**b**) $CaCl_2$, (**c**) KNO_3, (**d**) $NaNO_3$.

13.59 Consider water and glycerol, $CH_2(OH)CH(OH)CH_2OH$. (**a**) Would you expect them to be miscible in all proportions? (**b**) List the intermolecular attractions that occur between a water molecule and a glycerol molecule.

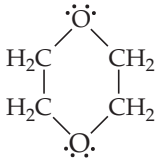
13.60 Would you expect alanine (an amino acid) to be more soluble in water or in hexane?



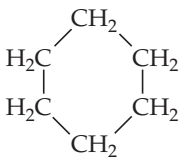
Alanine

13.61 (**a**) Would you expect stearic acid, $CH_3(CH_2)_{16}COOH$, to be more soluble in water or in carbon tetrachloride?

(**b**) Which would you expect to be more soluble in water, cyclohexane or dioxane?



Dioxane



Cyclohexane

13.62 Which of the following in each pair is likely to be more soluble in hexane, C_6H_{14}: (**a**) CCl_4 or $CaCl_2$, (**b**) benzene (C_6H_6) or glycerol, $CH_2(OH)CH(OH)CH_2OH$, (**c**) octanoic acid, $CH_3CH_2CH_2CH_2CH_2CH_2COOH$, or acetic acid, CH_3COOH? Explain your answer in each case.

13.63 Indicate whether each statement is true or false:

(**a**) The higher the temperature, the more soluble most gases are in water.

(**b**) The higher the temperature, the more soluble most ionic solids are in water.

(**c**) As you cool a saturated solution from high temperature to low temperature, solids start to crystallize out of solution if you achieve a supersaturated solution.

(**d**) If you take a saturated solution and raise its temperature, you can (usually) add more solute and make the solution even more concentrated.

13.64 The mole fraction of N_2 in air at sea level is 0.78. Using the data in Table 13.1, together with Henry's law, calculate the molar concentration of N_2 in the surface water of a mountain lake saturated with air at 20 °C and an atmospheric pressure of 86.6 kPa.

Concentrations of Solutions (Section 13.4)

13.65 (**a**) Calculate the mass percentage of $NaNO_3$ in a solution containing 13.6 g of $NaNO_3$ in 834 g of water. (**b**) An alloy contains 2.86 g of chromium per 100 kg of alloy. What is the concentration of chromium in ppm?

13.66 A solution is made containing 50.0 g of ethanol (C_2H_5OH) in 1000 g of H_2O. Calculate (**a**) the mole fraction of C_2H_5OH, (**b**) the mass percent of C_2H_5OH, (**c**) the molality of C_2H_5OH.

13.67 Calculate the molarity of the following aqueous solutions: (**a**) 0.640 g of $Mg(NO_3)_2$ in 500.0 mL of solution, (**b**) 50.0 g of $LiClO_4 \cdot 3\,H_2O$ in 250 mL of solution, (**c**) 125 mL of 3.00 *M* HNO_3 diluted to 1.00 L.

13.68 Calculate the molality of each of the following solutions: (**a**) 10.0 g of benzene (C_6H_6) dissolved in 50.0 g of carbon tetrachloride (CCl_4), (**b**) 5.00 g of NaCl dissolved in 0.100 L of water.

13.69 A sulfuric acid solution containing 697.6 g of H_2SO_4 per liter of solution has a density of 1.395 g/cm^3. Calculate (**a**) the mass percentage, (**b**) the mole fraction, (**c**) the molality, (**d**) the molarity of H_2SO_4 in this solution.

13.70 The density of acetonitrile (CH_3CN) is 0.786 g/mL and the density of methanol (CH_3OH) is 0.791 g/mL. A solution is made by dissolving 25.0 mL of CH_3OH in 100 mL of CH_3CN. (**a**) What is the mole fraction of methanol in the solution? (**b**) What is the molality of the solution? (**c**) Assuming that the volumes are additive, what is the molarity of CH_3OH in the solution?

13.71 The density of toluene (C_7H_8) is 0.867 g/mL, and the density of thiophene (C_4H_4S) is 1.065 g/mL. A solution is made by dissolving 8.10 g of thiophene in 250.0 mL of toluene. (**a**) Calculate the mole fraction of thiophene in the solution. (**b**) Calculate the molality of thiophene in the solution. (**c**) Assuming that the volumes of the solute and solvent are additive, what is the molarity of thiophene in the solution?

13.72 Calculate the number of moles of solute present in each of the following aqueous solutions: (**a**) 750 mL of 0.120 *M* $SrBr_2$, (**b**) 70.0 g of 0.200 *m* KCl, (**c**) 150.0 g of a solution that is 5.75% glucose ($C_6H_{12}O_6$) by mass.

13.73 Describe how you would prepare each of the following aqueous solutions, starting with solid KBr: (**a**) 0.75 L of 1.5×10^{-2} *M* KBr, (**b**) 125 g of 0.180 *m* KBr, (**c**) 1.85 L of a solution that is 12.0% KBr by mass (the density of the solution is 1.10 g/mL), (**d**) a 0.150 *M* solution of KBr that contains just enough KBr to precipitate 16.0 g of AgBr from a solution containing 0.480 mol of $AgNO_3$.

13.74 Describe how you would prepare each of the following aqueous solutions: (**a**) 1.50 L of 0.110 *M* $(NH_4)_2SO_4$ solution, starting with solid $(NH_4)_2SO_4$; (**b**) 225 g of a solution that is 0.65 *m* in Na_2CO_3, starting with the solid solute; (**c**) 1.20 L of a solution that is 15.0% $Pb(NO_3)_2$ by mass (the density of the solution is 1.16 g/mL), starting with solid solute; (**d**) a 0.50 *M* solution of HCl that would just neutralize 5.5 g of $Ba(OH)_2$ starting with 6.0 *M* HCl.

13.75 Commercial aqueous nitric acid has a density of 1.12 g/mL and is 3.7 *M*. Calculate the percent HNO_3 by mass in the solution.

13.76 Brass is a substitutional alloy consisting of a solution of copper and zinc. A particular sample of yellow brass consisting of 65.0 % Cu and 35.0 % Zn by mass has a density of 8470 kg/m^3. (**a**) What is the molality of Zn in the solid solution? (**b**) What is the molarity of Zn in the solution?

13.77 During a person's typical breathing cycle, the CO_2 concentration in the expired air rises to a peak of 4.6% by volume. (**a**) Calculate the partial pressure of the CO_2 in the expired air at its peak, assuming 101.3 kPa pressure and a body temperature of 37 °C. (**b**) What is the molarity of the CO_2 in the expired air at its peak, assuming a body temperature of 37 °C?

Colligative Properties (Section 13.5)

13.78 You make two solutions of a nonvolatile solute with a liquid solvent, 0.01 *M* and 1.00 *M*. Indicate whether each of the following statements is true or false. (**a**) The vapor pressure of the concentrated solution is higher than that of the diluted solution. (**b**) The osmotic pressure of the concentrated solution is higher than that of the diluted solution. (**c**) The boiling point of the concentrated solution is higher than that of the diluted solution. (**d**) The freezing point of the concentrated solution is higher than that of the diluted solution.

13.79 Consider two solutions, one formed by adding 150 g of glucose $(C_6H_{12}O_6)$ to 1 L of water and the other formed by adding 150 g of sucrose $(C_{12}H_{22}O_{11})$ to 1 L of water. Calculate the vapor pressure for each solution at 25 °C; the vapor pressure of pure water at this temperature is 3.17 kPa.

13.80 The vapor pressure of pure water at 70 °C is 31.2 kPa. The vapor pressure of water over a solution at 70 °C containing equal numbers of moles of water and glycerol $(C_3H_5(OH)_3$, a nonvolatile solute) is 13.3 kPa. Is the solution ideal according to Raoult's law?

13.81 (**a**) Calculate the vapor pressure of water above a solution prepared by adding 22.5 g of lactose $(C_{12}H_{22}O_{11})$ to 200.0 g of water at 338 K. (Vapor–pressure data for water are given in Appendix B.) (**b**) Calculate the mass of propene glycol $(C_3H_8O_2)$ that must be added to 0.340 kg of water to reduce the vapor pressure by 384 Pa at 40 °C.

13.82 At 20 °C, the vapor pressure of benzene (C_6H_6) is 10 kPa, and that of toluene (C_7H_8) is 2.9 kPa. Assume that benzene and toluene form an ideal solution. (**a**) What is the composition in mole fraction of a solution that has a vapor pressure of 4.7 kPa at 20 °C? (**b**) What is the mole fraction of benzene in the vapor above the solution described in part (a)?

13.83 (**a**) Does a 0.10 *m* aqueous solution of KCl have a higher freezing point, a lower freezing point, or the same freezing point as a 0.10 *m* aqueous solution of urea $(CO(NH_2)_2)$, (**b**) The experimental freezing point of the KCl solution is higher than that calculated assuming that KCl is completely dissociated in solution. Why is this the case?

13.84 Arrange the following aqueous solutions, each 10% by mass in solute, in order of increasing boiling point: glucose $(C_6H_{12}O_6)$, sucrose $(C_{12}H_{22}O_{11})$, sodium nitrate $(NaNO_3)$.

13.85 List the following aqueous solutions in order of increasing boiling point: 0.080 *M* KBr, 0.130 *M* urea $(CO(NH_2)_2)$, 0.080 *M* $Mg(NO_2)_2$.

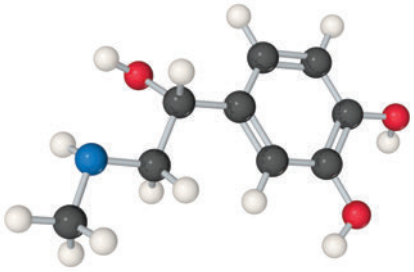
13.86 Using data from Table 13.3, calculate the freezing and boiling points of each of the following solutions: (**a**) 0.22 *m* glycerol $(C_3H_8O_3)$ in ethanol, (**b**) 0.240 mol of naphthalene $(C_{10}H_8)$ in 2.45 mol of chloroform, (**c**) 1.50 g NaCl in 0.250 kg of water, (**d**) 2.04 g KBr and 4.82 g glucose $(C_6H_{12}O_6)$ in 188 g of water.

13.87 How many grams of ethylene glycol $(C_2H_6O_2)$ must be added to 2.00 kg of water to produce a solution that freezes at −10.00 °C?

13.88 What is the freezing point of an aqueous solution that boils at 105.0 °C?

13.89 What is the osmotic pressure formed by dissolving 50.0 mg of acetylsalicylic acid $(C_9H_8O_4)$ in 0.100 L of water at 37 °C?

13.90 Adrenaline is the hormone that triggers the release of extra glucose molecules in times of stress or emergency. A solution of 0.64 g of adrenaline in 36.0 g of CCl_4 elevates the boiling point by 0.49 °C. Calculate the approximate molar mass of adrenaline from this data.



Adrenaline

13.91 Lauryl alcohol is obtained from coconut oil and is used to make detergents. A solution of 5.00 g of lauryl alcohol in 0.100 kg of benzene freezes at 4.1 °C. What is the molar mass of lauryl alcohol from this data?

13.92 A dilute aqueous solution of fructose in water is formed by dissolving 1.25 g of the compound in water to form 0.150 L of solution. The resulting solution has an osmotic pressure of 112.8 kPa at 20 °C. Assuming that the organic compound is a nonelectrolyte, what is its molar mass?

13.93 The osmotic pressure of a 0.010 *M* aqueous solution of $CaCl_2$ is found to be 68.3 kPa at 25 °C. Calculate the van't Hoff factor, *i*, for the solution.

Colloids (Section 13.6)

13.94 (**a**) Do colloids made only of gases exist? Why or why not? (**b**) In the 1850s, Michael Faraday prepared ruby-red colloids of gold nanoparticles in water that are still stable today. These brightly colored colloids look like solutions. What experiment(s) could you do to determine whether a given colored preparation is a solution or colloid?

13.95 An "emulsifying agent" is a compound that helps stabilize a hydrophobic colloid in a hydrophilic solvent (or a hydrophilic colloid in a hydrophobic solvent). Which of the following choices is the best emulsifying agent? (**a**) CH_3COOH, (**b**) $CH_3CH_2CH_2COOH$, (**c**) $CH_3(CH_2)_{11}COOH$, (**d**) $CH_3(CH_2)_{11}COONa$.

13.96 Proteins can be precipitated out of aqueous solution by the addition of an electrolyte; this process is called "salting out" the protein. (**a**) Do you think that all proteins would be precipitated out to the same extent by the same concentration of the same electrolyte? (**b**) If a protein has been salted out, are the protein–protein interactions stronger or weaker than they were before the electrolyte was added? (**c**) A friend of yours who is taking a biochemistry class says that salting out works because the waters of hydration that surround the protein prefer to surround the electrolyte as

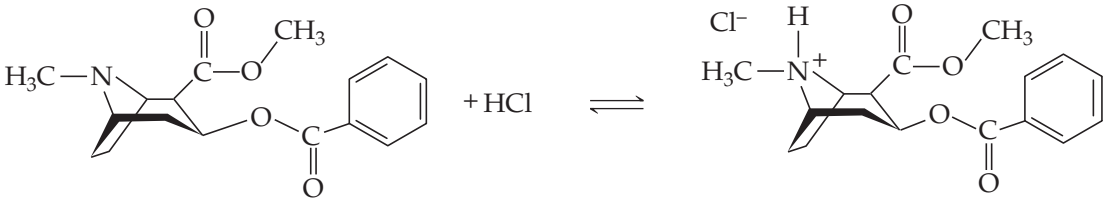
the electrolyte is added; therefore, the protein's hydration shell is stripped away, leading to protein precipitation. Another friend of yours in the same biochemistry class says that salting out works because the incoming ions adsorb tightly to the protein, making ion pairs on the protein surface, which end up giving the protein a zero net charge in water and therefore leading to precipitation. Discuss these two hypotheses. What kind of measurements would you need to make to distinguish between these two hypotheses?

Additional Exercises

13.97 The "free-base" form of cocaine ($C_{17}H_{21}NO_4$) and its protonated hydrochloride form ($C_{17}H_{22}ClNO_4$) are shown here; the free-base form can be converted to the hydrochloride form with one equivalent of HCl. For clarity, not all the carbon and hydrogen atoms are shown; each vertex represents a carbon atom with the appropriate number of hydrogen atoms so that each carbon makes four bonds to other atoms.

(**a**) One of these forms of cocaine is relatively water-soluble: which form, the free base or the hydrochloride?

(**b**) One of these forms of cocaine is relatively insoluble in water: which form, the free base or the hydrochloride?



Cocaine
(Free base)

Cocaine hydrochloride

(**c**) The free-base form of cocaine has a solubility of 1.00 g in 6.70 mL ethanol (CH_3CH_2OH). Calculate the molarity of a saturated solution of the free-base form of cocaine in ethanol.

(**d**) The hydrochloride form of cocaine has a solubility of 1.00 g in 0.400 mL water. Calculate the molarity of a saturated solution of the hydrochloride form of cocaine in water.

(**e**) How many mL of a concentrated 18.0 *M* HCl aqueous solution would it take to convert 1.00 kilograms (a "kilo") of the free-base form of cocaine into its hydrochloride form?

13.98 A supersaturated solution of sucrose ($C_{12}H_{22}O_{11}$) is made by dissolving sucrose in hot water and slowly letting the solution cool to room temperature. After a long time, the excess sucrose crystallizes out of the solution. Indicate whether each of the following statements is true or false:

(**a**) After the excess sucrose has crystallized out, the remaining solution is saturated.

(**b**) After the excess sucrose has crystallized out, the system is now unstable and is not in equilibrium.

(**c**) After the excess sucrose has crystallized out, the rate of sucrose molecules leaving the surface of the crystals to be hydrated by water is equal to the rate of sucrose molecules in water attaching to the surface of the crystals.

13.99 Some soft drinks contain up to 85 ppm oxygen. (**a**) What is this concentration in mol/L? (**b**) What partial pressure of O_2 above water is needed to obtain 85 ppm O_2 in water at 10 °C? (The Henry's law constant for O_2 at this temperature is 1.69×10^{-5} mol/m^3 Pa.)

13.100 The presence of the radioactive gas radon (Rn) in well water presents a possible health hazard in parts of the United States. (**a**) Assuming that the solubility of radon in water with 15.2 kPa pressure of the gas over the water at 30 °C is 0.109 *M*, what is the Henry's law constant for radon in water at this temperature? (**b**) A sample consisting of various gases contains 4.5-ppm radon (mole fraction). This gas at a total pressure of 5.07 MPa is shaken with water at 30 °C. Calculate the molar concentration of radon in the water.

13.101 Glucose makes up about 0.10% by mass of human blood. Calculate this concentration in (**a**) ppm, (**b**) molality. (**c**) What further information would you need to determine the molarity of the solution?

13.102 The maximum allowable concentration of lead in drinking water is 9.0 ppb. (**a**) Calculate the molarity of lead in a 9.0-ppb solution. (**b**) How many grams of lead are in a swimming pool containing 9.0 ppb lead in 60 m^3 of water?

13.103 Acetonitrile (CH_3CN) is a polar organic solvent that dissolves a wide range of solutes, including many salts. The density of a 1.80 *M* LiBr solution in acetonitrile is 0.826 g/cm^3. Calculate the concentration of the solution in (**a**) molality, (**b**) mole fraction of LiBr, (**c**) mass percentage of CH_3CN.

13.104 A "canned heat" product used to warm buffet dishes consists of a homogeneous mixture of ethanol (C_2H_5OH) and paraffin, which has an average formula of $C_{24}H_{50}$. What mass of C_2H_5OH should be added to 620 kg of the paraffin to produce 1.07 kPa of ethanol vapor pressure at 35 °C? The vapor pressure of pure ethanol at 35 °C is 13.3 kPa.

13.105 A solution contains 0.50 mol H_2O and an unknown number of moles of sodium chloride. The vapor pressure of the solution at 29 °C is 3.85 kPa. The vapor pressure of pure water at this temperature is 4.05 kPa. Calculate the number of grams of sodium chloride in the solution. (*Hint*: Remember that sodium chloride is a strong electrolyte.)

13.106 Two beakers are placed in a sealed box at 25 °C. One beaker contains 50.0 mL of a 0.050 *M* aqueous solution of a NaCl. The other beaker contains 50.0 mL of a 0.040 *M* aqueous solution of $CaCl_2$. The water vapor pressure of the two solutions reaches equilibrium. (**a**) In which beaker does the solution level rise, and in which one does it fall? (**b**) What are the volumes in the two beakers when equilibrium is attained, assuming ideal behavior?

13.107 The normal boiling point of ethanol, CH_3CH_2OH, is 78.4 °C. When 3.26 g of a soluble nonelectrolyte is dissolved in 100.0 g of ethanol at that temperature, the vapor pressure of the solution is 100 kPa. What is the molar mass of the solute?

13.108 Calculate the freezing point of a 0.100 *m* aqueous solution of K_2SO_4, (**a**) ignoring interionic attractions, and (**b**) taking interionic attractions into consideration by using the van't Hoff factor (Table 13.4).

13.109 Benzene (C_6H_6) boils at 80.1 °C and has a density of 0.876 g/mL. (**a**) When 0.100 mol of a nondissociating

solute is dissolved in 500 mL of C_6H_6, the solution boils at 79.52 °C. What is the molal boiling-point-elevation constant for C_6H_6? (**b**) When 10.0 g of a nondissociating unknown is dissolved in 500 mL of C_6H_6, the solution boils at 79.23 °C. What is the molar mass of the unknown?

13.110 A lithium salt used in lubricating grease has the formula $LiC_nH_{2n+1}O_2$. The salt is soluble in water to the extent of 0.036 g per 100 g of water at 25 °C. The osmotic pressure of this solution is found to be 7.61 kPa. Assuming that molality and molarity in such a dilute solution are the same and that the lithium salt is completely dissociated in the solution, determine an appropriate value of n in the formula for the salt.

Integrative Exercises

13.111 Fluorocarbons (compounds that contain both carbon and fluorine) were, until recently, used as refrigerants. The compounds listed in the following table are all gases at 25 °C, and their solubilities in water at 25 °C and 101.3 kPa fluorocarbon pressure are given as mass percentages. (**a**) For each fluorocarbon, calculate the molality of a saturated solution. (**b**) Which molecular property best predicts the solubility of these gases in water: molar mass, dipole moment, or ability to hydrogen-bond to water? (**c**) Infants born with severe respiratory problems are sometimes given *liquid ventilation*: They breathe a liquid that can dissolve more oxygen than air can hold. One of these liquids is a fluorinated compound, $CF_3(CF_2)_7Br$. The solubility of oxygen in this liquid is 66 mL O_2 per 100 mL liquid. In contrast, air is 21% oxygen by volume. Calculate the moles of O_2 present in an infant's lungs (volume: 15 mL) if the infant takes a full breath of air compared to taking a full "breath" of a saturated solution of O_2 in the fluorinated liquid. Assume a pressure of 101.3 kPa in the lungs.

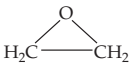
Fluorocarbon	Solubility (mass %)
CF_4	0.0015
$CClF_3$	0.009
CCl_2F_2	0.028
$CHClF_2$	0.30

13.112 At ordinary body temperature (37 °C), the solubility of N_2 in water at ordinary atmospheric pressure is 0.015 g/L. Air is approximately 78 mol % N_2. (**a**) Calculate the number of moles of N_2 dissolved per liter of blood, assuming blood is a simple aqueous solution. (**b**) At a depth of 30.5 m in water, the external pressure is 405 kPa. What is the solubility of N_2 from air in blood at this pressure? (**c**) If a scuba diver suddenly surfaces from this depth, how many milliliters of N_2 gas, in the form of tiny bubbles, are released into the bloodstream from each liter of blood?

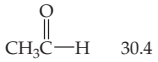
13.113 Consider the following values for enthalpy of vaporization (kJ/mol) of several organic substances:



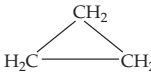
32.0
Acetone



28.5
Ethylene oxide



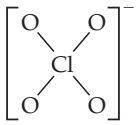
30.4
Acetaldehyde



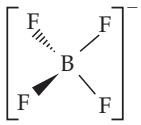
24.7
Cyclopropane

(**a**) Account for the variations in heats of vaporization for these substances, considering their relative intermolecular forces. (**b**) How would you expect the solubilities of these substances to vary in hexane as solvent? In ethanol? Use intermolecular forces, including hydrogen-bonding interactions where applicable, to explain your responses.

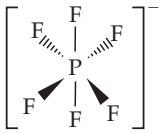
13.114 A series of anions is shown here:



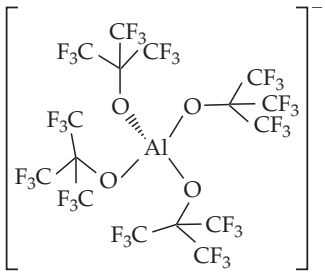
(i)



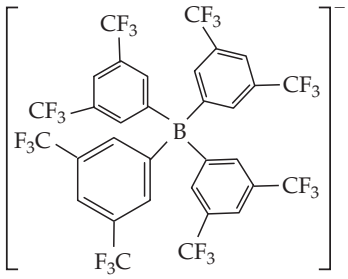
(ii)



(iii)



(iv)



(v)

The anion on the far right is called "BARF" by chemists, as its common abbreviation sounds similar to this word.

(**a**) What is the central atom and the number of electron-pair domains around the central atom in each of these anions?

(**b**) What is the electron-domain geometry around the central B in BARF?

(**c**) Which, if any, of these anions has an expanded octet around its central atom?

(**d**) Tetrabutylammonium, $(CH_3CH_2CH_2CH_2)_4N^+$ is a bulky cation. Which anion, when paired with the tetrabutylammonium cation, would lead to a salt that will be most soluble in nonpolar solvents?

13.115 (**a**) A sample of hydrogen gas is generated in a closed container by reacting 1.750 g of zinc metal with 50.0 mL of 1.00 *M* hydrochloric acid. Write the balanced equation for the reaction, and calculate the number of moles of hydrogen formed, assuming that the reaction is complete.

(**b**) The volume over the solution in the container is 150 mL. Calculate the partial pressure of the hydrogen gas in this volume at 25 °C, ignoring any solubility of the gas in the solution. (**c**) The Henry's law constant for hydrogen in water at 25 °C is 7.7×10^{-6} mol/m^3 Pa. Estimate the number of moles of hydrogen gas that remain dissolved in the solution. What fraction of the gas molecules in the system is dissolved in the solution? Was it reasonable to ignore any dissolved hydrogen in part (b)?

13.116 The following table presents the solubilities of several gases in water at 25 °C under a total pressure of gas and water vapor of 101.3 kPa. (**a**) What volume of $CH_4(g)$ under standard conditions of temperature and pressure is contained in 4.0 L of a saturated solution at 25 °C? (**b**) The solubilities (in water) of the hydrocarbons are as follows: methane ethane ethene. Is this because ethene is the most polar molecule? (**c**) What intermolecular interactions can these hydrocarbons have with water? (**d**) Draw the Lewis dot structures for the three hydrocarbons. Which of these hydrocarbons possess π bonds? Based on their solubilities, would you say π bonds are more or less polarizable than σ bonds? (**e**) Explain why NO is more soluble in water than either N_2 or O_2. (**f**) H_2S is more water-soluble than almost all the other gases in table. What intermolecular forces is H_2S likely to have with water? (**g**) SO_2 is by far the most water-soluble gas in table. What intermolecular forces is SO_2 likely to have with water?

Gas	Solubility (m*M*)
CH_4 (methane)	1.3
C_2H_6 (ethane)	1.8
C_2H_4 (ethene)	4.7
N_2	0.6
O_2	1.2
NO	1.9
H_2S	99
SO_2	1476

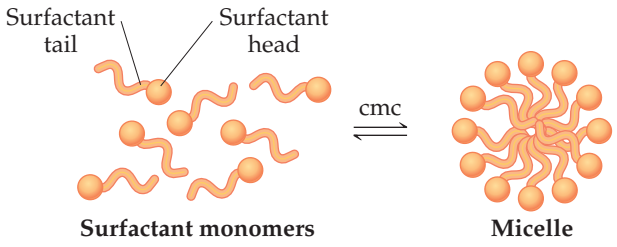
13.117 A small cube of sodium (density = 0.968 g/cm^3) measuring 1.0 mm on each edge is added to 0.100 L of water. The following reaction occurs:

$$2\,Na(s) + H_2O \longrightarrow 2\,NaOH(aq) + H_2(g)$$

What is the freezing point of the resulting solution, assuming that the reaction goes to completion?

13.118 At 35 °C the vapor pressure of acetone, $(CH_3)_2CO$, is 47.9 kPa, and that of carbon disulfide, CS_2, is 66.7 kPa. A solution composed of an equal number of moles of acetone and carbon disulfide has a vapor pressure of 86.7 kPa at 35 °C. (**a**) What would be the vapor pressure of the solution if it exhibited ideal behavior? (**b**) Based on the behavior of the solution, predict whether the mixing of acetone and carbon disulfide is an exothermic ($\Delta H_{soln} < 0$) or endothermic ($\Delta H_{soln} > 0$) process.

13.119 Compounds like sodium stearate, called "surfactants" in general, can form structures known as micelles in water, once the solution concentration reaches the value known as the critical micelle concentration (cmc). Micelles contain dozens to hundreds of molecules. The cmc depends on the substance, the solvent, and the temperature.



At and above the cmc, the properties of the solution vary drastically.

(**a**) The turbidity (the amount of light scattering) of solutions increases dramatically at the cmc. Suggest an explanation. (**b**) The ionic conductivity of the solution dramatically changes at the cmc. Suggest an explanation. (**c**) Chemists have developed fluorescent dyes that glow brightly only when the dye molecules are in a hydrophobic environment. Predict how the intensity of such fluorescence would relate to the concentration of sodium stearate as the sodium stearate concentration approaches and then increases past the cmc.

Design an Experiment

Based on Figure 13.17, you might think that the reason volatile solvent molecules in a solution are less likely to escape to the gas phase, compared to the pure solvent, is because the solute molecules are physically blocking the solvent molecules from leaving at the surface. This is a common misconception. Design an experiment to test the hypothesis that solute blocking of solvent vaporization is not the reason that solutions have lower vapor pressures than pure solvents.

WHAT'S AHEAD

14.1 ▶ Factors That Affect Reaction Rates

14.2 ▶ Reaction Rates

14.3 ▶ Concentration and Rate Laws

14.4 ▶ The Change of Concentration with Time

14.5 ▶ Temperature and Rate

14.6 ▶ Reaction Mechanisms

14.7 ▶ Catalysis

14

CHEMICAL KINETICS

14.1 | Factors That Affect Reaction Rates



Chemical reactions take time to occur. Some reactions, such as the rusting of iron, occur relatively slowly, requiring days, months, or years to complete. Others, such as the decomposition of sodium azide, the reaction used to inflate automobile air bags, occur so quickly they are difficult to measure. As chemists, we need to be concerned about the *speed* of chemical reactions as well as the products of those reactions.

The part of chemistry that deals with the speed of a chemical reaction is known as chemical kinetics. It plays an important role in processes as diverse as the production of chemicals on an industrial scale and the decay of radioactive isotopes used in medicine. Chemical kinetics is also useful in providing information about how reactions occur—the order in which chemical bonds are broken and formed during the course of a reaction. Chemical kinetics helps us formulate a reaction mechanism, which is a step-by-step, molecular-level view of the pathway from reactants to products.

The speed at which a chemical reaction occurs is called the **reaction rate**. One mechanism for controlling reaction rate is to adjust the temperature. Reaction rates slow down as the temperature decreases and speed up when the temperature increases. The chemical reactions that govern the metabolism of food, the transport of essential nutrients, and many other important physiological processes in the human body must proceed with the appropriate speeds. To do so, it is essential that our internal body temperature remain relatively constant regardless of the outside temperature. However, not all mammals operate within these strict confines. The body temperatures of animals that hibernate during the cold winter months often drop considerably in order to slow their metabolisms and conserve energy. The most extreme case is the arctic ground squirrel, an animal that hibernates for 7 to 8 months every year. Scientists have measured body temperatures as low as 3 °C in hibernating arctic ground squirrels! At these low temperatures, reaction rates are slowed by several orders of magnitude, which allow the squirrels to hibernate over such long periods.

By the end of this section, you should be able to

- List the factors that affect the rate of chemical reactions.

Four factors affect the rate at which any particular reaction occurs:

1. *Physical state of the reactants.* Reactants must come together to react. The more readily reactant molecules collide with one another, the more rapidly they react. Reactions may broadly be classified as *homogeneous*, involving either all gases or all liquids, or as *heterogeneous*, in which reactants are in different phases. Under heterogeneous conditions, a reaction is limited by the area of contact of the reactants. Thus, heterogeneous reactions that involve solids tend to proceed more rapidly if the surface area of the solid is increased. For example, a medicine in the form of a fine powder dissolves in the stomach and enters the blood more quickly than the same medicine in the form of a tablet.
2. *Reactant concentrations.* Most chemical reactions proceed more quickly if the concentration of one or more reactants is increased. For example, steel wool burns only slowly in air, which contains 20% O_2, but bursts into flame in pure oxygen (**Figure 14.1**). As reactant concentration increases, the frequency with which the reactant molecules collide increases, leading to increased rates.
3. *Reaction temperature.* Reaction rates generally increase as temperature is increased. The bacterial reactions that spoil milk, for instance, proceed more rapidly at room temperature than at the lower temperature of a refrigerator. Increasing temperature increases the kinetic energies of molecules. As molecules move more rapidly, they collide more frequently and with higher energy, leading to increased reaction rates.
4. *The presence of a catalyst. Catalysts* are agents that increase reaction rates without themselves being used up. They affect the kinds of collisions (and therefore alter the mechanism) that lead to reaction. Catalysts play many crucial roles in living organisms.

On a molecular level, reaction rates depend on the frequency of collisions between molecules. *The greater the frequency of collisions, the higher the reaction rate.* For a collision to lead to a reaction, however, it must occur with sufficient energy to break bonds and with suitable orientation for new bonds to form in the proper locations.

Go Figure

If a heated steel nail were placed in pure O_2, would you expect it to burn as readily as the steel wool does?



Steel wool heated in air (about 20% O_2) glows red-hot but oxidizes to Fe_2O_3 slowly.



Red-hot steel wool in 100% O_2 burns vigorously, forming Fe_2O_3 quickly.

▲ Figure 14.1 Effect of concentration on reaction rate. The difference in behavior is due to the different concentrations of O_2 in the two environments.

Self-Assessment Exercise

14.1 In a reaction involving molecules in the gas state, how does increasing the partial pressures of the gases affect the reaction rate?

(a) It will increase the rate
(b) It will decrease the rate
(c) The rate will remain unchanged

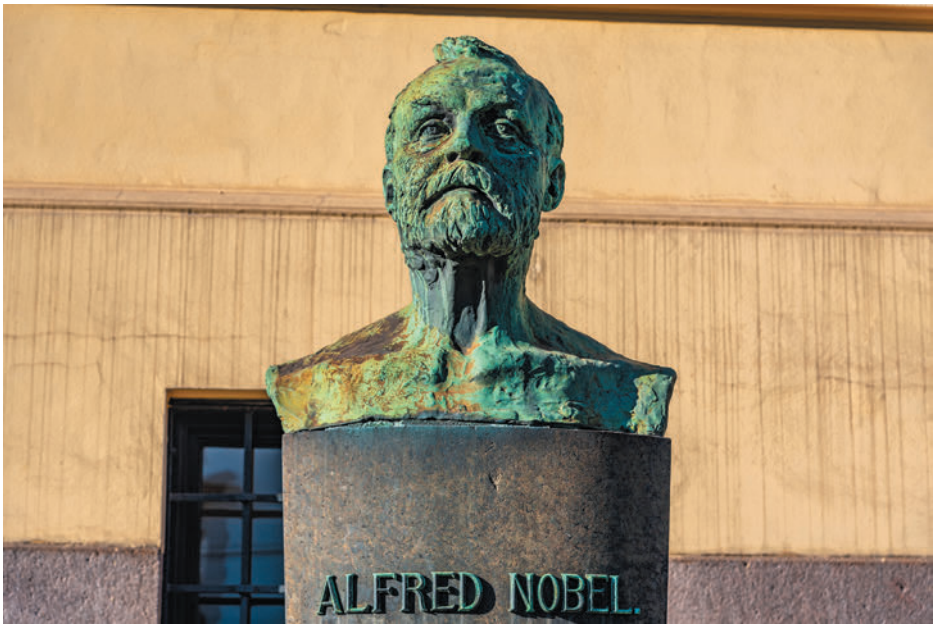
Exercises

14.2 (**a**) What is meant by the term *reaction rate*? (**b**) Name three factors that can affect the rate of a chemical reaction. (**c**) Is the rate of disappearance of reactants always the same as the rate of appearance of products?

Answers to Self-Assessment Exercises

14.1 (a)

14.2 Reaction Rates



An explosion is a chemical reaction that occurs very, very fast, coupled with one that is highly exothermic and produces gaseous products. Nitroglycerine fulfills these criteria but is an extremely unstable liquid and very difficult to use.

$$4\,C_3H_5N_3O_9\,(l) \rightarrow 6\,N_2\,(g) + 12\,CO_2\,(g) + 10\,H_2O\,(g) + O_2\,(g)$$

The Swedish inventor, Alfred Nobel, found that by mixing nitroglycerine with an absorbent solid material such as diatomaceous earth or cellulose, a solid explosive (*dynamite*) was produced and was much easier to handle than nitroglycerine. He had invented the most powerful military explosive to date, but he strongly supported international peace movements. His will stated that his fortune should be used to establish prizes awarding those who 'have conferred the greatest benefit on mankind', including the promotion of peace. The Nobel Prize is probably the most coveted award that a scientist, economist, writer, or peace advocate can receive

In this section, we introduce reaction rates and by the end of it you should be able to

- Determine the rate of a reaction by measuring the concentration of a reactant or product as a function of time.
- Relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction.

The *speed* of an event is defined as the *change* that occurs in a given *time* interval, which means that whenever we talk about speed, we necessarily bring in the notion of time. For example, the speed of a car is expressed as the change in the car's position over a certain time interval.

Similarly, the speed of a chemical reaction—its reaction rate—is the change in the concentration of reactants or products per unit of time. The units for reaction rate are usually molarity per second (M/s)—that is, the change in concentration measured in molarity divided by a time interval measured in seconds.

Let's consider the hypothetical reaction A $\longrightarrow$ B, depicted in **Figure 14.2**. Each red sphere represents 0.01 mol of A, each blue sphere represents 0.01 mol of B, and the container has a volume of 1.00 L. At the beginning of the reaction, there is 1.00 mol A, so the concentration is 1.00 mol/L = 1.00 M. After 20 s, the concentration of A has fallen to 0.54 M and the concentration of B has risen to 0.46 M. The sum of the concentrations is still 1.00 M because 1 mol of B is produced for each mole of A that reacts. After 40 s, the concentration of A is 0.30 M and that of B is 0.70 M.

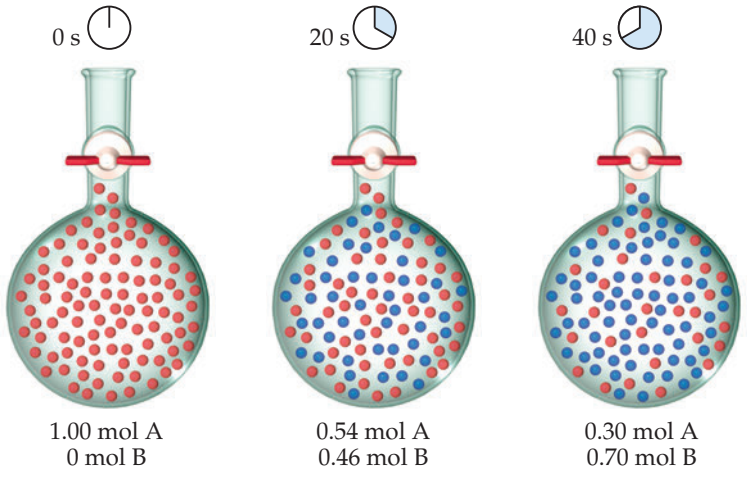
The rate of this reaction can be expressed either as the rate of disappearance of reactant A or as the rate of appearance of product B. The *average* rate of appearance of B over a particular time interval is given by the change in concentration of B divided by the change in time:

$$\text{Average rate of appearance of B} = \frac{\text{change in concentration of B}}{\text{change in time}} = \frac{[\text{B}]\text{ at } t_2 - [\text{B}]\text{ at } t_1}{t_2 - t_1} = \frac{\Delta[\text{B}]}{\Delta t} \qquad [14.1]$$

We use square brackets around a chemical formula, as in [B], to indicate molarity. The Greek letter delta, Δ, is read "change in" and is always equal to a final value minus an initial value. The average rate of appearance of B over the 20 s interval from the beginning of the reaction (t_1 = 0 s to t_2 = 20 s) is

$$\text{Average rate} = \frac{0.46\,M - 0.00\,M}{20\text{ s} - 0\text{ s}} = 2.3 \times 10^{-2}\,M/\text{s}$$

Go Figure Estimate the number of moles of A in the mixture after 30 s.



▲ **Figure 14.2 Progress of a hypothetical reaction A $\longrightarrow$ B.** The volume of the flask is 1.0 L.

We could equally well express the reaction rate in terms of the reactant, A. In this case, we would be describing the rate of disappearance of A, which we express as

$$\text{Average rate of disappearance of A} = -\frac{\text{change in concentration of A}}{\text{change in time}} = -\frac{\Delta[\text{A}]}{\Delta t} \qquad [14.2]$$

Notice the minus sign in this equation, which we use to indicate that the concentration of A decreases.

By convention, rates are always expressed as positive quantities.

Because [A] decreases, $\Delta[\text{A}]$ is a negative number. The minus sign we put in the equation converts the negative $\Delta[\text{A}]$ to a positive rate of disappearance.

Because one molecule of A is consumed for every molecule of B that forms, the average rate of disappearance of A equals the average rate of appearance of B:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.54\,M - 1.00\,M}{20\text{ s} - 0\text{ s}} = 2.3 \times 10^{-2}\,M/\text{s}$$

Sample Exercise 14.1

Calculating an Average Rate of Reaction

From the data in Figure 14.2, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

SOLUTION

Analyze We are given the concentration of A at 20 s (0.54 *M*) and at 40 s (0.30 *M*) and asked to calculate the average rate of reaction over this time interval.

Plan The average rate is given by the change in concentration, $\Delta[\text{A}]$, divided by the change in time, Δt. Because A is a reactant, a minus sign is used in the calculation to make the rate a positive quantity.

Solve

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30\,M - 0.54\,M}{40\text{ s} - 20\text{ s}} = 1.2 \times 10^{-2}\,M/\text{s}$$

Practice Exercise

If the experiment in Figure 14.2 is run for 60 s, 0.16 mol A remain. Which of the following statements is or are true?

(i) After 60 s there are 0.84 mol B in the flask.
(ii) The decrease in the number of moles of A from $t_1 = 0$ s to $t_2 = 20$ s is greater than that from $t_1 = 40$ to $t_2 = 60$ s.
(iii) The average rate for the reaction from $t_1 = 40$ s to $t_2 = 60$ s is $7.0 \times 10^{-3}\,M/\text{s}$.

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

Change of Rate with Time

Now let's consider the reaction between chlorobutane (C_4H_9Cl) and water to form butanol (C_4H_9OH) and hydrochloric acid:

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq) \qquad [14.3]$$

Suppose we prepare a 0.1000 *M* aqueous solution of C_4H_9Cl and then measure the concentration of C_4H_9Cl at various times after time zero (which is the instant at which the reactants are mixed, thereby initiating the reaction). We can use the resulting data, shown in the first two columns of **Table 14.1**, to calculate the average rate of disappearance of C_4H_9Cl over various time intervals; these rates are given in the third column. Notice that the average rate decreases over each 50 s interval for the first several measurements and continues to decrease over even larger intervals through the remaining measurements. *It is typical for rates to decrease as a reaction*

TABLE 14.1 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	
		1.9×10^{-4}
50.0	0.0905	
		1.7×10^{-4}
100.0	0.0820	
		1.6×10^{-4}
150.0	0.0741	
		1.4×10^{-4}
200.0	0.0671	
		1.22×10^{-4}
300.0	0.0549	
		1.01×10^{-4}
400.0	0.0448	
		0.80×10^{-4}
500.0	0.0368	
		0.560×10^{-4}
800.0	0.0200	
10,000	0	

proceeds because the concentration of reactants decreases. The change in rate as the reaction proceeds is also seen in a graph of $[C_4H_9Cl]$ versus time (**Figure 14.3**). Notice how the steepness of the curve decreases with time, indicating a decreasing reaction rate.

Instantaneous Rate

Graphs such as Figure 14.3 that show how the concentration of a reactant or product changes with time allow us to evaluate the **instantaneous rate** of a reaction, which is the rate at a particular instant during the reaction. The instantaneous rate is determined from the slope of the curve at a particular point in time. We have drawn two tangent lines in Figure 14.3, a dashed line running through the point at $t = 0$ s and a solid line running through the point at $t = 600$ s. The slopes of these tangent lines give the instantaneous rates at these two time points.* To determine the instantaneous rate at 600 s, for example, we construct horizontal and vertical lines to form the blue right triangle in Figure 14.3. The slope of the tangent line is the ratio of the height of the vertical side to the length of the horizontal side:

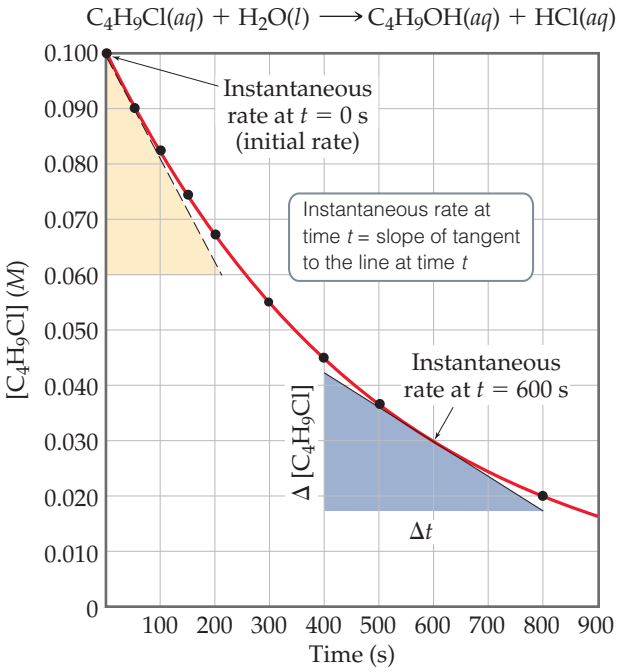
$$\text{Instantaneous rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.017 - 0.042)\,M}{(800 - 400)\,\text{s}}$$

$$= 6.3 \times 10^{-5}\,M/\text{s}$$

In discussions that follow, the term *rate* means instantaneous rate unless indicated otherwise. The instantaneous rate at $t = 0$ is called the *initial rate* of the reaction. To understand the difference between average and instantaneous rates, imagine you have just driven 160 km in 2.0 h. Your average speed for the trip is 80 km/hr, but your instantaneous speed at any moment during the trip is the speedometer reading at that moment.

Go Figure

Does the instantaneous rate increase, decrease, or remain the same as the reaction proceeds?



▲ **Figure 14.3 Concentration of butyl chloride (C_4H_9Cl) as a function of time.**

*You may wish to review graphical determination of slopes in Appendix A. If you are familiar with calculus, you may recognize that the average rate approaches the instantaneous rate as the time interval approaches zero. This limit, in the notation of calculus, is the negative of the derivative of the curve at time t, $-d[C_4H_9Cl]/dt$.

Sample Exercise 14.2

Calculating an Instantaneous Rate of Reaction

Using Figure 14.3, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ s (the initial rate).

SOLUTION

Analyze We are asked to determine an instantaneous rate from a graph of reactant concentration versus time.

Plan To obtain the instantaneous rate at $t = 0$ s, we must determine the slope of the curve at $t = 0$. The tangent is drawn on the graph as the hypotenuse of the tan triangle. The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (which, in the case of this example, is the change in molarity over change in time).

Solve The tangent line falls from $[C_4H_9Cl] = 0.100\,M$ to $0.060\,M$ in the time change from 0 s to 210 s. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\,M}{(210 - 0)\,\text{s}}$$
$$= 1.9 \times 10^{-4}\,M/\text{s}$$

Practice Exercise

Which of the following could be the instantaneous rate of the reaction in Figure 14.3 at $t = 1000$ s?
(**a**) $1.2 \times 10^{-4}\,M/\text{s}$
(**b**) $8.8 \times 10^{-5}\,M/\text{s}$
(**c**) $6.3 \times 10^{-5}\,M/\text{s}$
(**d**) $2.7 \times 10^{-5}\,M/\text{s}$
(**e**) More than one of these.

Reaction Rates and Stoichiometry

During our discussion of the hypothetical reaction A $\longrightarrow$ B, we saw that the stoichiometry requires that the rate of disappearance of A equal the rate of appearance of B. Likewise, the stoichiometry of Equation 14.3 indicates that 1 mol of C_4H_9OH is produced for each mole of C_4H_9Cl consumed. Therefore, the rate of appearance of C_4H_9OH equals the rate of disappearance of C_4H_9Cl:

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

What happens when the stoichiometric relationships are not one-to-one? For example, consider the reaction $2\,HI(g) \longrightarrow H_2(g) + I_2(g)$. We can measure either the rate of disappearance of HI or the rate of appearance of either H_2 or I_2. Because 2 mol of HI disappears for each mole of H_2 or I_2 that forms, the rate of disappearance of HI is *twice* the rate of appearance of either H_2 or I_2. How do we decide which number to use for the rate of the reaction? Depending on whether we monitor HI, I_2, or H_2, the rates can differ by a factor of 2. To fix this problem, we need to take into account the reaction stoichiometry. To arrive at a number for the reaction rate that does not depend on which component we measured, we must divide the rate of disappearance of HI by 2 (its coefficient in the balanced chemical equation):

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

In general, for the reaction

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

the rate is given by

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t} \qquad [14.4]$$

When we speak of the rate of a reaction without specifying a particular reactant or product, we utilize the definition in Equation 14.4.*

*Equation 14.4 does not hold true if substances other than C and D are formed in significant amounts. For example, sometimes intermediate substances build in concentration before forming the final products. In that case, the relationship between the rate of disappearance of reactants and the rate of appearance of products is not given by Equation 14.4. All reactions whose rates we consider in this chapter obey Equation 14.4.

Sample Exercise 14.3

Relating Rates at Which Products Appear and Reactants Disappear



(**a**) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2\,O_3(g) \longrightarrow 3\,O_2(g)$?

(**b**) If the rate at which O_2 appears, $\Delta[O_2]/\Delta t$, is $6.0 \times 10^{-5}\ M/s$ at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]/\Delta t$?

SOLUTION

Analyze We are given a balanced chemical equation and asked to relate the rate of appearance of the product to the rate of disappearance of the reactant.

Plan We can use the coefficients in the chemical equation as shown in Equation 14.4 to express the relative rates of reactions.

Solve

(**a**) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

(**b**) Solving the equation from part (a) for the rate at which O_3 disappears, $-\Delta[O_3]/\Delta t$, we have:

$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}(6.0 \times 10^{-5}\,M/s) = 4.0 \times 10^{-5}\,M/s$$

Check We can apply a stoichiometric factor to convert the O_2 formation rate to the O_3 disappearance rate:

$$-\frac{\Delta[O_3]}{\Delta t} = \left(6.0 \times 10^{-5}\,\frac{\text{mol } O_2/\text{L}}{\text{s}}\right)\left(\frac{2\text{ mol } O_3}{3\text{ mol } O_2}\right) = 4.0 \times 10^{-5}\,\frac{\text{mol } O_3/\text{L}}{\text{s}}$$

$$= 4.0 \times 10^{-5}\,M/s$$

Practice Exercise

At a certain time in a reaction, substance A is disappearing at a rate of $4.0 \times 10^{-2}\,M/s$, substance B is appearing at a rate of $2.0 \times 10^{-2}\,M/s$, and substance C is appearing at a rate of $6.0 \times 10^{-2}\,M/s$. Which of the following could be the stoichiometry for the reaction being studied?

(**a**) $2\,A + B \longrightarrow 3\,C$ (**b**) $A \longrightarrow 2\,B + 3\,C$
(**c**) $2\,A \longrightarrow B + 3\,C$ (**d**) $4\,A \longrightarrow 2\,B + 3\,C$
(**e**) $A + 2\,B \longrightarrow 3\,C$

Self-Assessment Exercises

14.3 In Figure 14.3, order the following three rates from fastest to slowest: (i) The average rate of the reaction between 0 s and 600 s, (ii) the instantaneous rate at t = 0 s, and (iii) the instantaneous rate at t = 600 s. You should not have to do any calculations.

(a) Average rate > Rate at t = 0 s > Rate at t = 600 s

(b) Rate at t = 600 s > Average rate > Rate at t = 0 s

(c) Rate at t = 0 s > Average rate > Rate at t = 600 s

14.4 For the reaction $N_2O_4\,(g) \rightarrow 2\,NO_2\,(g)$, how is the rate of disappearance of dinitrogen tetroxide related to the rate of appearance of nitrogen dioxide?

(a) $\text{Rate} = -\dfrac{\Delta[N_2O_4]}{\Delta t} = \dfrac{\Delta[NO_2]}{\Delta t}$

(b) $\text{Rate} = -\dfrac{1}{2}\dfrac{\Delta[N_2O_4]}{\Delta t} = \dfrac{\Delta[NO_2]}{\Delta t}$

(c) $\text{Rate} = -\dfrac{\Delta[N_2O_4]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[NO_2]}{\Delta t}$

Exercises

14.5 A flask is charged with 0.200 mol of A and allowed to react to form B according to the hypothetical gas-phase reaction $A(g) \longrightarrow B(g)$. The following data are collected:

Time (s)	0	50	100	150	200
Moles of A	0.200	0.141	0.100	0.071	0.050

(**a**) Calculate the number of moles of B at each time in the table, assuming that A is cleanly converted to B with no intermediates. (**b**) Calculate the average rate of disappearance of A for each 50 s interval in units of mol/s. (**c**) Which of the following would be needed to calculate the rate in units of concentration per time: (**i**) the partial pressure of the gases at

each time, (**ii**) the temperature, (**iii**) the volume of the reaction flask, or (**iv**) the molecular weights of A and B?

14.6 The rate of disappearance of HCl was measured for the following reaction:

$$CH_3OH(aq) + HCl(aq) \longrightarrow CH_3Cl(aq) + H_2O(l)$$

The following data were collected:

Time (min)	[HCl](M)
0.0	1.85
54.0	1.58
107.0	1.36
215.0	1.02
430.0	0.580

(**a**) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. (**b**) Calculate the average rate of reaction for the entire time for the data from $t = 0.0$ min to $t = 430.0$ min. (**c**) Which is greater, the average rate between $t = 54.0$ and $t = 215.0$ min, or between $t = 107.0$ and $t = 430.0$ min? (**d**) Graph [HCl] versus time and determine the instantaneous rates in M/min and M/s at $t = 75.0$ min and $t = 250$ min.

14.7 For each of the following gas-phase reactions, write the rate expression in terms of the appearance of each product and disappearance of each reactant:

(**a**) $O_3(g) + H_2O(g) \longrightarrow 2\,O_2(g) + H_2(g)$

(**b**) $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$

(**c**) $2\,C_2H_2(g) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 2\,H_2O(g)$

(**d**) $C_3H_7NH_2(g) \longrightarrow C_3H_6(g) + NH_3(g)$

14.8 (**a**) Consider the combustion of ethene, $C_2H_4(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(g)$. If the concentration of C_2H_4 is decreasing at the rate of 0.025 M/s, what are the rates of change in the concentrations of CO_2 and H_2O? (**b**) The rate of decrease in N_2H_4 partial pressure in a closed reaction vessel from the reaction $N_2H_4(g) + H_2(g) \longrightarrow 2\,NH_3(g)$ is 10 kPa per hour. What are the rates of change of NH_3 partial pressure and total pressure in the vessel?

Answers to Self-Assessment Exercises

14.3 (c) **14.4** (c)

14.3 Concentration and Rate Laws



Acid rain results largely from emissions from industry of sulfur dioxide and nitrogen oxide reacting with water in the atmosphere. Coal-fired power stations are a major source of these gases and their emissions increased significantly during the industrial revolution of the nineteenth century. Some statues and buildings, most notably those made of limestone, are sensitive to acidic solutions and erosion of the stone has been accelerated in the modern era as the rain in some regions has become more acidic.

By the end of this section, you should be able to

- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant.
- Determine the rate law and rate constant for a reaction from a series of data.

One way of studying the effect of concentration on reaction rate is to determine the way in which the initial rate of a reaction depends on the initial concentrations. For example, we might study the rate of the reaction

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\,H_2O(l)$$

A CLOSER LOOK Using Spectroscopic Methods to Measure Reaction Rates: Beer's Law

A variety of techniques can be used to monitor reactant and product concentration during a reaction, including spectroscopic methods, which rely on the ability of substances to absorb (or emit) light. Spectroscopic kinetic studies are often performed with the reaction mixture in the sample compartment of a *spectrometer*, an instrument that measures the amount of light transmitted or absorbed by a sample at different wavelengths. For kinetic studies, the spectrometer is set to measure the light absorbed at a wavelength characteristic of one of the reactants or products. In the decomposition of $HI(g)$ into $H_2(g)$ and $I_2(g)$, for example, both HI and H_2 are colorless, whereas I_2 is violet. During the reaction, the violet color of the reaction mixture gets more intense as I_2 forms. Thus, visible light of appropriate wavelength can be used to monitor the reaction (Figure 14.4).

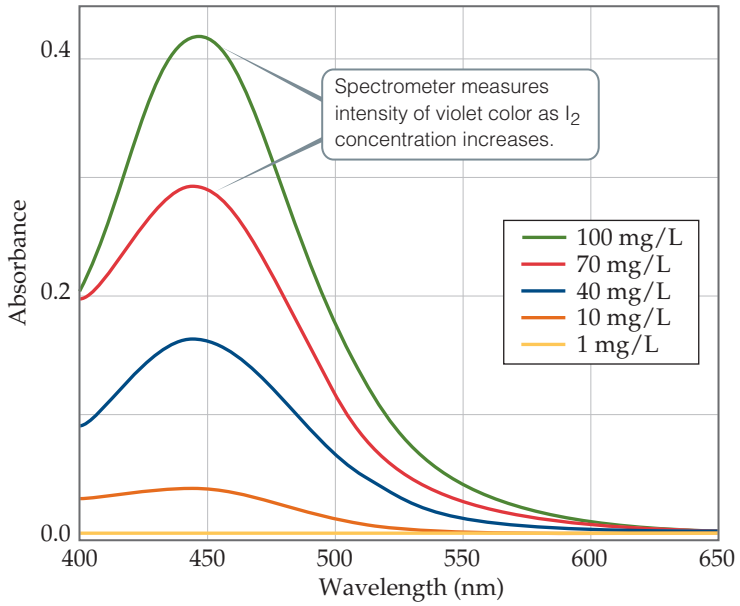
Figure 14.5 shows the components of a spectrometer. The spectrometer measures the amount of light absorbed by the sample by comparing the intensity of the light emitted from the light source with the intensity of the light transmitted through the sample, for various wavelengths. As the concentration of I_2 increases and its color becomes more intense, the amount of light absorbed by the reaction mixture increases, as Figure 14.4 shows, causing less light to reach the detector.

How can we relate the amount of light detected by the spectrometer to the concentration of a species? A relationship called *Beer's law* gives us a direct route to the information we seek. Beer's law connects the amount of light absorbed to the concentration of the absorbing substance:

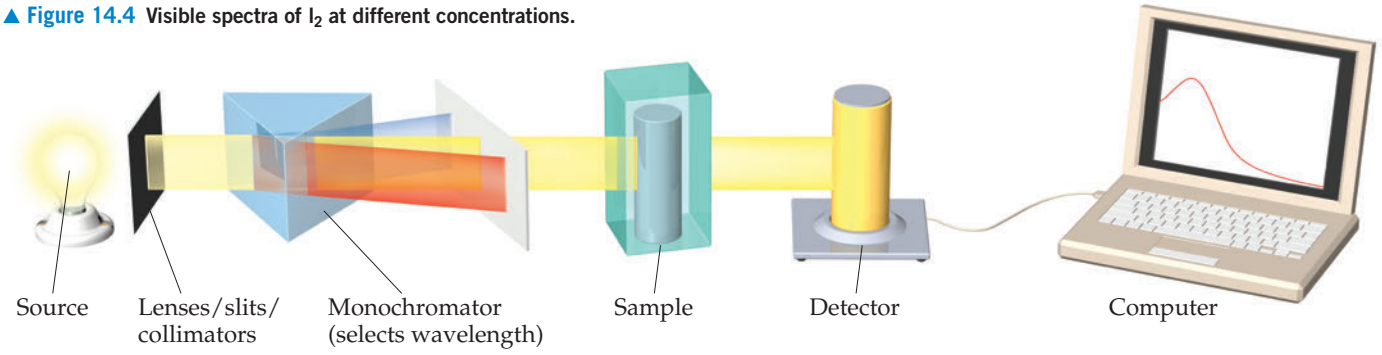
$$A = \varepsilon l c \qquad [14.5]$$

In this equation, A is the measured absorbance, ε is the extinction coefficient (a characteristic of the substance being monitored at a given wavelength of light), l is the path length through which the light passes, and c is the molar concentration of the absorbing substance. Thus, the concentration is directly proportional to absorbance. Many chemical and pharmaceutical companies routinely use Beer's law to calculate the concentration of purified solutions of the compounds that they make. In the laboratory portion of your course, you may very well perform one or more experiments in which you use Beer's law to relate absorption of light to concentration.

Related Exercises: 14.111, 14.112, Design an Experiment



▲ **Figure 14.4** **Visible spectra of I_2 at different concentrations.**



▲ **Figure 14.5** Components of a spectrometer.

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

by measuring the concentration of NH_4^+ or NO_2^- as a function of time or by measuring the volume of N_2 collected as a function of time. Because the stoichiometric coefficients on NH_4^+, NO_2^-, and N_2 are the same, all of these rates are the same.

Table 14.2 shows that changing the initial concentration of either reactant changes the initial reaction rate. If we double $[NH_4^+]$ while holding $[NO_2^-]$ constant, the rate doubles (compare experiments 1 and 2). If we increase $[NH_4^+]$ by a factor of 4 but leave $[NO_2^-]$ unchanged (experiments 1 and 3), the rate changes by a factor of 4, and so forth. These results indicate that the initial reaction rate is proportional to $[NH_4^+]$. When $[NO_2^-]$ is similarly varied while $[NH_4^+]$ is held constant, the rate is affected in the same manner. Thus, the rate is also directly proportional to the concentration of $[NO_2^-]$.

We express the way in which the rate depends on the reactant concentrations by the equation

$$\text{Rate} = k[NH_4^+][NO_2^-] \qquad [14.6]$$

An equation such as Equation 14.6, which shows how the rate depends on reactant concentrations, is called a **rate law**. For the general reaction

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

the rate law generally has the form

$$\text{Rate} = k[A]^m[B]^n \qquad [14.7]$$

Notice that only the concentrations of the reactants generally appear in the rate law. The constant k is called the **rate constant**. The magnitude of k changes with temperature and therefore determines how temperature affects rate, as we will see in Section 14.5. The exponents m and n are typically small whole numbers, whose values are not necessarily equal to the coefficients a and b from the balanced equation. As we will learn shortly, if we know m and n for a reaction, we can gain great insight into the individual steps that occur during the reaction.

Once we know the rate law for a reaction and the reaction rate for a set of reactant concentrations, we can calculate the value of k. For example, using the values for experiment 1 in Table 14.2, we can substitute into Equation 14.6:

$$5.4 \times 10^{-7}\,M/\text{s} = k(0.0100\,M)(0.200\,M)$$

$$k = \frac{5.4 \times 10^{-7}\,M/\text{s}}{(0.0100\,M)(0.200\,M)} = 2.7 \times 10^{-4}\,M^{-1}\text{s}^{-1}$$

You should verify that this same value of k is obtained using any of the other experimental results in Table 14.2.

Once we have both the rate law and the k value for a reaction, we can calculate the reaction rate for any set of concentrations. For example, using Equation 14.7 with

$k = 2.7 \times 10^{-4}\,M^{-1}\,s^{-1}$, $m = 1$, and $n = 1$, we can calculate the rate for $[NH_4^+] = 0.100\,M$ and $[NO_2^-] = 0.100\,M$:

$$\text{Rate} = (2.7 \times 10^{-4}\,M^{-1}\,s^{-1})(0.100\,M)(0.100\,M) = 2.7 \times 10^{-6} M/s$$

Reaction Orders: The Exponents in the Rate Law

The rate law for most reactions has the form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots \qquad [14.8]$$

The exponents m and n are called **reaction orders**. For example, consider again the rate law for the reaction of NH_4^+ with NO_2^-:

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

Because the exponent of $[NH_4^+]$ is 1, the rate is *first order* in NH_4^+. The rate is also first order in NO_2^-. (The exponent 1 is not shown in rate laws.) The **overall reaction order** is the sum of the orders with respect to each reactant represented in the rate law. Thus, for the reaction between NH_4^+ and NO_2^- the rate law has an overall reaction order of $1 + 1 = 2$, and the reaction is *second order overall*.

The exponents in a rate law indicate how the rate is affected by each reactant concentration. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[NH_4^+]$ raised to the first power, the rate doubles when $[NH_4^+]$ doubles, triples when $[NH_4^+]$ triples, and so forth. Doubling or tripling $[NO_2^-]$ likewise doubles or triples the rate. If a rate law is second order with respect to a reactant, $[A]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple because $[2]^2 = 4$, whereas tripling the concentration causes the rate to increase ninefold: $[3]^2 = 9$.

The following are some additional examples of experimentally determined rate laws:

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \quad \text{Rate} = k[N_2O_5] \qquad [14.9]$$

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \quad \text{Rate} = k[H_2][I_2] \qquad [14.10]$$

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g) \quad \text{Rate} = k[CHCl_3][Cl_2]^{1/2} \qquad [14.11]$$

Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case, as Equations 14.9 and 14.11 show.

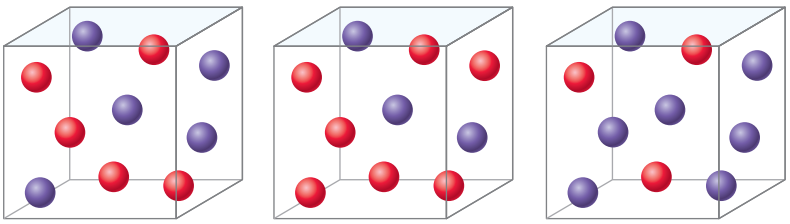
For any reaction, the rate law must be determined experimentally.

In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional (as is the case with Equation 14.11) or even negative.

Sample Exercise 14.4

Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction A + B ⟶ C for which rate $= k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.



(1) (2) (3)

SOLUTION

Analyze We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Continued

Solve Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (Box 2), and the highest is $147k$ (Box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Check Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a larger reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

Practice Exercise

Suppose the rate law for the reaction in this Sample Exercise were rate $= k[\text{A}]^2[\text{B}]$. What would be the ordering of the rates for the three mixtures in this Sample Exercise, from slowest to fastest?

(**a**) $1 < 2 < 3$
(**b**) $1 < 3 < 2$
(**c**) $3 < 2 < 1$
(**d**) $2 < 1 < 3$
(**e**) $3 < 1 < 2$

Magnitudes and Units of Rate Constants

If chemists want to compare reactions to evaluate which ones are relatively fast and which ones are relatively slow, the quantity of interest is the rate constant. A good general rule is that a large value of k ($\sim 10^9$ or higher) means a fast reaction and a small value of k (10 or lower) means a slow reaction.

The units of the rate constant depend on the overall reaction order of the rate law. In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, in our usual units of molarity for concentration and seconds for time, we have

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/\text{s}}{M^2} = M^{-1}\,\text{s}^{-1}$$

Sample Exercise 14.5

Determining Reaction Orders and Units for Rate Constants

(**a**) What are the overall reaction orders for the reactions described in Equations 14.9 and 14.11?

(**b**) What are the units of the rate constant for the rate law in Equation 14.9?

SOLUTION

Analyze We are given two rate laws and asked to express (**a**) the overall reaction order for each and (**b**) the units for the rate constant for the first reaction.

Plan The overall reaction order is the sum of the exponents in the rate law. The units for the rate constant, k, are found by using the normal units for rate (M/s) and concentration (M) in the rate law and applying algebra to solve for k.

Solve

(**a**) The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.11 is first order in $CHCl_3$ and one-half order in Cl_2. The overall reaction order is three halves.

(**b**) For the rate law for Equation 14.9, we have

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

so

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{M/\text{s}}{M} = \text{s}^{-1}$$

Note that if the reaction order changes, the units of the rate constant change.

Practice Exercise

Which of the following are the units of the rate constant for Equation 14.11?

(**a**) $M^{-1/2}\text{s}^{-1}$ (**b**) $M^{-1/2}\text{s}^{-1/2}$ (**c**) $M^{1/2}\text{s}^{-1}$ (**d**) $M^{-3/2}\text{s}^{-1}$ (**e**) $M^{-3/2}\text{s}^{-1/2}$

Using Initial Rates to Determine Rate Laws

We have seen that the rate law for most reactions has the general form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots$$

Thus, the task of determining the rate law becomes one of determining the reaction orders, m and n. In most reactions, the reaction orders are 0, 1, or 2. As noted earlier in this section, we can use the response of the reaction rate to a change in initial concentration to determine the reaction order.

In working with rate laws, it is important to realize that the *rate* of a reaction depends on concentration but the *rate constant* does not. As we will see later in this chapter, the rate constants (and hence the reaction rate) are affected by temperature and by the presence of a catalyst.

Sample Exercise 14.6

Determining a Rate Law from Initial Rate Data

The initial rate of a reaction A + B ⟶ C was measured for three different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (**a**) the rate law for the reaction, (**b**) the rate constant, (**c**) the rate of the reaction when [A] = 0.050M and [B] = 0.100 M.

SOLUTION

Analyze We are given a table of data that relates concentrations of reactants with initial rates of reaction and asked to determine (**a**) the rate law, (**b**) the rate constant, and (**c**) the rate of reaction for a set of concentrations not listed in the table.

Plan (**a**) We assume that the rate law has the following form: Rate = $k[\text{A}]^m[\text{B}]^n$. We will use the given data to deduce the reaction orders m and n by determining how changes in the concentration change the rate. (**b**) Once we know m and n, we can use the rate law and one of the sets of data to determine the rate constant k. (**c**) Upon determining both the rate constant and the reaction orders, we can use the rate law with the given concentrations to calculate rate.

Solve

(**a**) If we compare experiments 1 and 2, we see that [A] is held constant and [B] is doubled. Thus, this pair of experiments shows how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B.

$$\frac{\text{Rate 1}}{\text{Rate 2}} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_2]^m[\text{B}_2]^n}$$

Inserting values of rate and concentration from the experiments gives:

$$\frac{4.0 \times 10^{-5}\ \cancel{M/s}}{4.0 \times 10^{-5}\ \cancel{M/s}} = \frac{k[0.100\ \cancel{M}]^m[0.100\ \cancel{M}]^n}{k[0.100\ \cancel{M}]^m[0.200\ \cancel{M}]^n}$$

$$1 = (1/2)^n$$

The only way this equation can be true is if $n = 0$. Therefore, the rate law is zero order in B, which means that the rate is independent of [B].

In experiments 1 and 3, [B] is held constant, so these data allow us to determine the order of the rate law with respect to [A].

$$\frac{\text{Rate 1}}{\text{Rate 3}} = \frac{k[\text{A}_1]^m[\text{B}_1]^n}{k[\text{A}_3]^m[\text{B}_3]^n}$$

Inserting values of rate and concentration from the experiments gives:

$$\frac{16.0 \times 10^{-5}\ \cancel{M/s}}{4.0 \times 10^{-5}\ \cancel{M/s}} = \frac{k[0.200\cancel{M}]^m[0.100\cancel{M}]^n}{k[0.100\cancel{M}]^m[0.100\cancel{M}]^n}$$

$$4 = (2)^m$$

Because the rate increases by a factor of four when [A] is doubled, we can conclude that $m = 2$ and the rate law is second order in B.

Combining these results, we arrive at the rate law:

$$\text{Rate} = k[\text{A}]^2[\text{B}]^0 = k[\text{A}]^2$$

Continued

(**b**) Using the rate law and the data from experiment 1, we have:

$$k = \frac{\text{rate}}{[\text{A}]^2} = \frac{4.0 \times 10^{-5}\,M/\text{s}}{(0.100\,M)^2} = 4.0 \times 10^{-3}\,M^{-1}\,\text{s}^{-1}$$

(**c**) Using the rate law from part (a) and the rate constant from part (b), we have:

Because [B] is not part of the rate law, it is irrelevant to the rate if there is at least some B present to react with A.

$$\begin{aligned}\text{Rate} &= k[\text{A}]^2 \\ &= (4.0 \times 10^{-3}\,M^{-1}\text{s}^{-1})(0.050\,M)^2 \\ &= 1.0 \times 10^{-5}\,M/\text{s}\end{aligned}$$

Check A good way to check our rate law is to use the concentrations in experiment 2 or 3 and see if we can correctly calculate the rate. Using data from experiment 3, we have

$$\begin{aligned}\text{Rate} &= k[\text{A}]^2 = (4.0 \times 10^{-3}\,M^{-1}\,\text{s}^{-1})(0.200\,M)^2 \\ &= 1.6 \times 10^{-4}\,M/\text{s}\end{aligned}$$

Thus, the rate law correctly reproduces the data, giving both the correct number and the correct units for the rate.

Practice Exercise

Consider the reaction examined in the Sample Exercise, A + B → C. If the concentration of B is doubled, the rate of disappearance of B _____, whereas if the concentration of A is doubled, the rate of disappearance of B _____.

(**a**) does not change; does not change
(**b**) increases by a factor of two; increases by a factor of two
(**c**) increases by a factor of four; increases by a factor of two
(**d**) does not change; increases by a factor of four
(**e**) increases by a factor of four; does not change

- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant.
- Determine the rate law and rate constant for a reaction from a series of data.

Self-Assessment Exercises

14.9 The experimentally determined rate law for the substitution reaction $(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + HCl$ is Rate = k[$(CH_3)_3CCl$].

If the concentration of CH_3OH is doubled, how will the reaction rate change?

(**a**) The reaction rate will remain the same

(**b**) The reaction rate will double

(**c**) The reaction rate will quadruple

14.10 From the given data, determine the rate equation and value of the rate constant for the reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Experiment Number	$[NO_2]$ (M)	[CO] (M)	Initial Rate (M/s)
1	0.10	0.10	0.0050
2	0.40	0.10	0.080
3	0.10	0.20	0.0050

(**a**) Rate = $k[NO_2][CO]$ where $k = 0.50\,M^{-1}\,\text{s}^{-1}$

(**b**) Rate = $k[NO_2]^2$ where $k = 0.50\,M^{-1}\,\text{s}^{-1}$

(**c**) Rate = $k[CO]^2$ where $k = 0.50\,M^{-1}\,\text{s}^{-1}$

Exercises

14.11 Consider a hypothetical reaction between A, B, and C that is zero order in A, second order in B, and first order in C. (**a**) Write the rate law for the reaction. (**b**) How does the rate change when [A] is tripled and the other reactant concentrations are held constant? (**c**) How does the rate change when [B] is doubled and the other reactant concentrations are held constant? (**d**) How does the rate change when [C] is tripled and the other reactant concentrations are held constant? (**e**) By what factor does the rate change when the concentrations of all three reactants are doubled? (**f**) By what factor does the rate change when the concentrations of all three reactants are cut in half?

14.12 The decomposition reaction of N_2O_5 in tetrachloromethne is $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$. The rate law is first order in N_2O_5. At 55 °C the rate constant is $4.12 \times 10^{-3}\,\text{s}^{-1}$. (**a**) Write the rate law for the reaction. (**b**) What is the rate of reaction when $[N_2O_5] = 0.050\,M$? (**c**) What happens to the rate when the concentration of N_2O_5 is tripled to 0.150 M? (**d**) What happens to the rate when the concentration of N_2O_5 is reduced by 10% to 0.045 M?

14.13 The reaction between bromoethane (C_2H_5Br) and hydroxide ion in ethanol at 330 K, $C_2H_5Br(alc) + OH^-(alc) \longrightarrow C_2H_5OH(l) + Br^-(alc)$, is first order each in bromoethane and hydroxide ion. When $[C_2H_5Br]$ is 0.0477 M and $[OH^-]$

is 0.100 *M*, the rate of disappearance of bromoethane is $1.7 \times 10^{-7}\,M/s$. (**a**) What is the value of the rate constant? (**b**) What are the units of the rate constant? (**c**) How would the rate of disappearance of bromoethane change if the solution were diluted by adding an equal volume of pure ethanol to the solution?

14.14 The reaction $2\,ClO_2(aq) + 2\,OH^-(aq) \longrightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$ was studied with the following results:

Experiment	$[ClO_2]\,(M)$	$[OH^-]\,(M)$	Initial Rate (M/s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

(**a**) Determine the rate law for the reaction. (**b**) Calculate the rate constant with proper units. (**c**) Calculate the rate when $[ClO_2] = 0.100\,M$ and $[OH^-] = 0.050\,M$.

14.15 The following data were collected for the rate of disappearance of NO in the reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$:

Experiment	$[NO]\,(M)$	$[O_2]\,(M)$	Initial Rate (M/s)
1	0.0126	0.0125	1.41×10^{-2}
2	0.0252	0.0125	5.64×10^{-2}
3	0.0252	0.0250	1.13×10^{-1}

(**a**) What is the rate law for the reaction? (**b**) What are the units of the rate constant? (**c**) What is the average value of the rate constant calculated from the three data sets? (**d**) What is the rate of disappearance of NO when $[NO] = 0.0750\,M$ and $[O_2] = 0.0100\,M$? (**e**) What is the rate of disappearance of O_2 at the concentrations given in part (d)?

14.16 Consider the reaction of peroxydisulfate ion ($S_2O_8^{2-}$) with iodide ion (I^-) in aqueous solution:

$$S_2O_8^{2-}(aq) + 3\,I^-(aq) \longrightarrow 2\,SO_4^{2-}(aq) + I_3^-(aq)$$

At a particular temperature, the initial rate of disappearance of $S_2O_8^{2-}$ varies with reactant concentrations in the following manner:

Experiment	$[S_2O_8^{2-}]\,(M)$	$[I^-]\,(M)$	Initial Rate (M/s)
1	0.018	0.036	2.6×10^{-6}
2	0.027	0.036	3.9×10^{-6}
3	0.036	0.054	7.8×10^{-6}
4	0.050	0.072	1.4×10^{-5}

(**a**) Determine the rate law for the reaction and state the units of the rate constant. (**b**) What is the average value of the rate constant for the disappearance of $S_2O_8^{2-}$ based on the four sets of data? (**c**) How is the rate of disappearance of $S_2O_8^{2-}$ related to the rate of disappearance of I^-? (**d**) What is the rate of disappearance of I^- when $[S_2O_8^{2-}] = 0.025\,M$ and $[I^-] = 0.050\,M$?

Answers to Self-Assessment Exercises

14.9 (a) **14.10** (b)

14.4 The Change of Concentration with Time



The Iron pillar of Delhi dates from the late fourth to early fifth century and was constructed in the reign of King Chandragupta II. Over the course of time, it has shown great resistance to corrosion, attracting the attention of metallurgists as well as archaeologists. The pillar's endurance is attributed to a natural protective film on the surface of the pillar resulting from a relatively high phosphorous content in the iron. It has outlasted the ravages of time and weather!

At the end of this section, you should be able to

- Apply the integrated form of a rate law to determine the concentration of a reactant at a given time.
- Relate the rate constant for a first order reaction to the reaction half-life.

The rate laws we have examined so far enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. In this section, we will show that rate laws can also be converted into equations that show the relationship between concentrations of reactants or products and time. The mathematics required to accomplish this conversion involves calculus. We do not expect you to be able to perform the calculus operations, but you should be able to use the resulting equations. We will apply this conversion to three of the simplest rate laws: those that are first order overall, those that are second order overall, and those that are zero order overall.

First-Order Reactions

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power. If a reaction of the type A $\longrightarrow$ products is first order, the rate law is:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

This form of a rate law, which expresses how rate depends on concentration, is called the *differential rate law*. Using the operation from calculus called integration, we see that this relationship can be transformed into an equation known as the *integrated rate law* for a first-order reaction that relates the initial concentration of A, $[\text{A}]_0$, to its concentration at any other time t, $[\text{A}]_t$:

$$\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt \quad \text{or} \quad \ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt \qquad [14.12]$$

The function "ln" in Equation 14.12 is the natural logarithm (Appendix A.2). Equation 14.12 can also be rearranged to

$$\ln[\text{A}]_t = -kt + \ln[\text{A}]_0 \qquad [14.13]$$

Equations 14.12 and 14.13 can be used with any concentration units as long as the units are the same for both $[\text{A}]_t$ and $[\text{A}]_0$. When dealing with gases, we can use partial pressure as a concentration in Equations 14.12 and 14.13. This substitution follows from the fact that the ideal gas law (see Section 10.4) dictates that at constant temperature the pressure is directly proportional to the concentration (n/V).

For a first-order reaction, Equation 14.12 or 14.13 can be used in several ways. Given any three of the following quantities, we can solve for the fourth: k, t, $[\text{A}]_0$, and $[\text{A}]_t$. Thus, you can use these equations to determine (1) the concentration of a reactant remaining at any time after the reaction has started, (2) the time interval required for a given fraction of a sample to react, or (3) the time interval required for a reactant concentration to fall to a certain level.

Sample Exercise 14.7

Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water at 12 °C follows first-order kinetics with a rate constant of $1.45\ yr^{-1}$. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of $5.0 \times 10^{-7}\ g/cm^3$. Assume that the temperature of the lake is constant (so that there are no effects of temperature variation on the rate). (**a**) What is the concentration of the insecticide on June 1 of the following year? (**b**) How long will it take for the insecticide concentration to decrease to $3.0 \times 10^{-7}\ g/cm^3$?

SOLUTION

Analyze We are given the rate constant for a reaction that obeys first-order kinetics, as well as information about concentrations and times, and asked to calculate how much reactant (insecticide) remains after 1 yr. We must also determine the time interval needed to reach a particular insecticide concentration.

Plan In part (a) we are given the rate constant, a period of time, and the initial concentration of the reactant, so we can use Equation 14.13 to determine the concentration of the reactant after 1 year has passed. In part (b) we are given the initial and final concentrations and the rate constant. In this case we can use Equation 14.13 to calculate the time that must pass to reach the desired concentration.

Solve

(**a**) Substituting the known quantities into Equation 14.13, we have:

$$\ln[\text{insecticide}]_{t=1\,yr} = -(1.45\ yr^{-1})(1.00\ yr) + \ln(5.0 \times 10^{-7})$$

We use the ln function on a calculator to evaluate the second term on the right [that is, $\ln(5.0 \times 10^{-7})$], giving:

$$\ln[\text{insecticide}]_{t=1\,yr} = -1.45 + (-14.51) = -15.96$$

To obtain $[\text{insecticide}]_{t=1\,yr}$, we use the inverse natural logarithm, or e^x, function on the calculator:

$$[\text{insecticide}]_{t=1\,yr} = e^{-15.96} = 1.2 \times 10^{-7}\ g/cm^3$$

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(**b**) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7}\ g/cm^3$, gives:

$$\ln(3.0 \times 10^{-7}) = -(1.45\ yr^{-1})(t) + \ln(5.0 \times 10^{-7})$$

Solving for t gives:

$$t = -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45\ yr^{-1}$$
$$= -(-15.02 + 14.51)/1.45\ yr^{-1} = 0.35\ yr$$

Check In part (a) the concentration remaining after 1.00 yr (that is, $1.2 \times 10^{-7}\ g/cm^3$) is less than the original concentration ($5.0 \times 10^{-7}\ g/cm^3$), as it should be. In (b) the given concentration ($3.0 \times 10^{-7}\ g/cm^3$) is greater than that remaining after 1.00 yr, indicating that the time must be less than a year. Thus, $t = 0.35$ yr is a reasonable answer.

Practice Exercise

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510 °C is a first-order process with a rate constant of $6.8 \times 10^{-4}\ s^{-1}$:

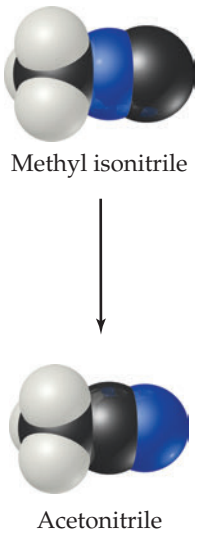
$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

If the initial pressure of $(CH_3)_2O$ is 18 kPa, what is its pressure after 1420 s?

Equation 14.13 can be used to verify whether a reaction is first order and to determine its rate constant. This equation has the form of the general equation for a straight line, $y = mx + b$, in which m is the slope and b is the y-intercept of the line (Appendix A.4):

$$\ln [A]_t = -kt + \ln [A]_0$$
$$\updownarrow \quad \updownarrow \quad \updownarrow$$
$$y = mx + b$$

For a first-order reaction, therefore, a graph of $\ln[A]_t$ versus time gives a straight line with a slope of $-k$ and a y-intercept of $\ln[A]_0$. A reaction that is not first order will not yield a straight line.



▲ **Figure 14.6** **The first-order reaction of CH_3NC conversion into CH_3CN.**

As an example, consider the conversion of methyl isonitrile (CH_3NC) to its isomer acetonitrile (CH_3CN) (**Figure 14.6**). Because experiments show that the reaction is first order, we can write the rate equation:

$$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0$$

We run the reaction at a temperature at which methyl isonitrile is a gas (199 °C), and **Figure 14.7**(**a**) shows how the pressure of this gas varies with time. Figure 14.7(**b**) shows that a plot of the natural logarithm of the pressure versus time is a straight line. The slope of this line is $-5.1 \times 10^{-5}\ s^{-1}$. (You should verify this for yourself, remembering that your result may vary slightly from ours because of inaccuracies associated with reading the graph.) Because the slope of the line equals $-k$, the rate constant for this reaction equals $5.1 \times 10^{-5}\ s^{-1}$.

Second-Order Reactions

A **second-order reaction** is one for which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power. For simplicity, let's consider reactions of the type A ⟶ products or A + B ⟶ products that are second order in just one reactant, A:

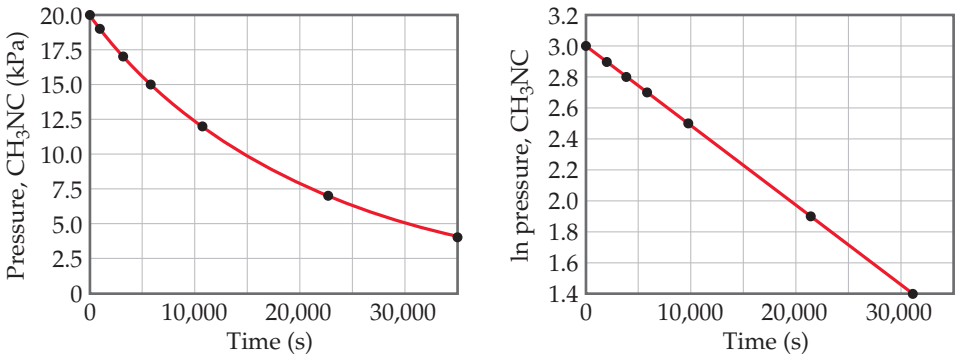
$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

With the use of calculus, this differential rate law can be used to derive the integrated rate law for second-order reactions:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \qquad [14.14]$$

This equation, like Equation 14.13, has four variables, k, t, $[A]_0$, and $[A]_t$, and any one of these can be calculated knowing the other three. Equation 14.14 also has the form of a straight line ($y = mx + b$). If the reaction is second order, a plot of $1/[A]_t$ versus t yields a straight line with slope k and y-intercept $1/[A]_0$. One way to distinguish between first- and second-order rate laws is to graph both $\ln[A]_t$ and $1/[A]_t$ against t. If the $\ln[A]_t$ plot is linear, the reaction is first order; if the $1/[A]_t$ plot is linear, the reaction is second order.

Go Figure What can you conclude given that the plot of ln *P* versus *t* is linear?



▲ **Figure 14.7** **Kinetic data for conversion of methyl isonitrile into acetonitrile.**

Sample Exercise 14.8

Determining Reaction Order from the Integrated Rate Law

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C, $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$. Is the reaction first or second order in NO_2?

Time (s)	$[NO_2](M)$
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

SOLUTION

Analyze We are given the concentrations of a reactant at various times during a reaction and asked to determine whether the reaction is first or second order.

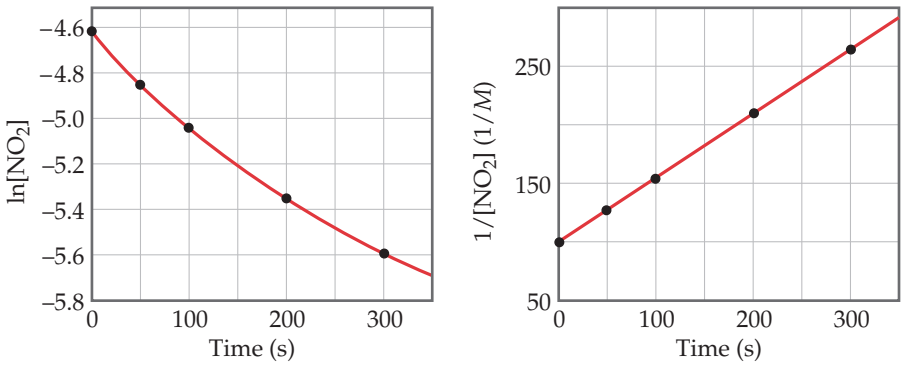
Plan We can plot $\ln[NO_2]$ and $1/[NO_2]$ against time. If one plot or the other is linear, we will know the reaction is either first or second order.

Solve

To graph $\ln[NO_2]$ and $1/[NO_2]$ against time, we first make the following calculations from the data given:

Time (s)	$[NO_2](M)$	$\ln[NO_2]$	$1/[NO_2]$ $(1/M)$
0.0	0.01000	−4.605	100
50.0	0.00787	−4.845	127
100.0	0.00649	−5.037	154
200.0	0.00481	−5.337	208
300.0	0.00380	−5.573	263

As Figure 14.8 shows, only the plot of $1/[NO_2]$ versus time is linear. Thus, the reaction obeys a second-order rate law: Rate $= k[NO_2]^2$. From the slope of this straight-line graph, we determine that $k = 0.543\ M^{-1}\,s^{-1}$ for the disappearance of NO_2.



▲ **Figure 14.8** Kinetic data for decomposition of NO_2.

Practice Exercise

For a certain reaction A $\longrightarrow$ products, a plot of ln[A] versus time produces a straight line with a slope of $-3.0 \times 10^{-2}\,s^{-1}$. Which of the following statements is or are true?

(i) The reaction follows first-order kinetics.
(ii) The rate constant for the reaction is $3.0 \times 10^{-2}\,s^{-1}$.
(iii) The initial concentration of [A] was 1.0 *M*.

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

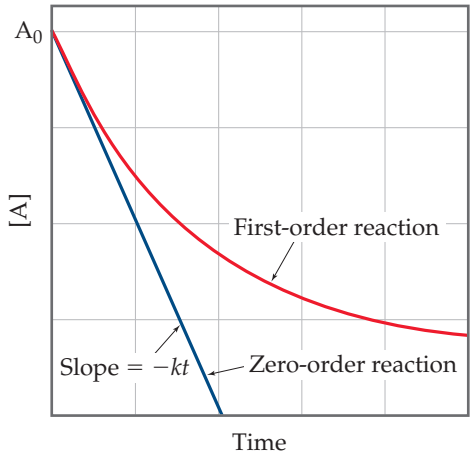
Zero-Order Reactions

We have seen that in a first-order reaction the concentration of a reactant A decreases nonlinearly, as shown by the red curve in Figure 14.9. As [A] declines, the *rate* at which it disappears declines in proportion. A **zero-order reaction** is one in which the rate of disappearance of A is *independent* of [A]. The rate law for a zero-order reaction is

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k \qquad [14.15]$$

Go Figure

At which times during the reaction would you have trouble distinguishing a zero-order reaction from a first-order reaction?



▲ **Figure 14.9** **Comparison of first-order and zero-order reactions for the disappearance of reactant A with time.**

The integrated rate law for a zero-order reaction is

$$[A]_t = -kt + [A]_0 \qquad [14.16]$$

where $[A]_t$ is the concentration of A at time t and $[A]_0$ is the initial concentration. This is the equation for a straight line with vertical intercept $[A]_0$ and slope $-k$, as shown in the blue curve in Figure 14.9.

The most common type of zero-order reaction occurs when a gas undergoes decomposition on the surface of a solid. If the surface is completely covered by decomposing molecules, the rate of reaction is constant because the number of reacting surface molecules is constant, so long as there is some gas-phase substance left.

Half-Life

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach half its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process. A fast reaction has a short half-life.

We can determine the half-life of a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12:

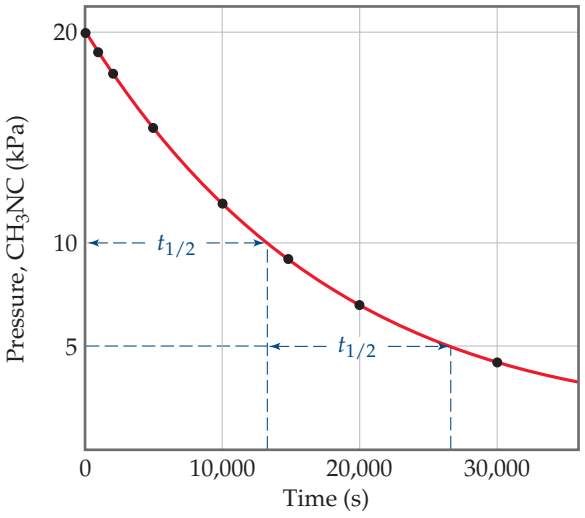
$$\ln\frac{\frac{1}{2}[A]_0}{[A]_0} = -kt_{1/2}$$

$$\ln\tfrac{1}{2} = -kt_{1/2}$$

$$t_{1/2} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k} \qquad [14.17]$$

From Equation 14.17, we see that $t_{1/2}$ for a first-order rate law does not depend on the initial concentration of any reactant. Consequently, the half-life remains constant throughout the reaction. If, for example, the initial concentration of a reactant is 0.120 M it will be $\frac{1}{2}(0.120\ M) = 0.060\ M$ after one half-life. After one more half-life passes, the concentration will drop to 0.030 M, and so on. Equation 14.17 also indicates that, for a first-order reaction, we can calculate $t_{1/2}$ if we know k and calculate k if we know $t_{1/2}$.

The change in concentration over time for the first-order rearrangement of gaseous methyl isonitrile at 199 °C is graphed in **Figure 14.10**. Because the concentration of this gas is directly proportional to its pressure during the reaction, we have chosen to plot pressure rather than concentration in this graph. The first half-life occurs at 13,600 s (3.78 h). At a time 13,600 s later, the methyl isonitrile pressure (and therefore, concentration) has decreased to half of one-half, or one-fourth, of the initial value.



▲ **Figure 14.10** **Kinetic data for the rearrangement of methyl isonitrile to acetonitrile at 199 °C, showing the half-life of the reaction.**

In a first-order reaction, the concentration of the reactant decreases by one-half *in each of a series of regularly spaced time intervals, each interval equal to* $t_{1/2}$.

The half-life for second-order and other reactions depends on reactant concentrations and therefore changes as the reaction progresses. We obtained Equation 14.17 for the half-life for a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12. We find the half-life of a second-order reaction by making the same substitutions into Equation 14.14:

$$\frac{1}{\frac{1}{2}[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0} \qquad [14.19]$$

In this case, the half-life depends on the initial concentration of reactant—the lower the initial concentration, the longer the half-life.

CHEMISTRY PUT TO WORK Bromomethane in the Atmosphere

The compounds known as chlorofluorocarbons (CFCs) are well-known agents responsible for the destruction of Earth's protective ozone layer. Another simple molecule that has the potential to destroy the stratospheric ozone layer is bromomethane, CH_3Br (Figure 14.11). Because this substance has a wide range of uses, including antifungal treatment of plant seeds, it has been produced in large quantities in the past (at the height of its production in 1997 about 70 000 tonnes per year worldwide). In the stratosphere, the C—Br bond is broken through absorption of short-wavelength radiation. The resultant Br atoms then catalyze decomposition of O_3.

Bromomethane is removed from the lower atmosphere by a variety of mechanisms, including a slow reaction with ocean water:

$$CH_3Br(g) + H_2O(l) \longrightarrow CH_3OH(aq) + HBr(aq) \qquad [14.18]$$

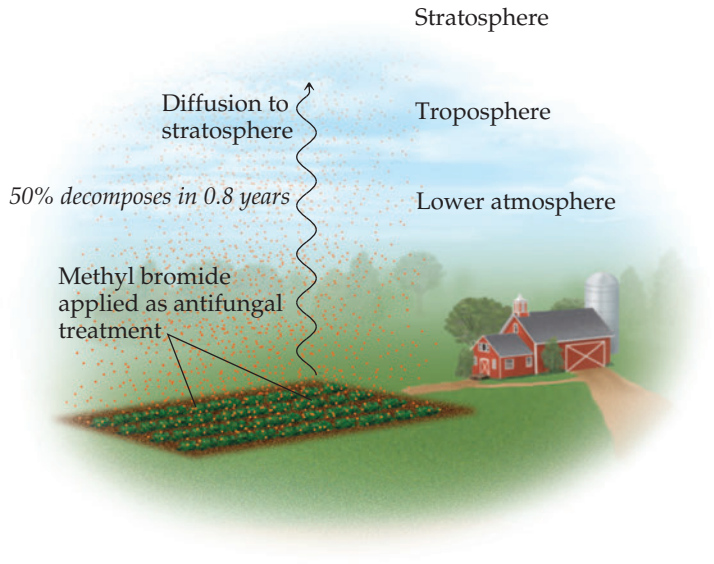
To determine the potential importance of CH_3Br in destruction of the ozone layer, it is important to know how rapidly the reaction in Equation 14.18 and all other reactions remove CH_3Br from the lower atmosphere before it can diffuse into the stratosphere.

The average lifetime of CH_3Br in Earth's lower atmosphere is difficult to measure because the conditions that exist in the atmosphere are too complex to be simulated in the laboratory. Instead, scientists analyzed nearly 4000 atmospheric samples collected above the Pacific Ocean for the presence of several trace organic substances, including bromomethane. From these measurements, it was possible to estimate the *atmospheric residence time* for CH_3Br.

The atmospheric residence time is related to the half-life for CH_3Br in the lower atmosphere, assuming CH_3Br decomposes by a first-order process. From the experimental data, the half-life for bromomethane in the lower atmosphere is estimated to be 0.8 ± 0.1 yr. That is, a collection of CH_3Br molecules present at any given time will, on average, be 50% decomposed after 0.8 yr, 75% decomposed after 1.6 yr, and so on. A half-life of 0.8 yr, while comparatively short, is still sufficiently long so that CH_3Br contributes significantly to the destruction of the ozone layer.

In 1997 an international agreement was reached to phase out use of bromomethane in developed countries by 2005. Although exemptions for critical agricultural use have been granted, global consumption in 2013 was only 3% of the levels seen in the early 1990s.

Related Exercise: 14.131



▲ **Figure 14.11** Distribution and fate of methyl bromide in Earth's atmosphere.

Sample Exercise 14.9

Determining the Half-Life of a First-Order Reaction

The reaction of C_4H_9Cl with water is a first-order reaction. (**a**) Use Figure 14.3 to estimate the half-life for this reaction. (**b**) Use the half-life from (a) to calculate the rate constant.

SOLUTION

Analyze We are asked to estimate the half-life of a reaction from a graph of concentration versus time and then to use the half-life to calculate the rate constant for the reaction.

Plan

(**a**) To estimate a half-life, we can select a concentration and then determine the time required for the concentration to decrease to half of that value.
(**b**) Equation 14.17 is used to calculate the rate constant from the half-life.

Solve

(**a**) From the graph, we see that the initial value of $[C_4H_9Cl]$ is 0.100 *M*. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 *M*, which we can read off the graph. This point occurs at approximately 340 s.

(**b**) Solving Equation 14.17 for *k*, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\ \text{s}} = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

Check At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 *M*. Inspection of the graph shows that this is indeed the case.

Practice Exercise

(**a**) Using Equation 14.17, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7.
(**b**) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Self-Assessment Exercises

14.17 In 1 L of a solution, 10.0 g of substance A remain after three-half-lives of a first order reaction. What was the original amount of substance A before the start of the reaction?

(a) 3.33 g

(b) 30.0 g

(c) 80.0 g

14.18 An antibiotic breaks down in the body with a first order rate constant of $k = 1.9 \times 10^{-2}$ min^{-1}. What is the half-life of the antibiotic?

(a) 16 min

(b) 36 min

(c) 52 min

Exercises

14.19 (**a**) For the generic reaction A → B what quantity, when graphed versus time, will yield a straight line for a first-order reaction? (**b**) How can you calculate the rate constant for a first-order reaction from the graph you made in part (a)?

14.20 (**a**) The gas-phase decomposition of sulfuryl chloride (SO_2Cl_2), $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is first order in SO_2Cl_2. At 300 °C the half-life for this process is two and a half days. What is the rate constant at this temperature? (**b**) At 400 °C the rate constant is 0.19 min^{-1}. What is the half-life at this temperature?

14.21 As described in Exercise 14.20, the decomposition of sulfuryl chloride (SO_2Cl_2) is a first-order process. The rate constant for the decomposition at 660 K is 4.5×10^{-2} s^{-1}. (**a**) If we begin with an initial SO_2Cl_2 pressure of 60 kPa, what is the partial pressure of this substance after 60 s? (**b**) At what time will the partial pressure of SO_2Cl_2 decline to one-tenth its initial value?

14.22 From the following data for the second-order gas-phase decomposition of HI at 430 °C, calculate the second-order rate constant and half-life for the reaction:

Time (s)	[HI]/mol dm^{-3}
0	1
100	0.89
200	0.8
300	0.72
400	0.66

14.23 Consider the data presented in Exercise 14.5. (**a**) Determine whether the reaction is first order or second order. (**b**) What is the rate constant? (**c**) What is the half-life?

14.24 Sucrose ($C_{12}H_{22}O_{11}$), commonly known as table sugar, reacts in dilute acid solutions to form two simpler sugars, glucose and fructose, both of which have the formula $C_6H_{12}O_6$. At 23 °C and in 0.5 *M* HCl, the following data were obtained for the disappearance of sucrose:

Time (min)	[$C_{12}H_{22}O_{11}$] (*M*)
0	0.316
39	0.274
80	0.238
140	0.190
210	0.146

(**a**) Is the reaction first order or second order with respect to [$C_{12}H_{22}O_{11}$]? (**b**) What is the rate constant? (**c**) Using this rate constant, calculate the concentration of sucrose at 39, 80, 140, and 210 min if the initial sucrose concentration was 0.316 *M* and the reaction were zero order in sucrose.

Answers to Self-Assessment Exercises

14.17 (c) **14.18** (c)

14.5 Temperature and Rate

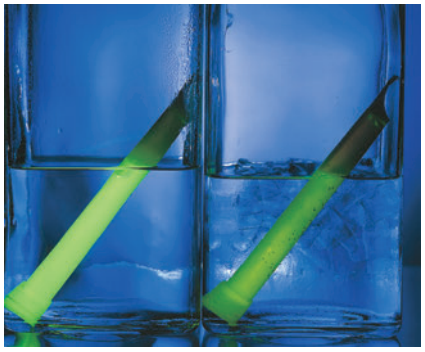


The rates of most chemical reactions increase as the temperature rises. For example, dough rises faster at room temperature than when refrigerated, and plants grow more rapidly in warm weather than in cold. We can see the effect of temperature on reaction rate by observing a chemiluminescence reaction (one that produces light), such as that in Cyalume® light sticks (**Figure 14.12**).

By the end of this section, you should be able to

- Explain how the activation energy affects a rate and be able to use the Arrhenius equation.

How is this experimentally observed temperature effect reflected in the rate law? The faster rate at higher temperature is due to an increase in the rate constant with increasing temperature. For example, let's reconsider the first-order reaction we saw in Figure 14.6 namely, $CH_3NC \longrightarrow CH_3CN$. **Figure 14.13** shows the rate constant for this reaction as a function of temperature. The rate constant and, hence, the rate of the reaction increase rapidly with temperature, approximately doubling for each 10 °C rise.



▲ **Figure 14.12 Temperature affects the rate of the chemiluminescence reaction in light sticks: The chemiluminescent reaction occurs more rapidly in hot water, and more light is produced.**

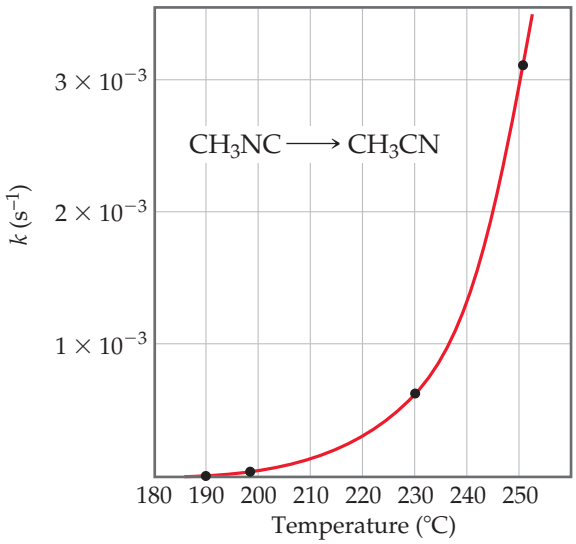
The Collision Model

Reaction rates are affected both by reactant concentrations and by temperature. The **collision model**, based on the kinetic-molecular theory, accounts for both of these effects at the molecular level. The central idea of the collision model is that molecules must collide to react. The greater the number of collisions per second, the greater the reaction rate. As reactant concentration increases, therefore, the number of collisions increases, leading to an increase in reaction rate. According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, both of which increase the reaction rate.

For a reaction to occur, though, more is required than simply a collision—it must be the right kind of collision. For most reactions, in fact, only a tiny fraction of collisions leads to a reaction. For example, in a mixture of H_2 and I_2 at ordinary temperatures and pressures, each molecule undergoes about 10^{10} collisions per second. If every collision between H_2 and I_2 resulted in the formation of HI, the reaction would be over in much less than a second. Instead, at room temperature the reaction proceeds very slowly because only about one in every 10^{13} collisions produces a reaction. What keeps the reaction from occurring more rapidly?

Go Figure

Would you expect this curve to eventually go back down to lower values? Why or why not?



▲ **Figure 14.13 Temperature dependence of the rate constant for methyl isonitrile conversion to acetonitrile.** The four points indicated are used in Sample Exercise 14.11.

The Orientation Factor

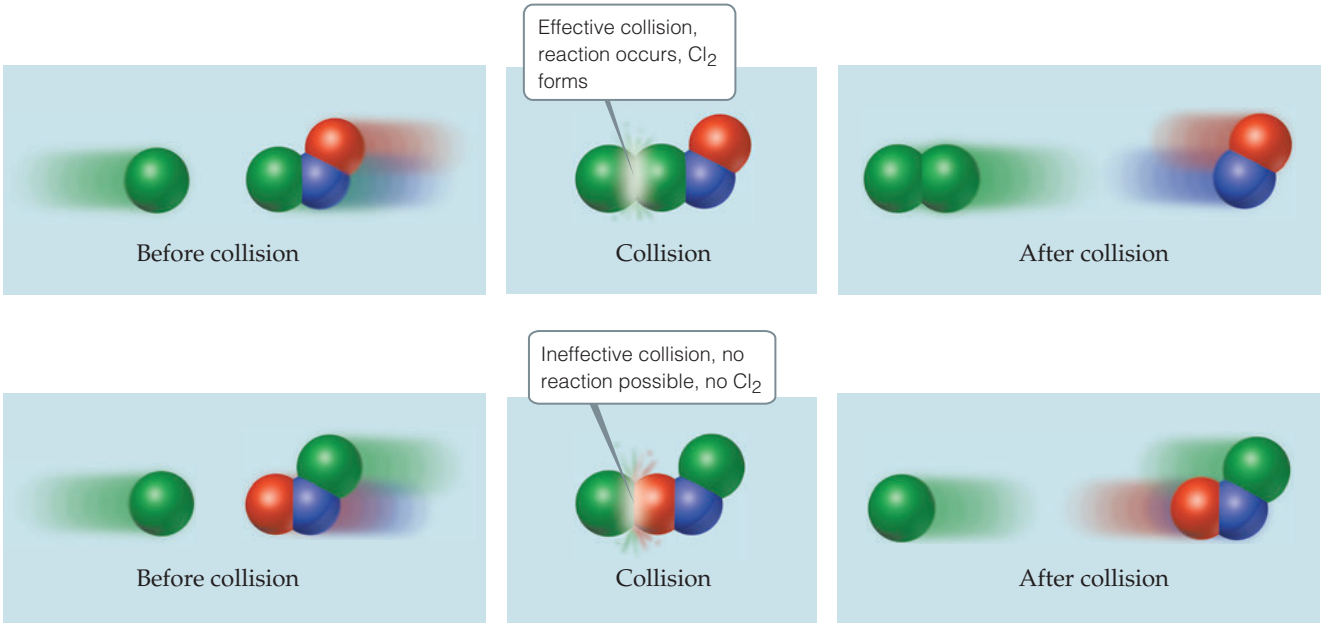
In most reactions, collisions between molecules result in a chemical reaction only if the molecules are oriented in a certain way when they collide. The relative orientations of the molecules during collision determine whether the atoms are suitably positioned to form new bonds. For example, consider the reaction

$$Cl + NOCl \longrightarrow NO + Cl_2$$

which takes place if the collision brings Cl atoms together to form Cl_2, as shown in the top panel of **Figure 14.14**. In contrast, in the collision shown in the lower panel, the two Cl atoms are not colliding directly with one another, and no products are formed.

Activation Energy

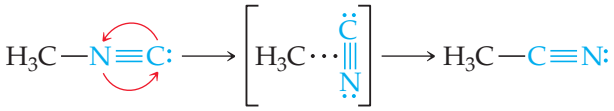
Molecular orientation is not the only factor influencing whether a molecular collision will produce a reaction. In 1888 the Swedish chemist Svante Arrhenius suggested that molecules must possess a certain minimum amount of energy to react. According to the collision model, this energy comes from the kinetic energies of the colliding molecules. Upon collision, the kinetic energy of the molecules can be used to stretch, bend, and ultimately break bonds, leading to chemical reactions. That is, the kinetic energy is used to change the potential energy



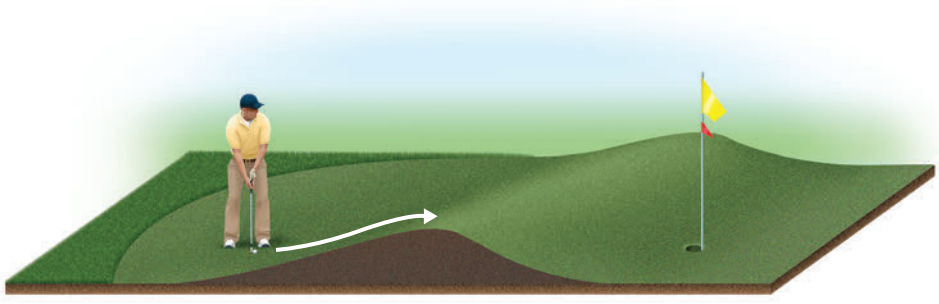
▲ **Figure 14.14** **Molecular collisions may or may not lead to a chemical reaction between Cl and NOCl.**

of the molecule. If molecules are moving too slowly—in other words, with too little kinetic energy—they merely bounce off one another without changing. The minimum energy required to initiate a chemical reaction is called the **activation energy**, E_a, and its value varies from reaction to reaction.

The situation during reactions is analogous to that shown in **Figure 14.15**. The golfer hits the ball to make it move over the hill in the direction of the cup. The hill is a *barrier* between ball and cup. To reach the cup, the player must impart enough kinetic energy with the putter to move the ball to the top of the barrier. If he does not impart enough energy, the ball will roll partway up the hill and then back down toward him. In the same way, molecules require a certain minimum energy to break existing bonds during a chemical reaction. We can think of this minimum energy as an *energy barrier*. In the rearrangement of methyl isonitrile to acetonitrile, for example, we might imagine the reaction passing through an intermediate state in which the N≡C portion of the methyl isonitrile molecule is sideways:



Go Figure Which of the following determines how hard the golfer must strike the ball: the difference in elevation between the ball and the hole or between the ball and the top of the barrier?



▲ **Figure 14.15** **Energy is needed to overcome a barrier between initial and final states.**

Figure 14.16 shows that energy must be supplied to stretch the bond between the H_3C group and the N≡C group to allow the N≡C group to rotate. After the N≡C group has twisted sufficiently, the C—C bond begins to form, and the energy of the molecule drops. Thus, the barrier to formation of acetonitrile represents the energy necessary to force the molecule through the relatively unstable intermediate state, analogous to forcing the ball in Figure 14.15 over the hill. The difference between the energy of the starting molecule and the highest energy along the reaction pathway is the activation energy, E_a. The molecule having the arrangement of atoms shown at the top of the barrier is called either the **activated complex** or the **transition state**.

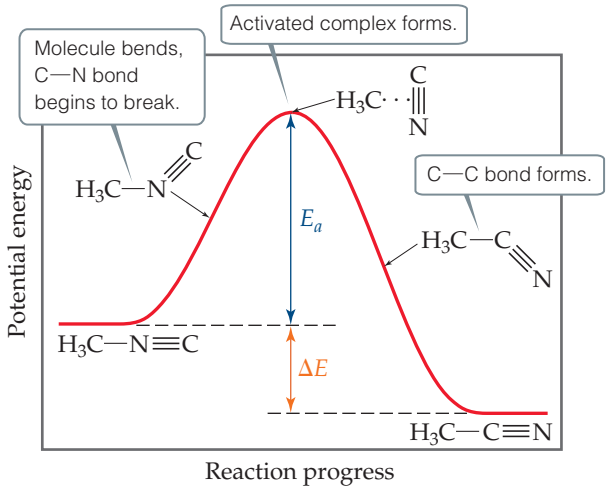
The conversion of $H_3C—N{\equiv}C$ to $H_3C—C{\equiv}N$ is exothermic. Figure 14.16 therefore shows the product as having a lower energy than the reactant. The energy change for the reaction, ΔE, has no effect on reaction rate, however.

The rate constant depends on the magnitude of E_a; generally, the lower the value of E_a is, the larger the rate constant and the faster the reaction.

Notice that the reverse reaction is endothermic. The activation energy for the reverse reaction is equal to the energy that must be overcome if approaching the barrier from the right: $\Delta E + E_a$. Thus, to reach the activated complex for the reverse reaction requires more energy than for the forward reaction—for this reaction, there is a larger barrier to overcome going from right to left than from left to right.

Go Figure

How does the energy needed to overcome the energy barrier compare with the overall change in energy for this reaction?



▲ **Figure 14.16** **Energy profile for conversion of methyl isonitrile (H_3CNC) to its isomer acetonitrile (H_3CCN).**

Any particular methyl isonitrile molecule acquires sufficient energy to overcome the energy barrier through collisions with other molecules. Recall from the kinetic-molecular theory of gases that, at any instant, gas molecules are distributed in energy over a wide range. **Figure 14.17** shows the distribution of kinetic energies for two temperatures, comparing them with the minimum energy needed for reaction, E_a. At the higher temperature a much greater fraction of the molecules have kinetic energy greater than E_a, which leads to a greater rate of reaction.

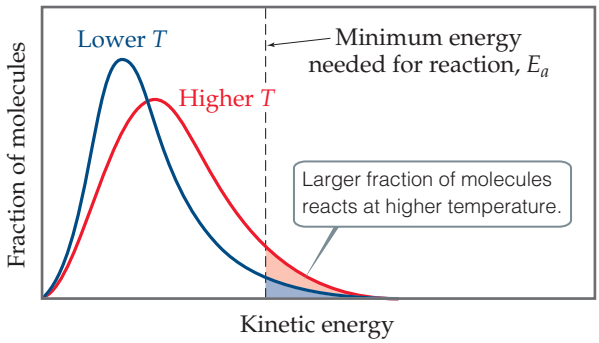
For a collection of molecules in the gas phase, the fraction of molecules that have kinetic energy equal to or greater than E_a is given by the expression

$$f = e^{-E_a/RT} \qquad [14.20]$$

In this equation, R is the gas constant (18.314 J/mol K) and T is the absolute temperature. To get an idea of the magnitude of f, let's suppose that E_a is 100 kJ/mol, a value typical of many reactions, and that T is 300 K. The calculated value of f is 3.9×10^{-18}, an extremely small

Go Figure

What would the curve look like for a temperature higher than that for the red curve in the figure?



▲ **Figure 14.17** **The effect of temperature on the distribution of kinetic energies of molecules in a sample.**

number! At 320 K, $f = 4.7 \times 10^{-17}$. Thus, only a 20° increase in temperature produces a more than tenfold increase in the fraction of molecules possessing at least 100 kJ/mol of energy.

The Arrhenius Equation

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear (Figure 14.13). He found that most reaction-rate data obeyed an equation based on (a) the fraction of molecules possessing energy E_a or greater, (b) the number of collisions per second, and (c) the fraction of collisions that have the appropriate orientation. These three factors are incorporated into the **Arrhenius equation**:

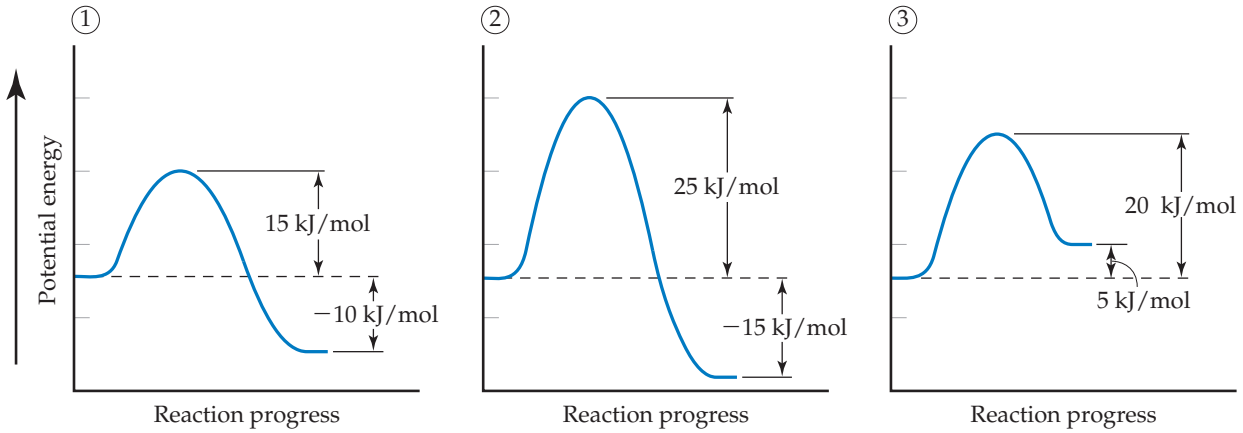
$$k = Ae^{-E_a/RT} \qquad [14.21]$$

In this equation, k is the rate constant, E_a is the activation energy, R is the gas constant (18.314 J/mol K), and T is the absolute temperature. The **frequency factor**, A, is constant, or nearly so, as temperature is varied. This factor is related to the frequency of collisions and the probability that the collisions are favorably oriented for reaction.* As the magnitude of E_a increases, k decreases because the fraction of molecules that possess the required energy is smaller. Thus, at fixed values of T and A, *the rate constant decreases as E_a increases*.

Sample Exercise 14.10

Activation Energies and Speeds of Reaction

Consider a series of reactions having these energy profiles:



Rank the forward rate constants from smallest to largest assuming all three reactions have nearly the same value for the frequency factor A.

SOLUTION

The lower the activation energy, the larger the rate constant and the faster the reaction. The value of ΔE does not affect the value of the rate constant. Hence, the order of the rate constants is $2 < 3 < 1$.

Practice Exercise

Which of the following changes *always* leads to an increase in the rate constant for a reaction:

(i) Decreasing the temperature
(ii) Decreasing the activation energy
(iii) Making the value of ΔE more negative

(**a**) Only one—(i), or (ii), or (iii)—increases the reaction rate.
(**b**) (i) and (ii)
(**c**) (i) and (iii)
(**d**) (ii) and (iii)
(**e**) All three—(i), (ii), and (iii)—increase the reaction rate.

*Because collision frequency increases with temperature, A also has some temperature dependence, but this dependence is much smaller than the exponential term. Therefore, A is considered to be approximately constant.

Determining the Activation Energy

We can calculate the activation energy for a reaction by manipulating the Arrhenius equation. Taking the natural log of both sides of Equation 14.21, we obtain

$$\ln k = \ln Ae^{-E_a/RT}$$

$$\ln k = \ln e^{-E_a/RT} + \ln A$$

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad [14.22]$$

$$y = mx + b$$

which has the form of the equation for a straight line. A graph of $\ln k$ versus $1/T$ is a line with a slope equal to $-E_a/R$ and a y-intercept equal to $\ln A$. Thus, the activation energy can be determined by measuring k at a series of temperatures, graphing $\ln k$ versus $1/T$, and calculating E_a from the slope of the resultant line.

We can also use Equation 14.22 to evaluate E_a in a nongraphical way if we know the rate constant of a reaction at two or more temperatures. For example, suppose that at two different temperatures T_1 and T_2 a reaction has rate constants k_1 and k_2. For each condition, we have

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \left(-\frac{E_a}{RT_1} + \ln A\right) - \left(-\frac{E_a}{RT_2} + \ln A\right)$$

Assuming temperature-dependent changes in the frequency factor A are negligible, we can simplify to obtain

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad [14.23]$$

Equation 14.23 provides a convenient way to calculate a rate constant k_1 at some temperature T_1 when we know the activation energy and the rate constant k_2 at some other temperature T_2.

Sample Exercise 14.11

Determining the Activation Energy

The table at right shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data points in Figure 14.13):

(**a**) From these data, calculate the activation energy for the reaction.
(**b**) What is the value of the rate constant at 430.0 K?

Temperature (°C)	k (s^{-1})
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

SOLUTION

Analyze We are given rate constants, k, measured at several temperatures and asked to determine the activation energy, E_a, and the rate constant, k, at a particular temperature.

Plan We can obtain E_a from the slope of a graph of $\ln k$ versus $1/T$. Once we know E_a, we can use Equation 14.23 together with the given rate data to calculate the rate constant at 430.0 K.

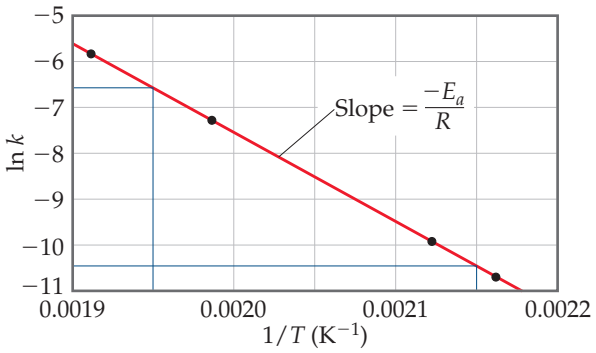
Solve

(**a**) We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the following table:

T (K)	$1/T$ (K^{-1})	$\ln k$
462.9	2.160×10^{-3}	−10.589
472.1	2.118×10^{-3}	−9.855
503.5	1.986×10^{-3}	−7.370
524.4	1.907×10^{-3}	−5.757

Continued

A graph of ln k versus $1/T$ is a straight line (Figure 14.18).



▲ **Figure 14.18** **Graphical determination of activation energy E_a.**

The slope of the line is obtained by choosing any two well-separated points and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1}. Thus, the overall units for the slope are K. The slope equals $-E_a/R$. We use the value for the gas constant R in units of J/mol K (Table 10.2). We thus obtain

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -(\text{slope})(R) = -(-1.9 \times 10^4\,\cancel{K})\left(8.314\frac{J}{\text{mol}\,\cancel{K}}\right)\left(\frac{1\,\text{kJ}}{1000\,\cancel{J}}\right)$$

$$= 1.6 \times 10^2\,\text{kJ/mol} = 160\,\text{kJ/mol}$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.18.

(**b**) To determine the rate constant, k_1, at $T_1 = 430.0$ K, we can use Equation 14.23 with $E_a = 160$ kJ/mol and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5}\,s^{-1}$ and $T_2 = 462.9$ K:

$$\ln\left(\frac{k_1}{2.52 \times 10^{-5}\,s^{-1}}\right) =$$

$$\left(\frac{160\,\cancel{\text{kJ}}/\text{mol}}{8.314\,\cancel{J}/\text{mol}\,\cancel{K}}\right)\left(\frac{1}{462.9\,\cancel{K}} - \frac{1}{430.0\,\cancel{K}}\right)\left(\frac{1000\,\cancel{J}}{1\,\cancel{\text{kJ}}}\right) = -3.18$$

Thus,

$$\frac{k_1}{2.52 \times 10^{-5}\,s^{-1}} = e^{-3.18} = 4.15 \times 10^{-2}$$

$$k_1 = (4.15 \times 10^{-2})(2.52 \times 10^{-5}\,s^{-1}) = 1.0 \times 10^{-6}\,s^{-1}$$

Note that the units of k_1 are the same as those of k_2 and the rate constant at 430.0 K is smaller than it is at 462.9 K, as it should be.

Practice Exercise

Using the data in Sample Exercise 14.11, which of the following is the rate constant for the rearrangement of methyl isonitrile at 320 °C?
(**a**) $8.1 \times 10^{-15}\,s^{-1}$ (**b**) $2.2 \times 10^{-13}\,s^{-1}$ (**c**) $2.7 \times 10^{-9}\,s^{-1}$
(**d**) $2.3 \times 10^{-1}\,s^{-1}$ (**e**) $9.2 \times 10^{3}\,s^{-1}$

Self-Assessment Exercise

14.25 If a reaction has a rate constant of $2.0 \times 10^{-5}\,s^{-1}$ at 20 °C and $7.3 \times 10^{-5}\,s^{-1}$ at 30 °C, what is the activation energy?
(a) 280 J/mol
(b) 650 J/mol
(c) 42 kJ/mol
(d) 96 kJ/mol

Exercises

14.26 (**a**) What factors determine whether a collision between two molecules will lead to a chemical reaction? (**b**) Does the rate constant for a reaction generally increase or decrease with an increase in reaction temperature? (**c**) Which factor is most sensitive to changes in temperature—the frequency of collisions, the orientation factor, or the fraction of molecules with energy greater than the activation energy?

14.27 (**a**) The activation energy for the reaction $A(g) \longrightarrow B(g)$ is 100 kJ/mol. Calculate the fraction of the molecule A that has an energy equal to or greater than the activation energy at 400 K. (**b**) Calculate this fraction for a temperature of 500 K. What is the ratio of the fraction at 500 K to that at 400 K?

14.28 For the elementary process $N_2O_5(g) \longrightarrow NO_2(g) + NO_3(g)$ the activation energy (E_a) and overall ΔE are 154 kJ/mol and 136 kJ/mol, respectively. (**a**) Sketch the energy profile for this reaction, and label E_a and ΔE. (**b**) What is the activation energy for the reverse reaction?

14.29 Indicate whether each statement is true or false.
(**a**) If you measure the rate constant for a reaction at different temperatures, you can calculate the overall enthalpy change for the reaction.
(**b**) Exothermic reactions are faster than endothermic reactions.
(**c**) If you double the temperature for a reaction, you cut the activation energy in half.

14.30 Data for a forward reaction is:
(**a**) $E_a = 75$ kJ/mol; $\Delta E = -20$ kJ/mol
(**b**) $E_a = 100$ kJ/mol; $\Delta E = +30$ kJ/mol
(**c**) $E_a = 85$ kJ/mol; $\Delta E = -50$ kJ/mol

Which of these reactions will be the fastest in the *reverse* direction? Which will be slowest?

14.31 Understanding the high-temperature behavior of nitrogen oxides is essential for controlling pollution generated in car engines. The decomposition of nitric oxide (NO) to N_2 and O_2 is second order with a rate constant of 0.0796 $M^{-1}s^{-1}$ at 737 °C and 0.0815 $M^{-1}s^{-1}$ at 947 °C. Calculate the activation energy for the reaction.

14.32 The temperature dependence of the rate constant for a reaction is tabulated as follows:

Temperature (K)	k (M^{-1} s^{-1})
600	0.028
650	0.22
700	1.3
750	6.0
800	23

Calculate E_a and A.

Answers to Self-Assessment Exercises

14.25 (d)

14.6 Reaction Mechanisms



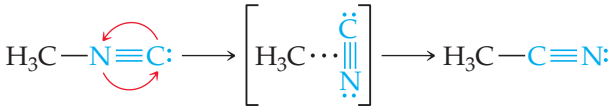
A reaction mechanism is a little like a climber of a rock face. The climber may be faced with a number of possible routes from bottom to top and it's by testing out the possibilities that the best one to accomplish the task is found.

A balanced equation for a chemical reaction indicates the substances present at the start of the reaction and those present at the end of the reaction. It provides no information, however, about the detailed steps that occur at the molecular level as the reactants are turned into products. The steps by which a reaction occurs is called the **reaction mechanism**. At the most sophisticated level, a reaction mechanism describes the order in which bonds are broken and formed and the changes in relative positions of the atoms in the course of the reaction. As we are unable to observe individual molecules as they collide and react, a reaction mechanism is always a hypothesis, however much confidence we have in our interpretation of the data. By the end of this section, you should be able to

- Connect the rate law for a reaction to a mechanism given the individual steps in the mechanism.

Elementary Reactions

We have seen that reactions take place because of collisions between reacting molecules. For example, the collisions between molecules of methyl isonitrile (CH_3NC) can provide the energy to allow the CH_3NC to rearrange to acetonitrile:



Similarly, the reaction of NO and O_3 to form NO_2 and O_2 appears to occur as a result of a single collision involving suitably oriented and sufficiently energetic NO and O_3 molecules:

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g) \qquad [14.24]$$

Both reactions occur in a single event or step and are called **elementary reactions**.

The number of molecules that participate as reactants in an elementary reaction defines the **molecularity** of the reaction. If a single molecule is involved, the reaction is **unimolecular**. The rearrangement of methyl isonitrile is a unimolecular process. Elementary reactions involving the collision of two reactant molecules are **bimolecular**. The reaction between NO and O_3 is bimolecular. Elementary reactions involving the simultaneous collision of three molecules are **termolecular**. Termolecular reactions are far less probable than unimolecular or bimolecular processes and are extremely rare. The chance that four or more molecules will collide simultaneously with any regularity is even more remote; consequently, such collisions are never proposed as part of a reaction mechanism. Thus, nearly all reaction mechanisms contain only unimolecular and bimolecular elementary reactions.

Multistep Mechanisms

The net change represented by a balanced chemical equation often occurs by a *multistep mechanism* consisting of a sequence of elementary reactions. For example, below 225 °C, the reaction

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \qquad [14.25]$$

appears to proceed in two elementary reactions (or two *elementary steps*), each of which is bimolecular. First, two NO_2 molecules collide, and an oxygen atom is transferred from one to the other. The resultant NO_3 then collides with a CO molecule and transfers an oxygen atom to it:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$$

Thus, we say that the reaction occurs by a two-step mechanism.

The chemical equations for the elementary reactions in a multistep mechanism must always add to give the chemical equation of the overall process.

In the present example, the sum of the two elementary reactions is

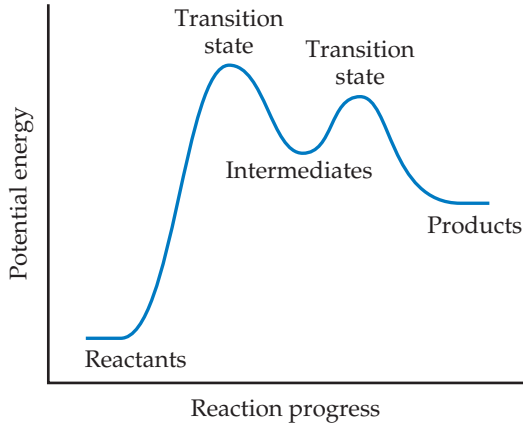
$$2\,NO_2(g) + NO_3(g) + CO(g) \longrightarrow NO_2(g) + NO_3(g) + NO(g) + CO_2(g)$$

Simplifying this equation by eliminating substances that appear on both sides gives Equation 14.25, the net equation for the process.

Because NO_3 is neither a reactant nor a product of the reaction—it is formed in one elementary reaction and consumed in the next—it is called an **intermediate**. Multistep mechanisms involve one or more intermediates. Intermediates are not the same as transition states, as shown in Figure 14.19. Intermediates can be stable and can therefore sometimes be identified and even isolated. Transition states, on the other hand, are always inherently unstable and as such can never be isolated. Nevertheless, the use of advanced "ultrafast" techniques sometimes allows us to characterize them.

Go Figure

For this profile, which elementary reaction rate is faster, intermediates converting to products or intermediates converting back to reactants?



▲ **Figure 14.19** **The energy profile of a reaction, showing transition states and an intermediate.**

Sample Exercise 14.12

Determining Molecularity and Identifying Intermediates

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$

(**a**) Describe the molecularity of each elementary reaction in this mechanism.
(**b**) Write the equation for the overall reaction.
(**c**) Identify the intermediate(s).

SOLUTION

Analyze We are given a two-step mechanism and asked for (a) the molecularities of each of the two elementary reactions, (b) the equation for the overall process, and (c) the intermediate.

Plan The molecularity of each elementary reaction depends on the number of reactant molecules in the equation for that reaction. The overall equation is the sum of the equations for the elementary reactions. The intermediate is a substance formed in one step of the mechanism and used in another and therefore not part of the equation for the overall reaction.

Solve

(**a**) The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.

(**b**) Adding the two elementary reactions gives

$$2\,O_3(g) + O(g) \longrightarrow 3\,O_2(g) + O(g)$$

Because $O(g)$ appears in equal amounts on both sides of the equation, it can be eliminated to give the net equation for the chemical process:

$$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

(**c**) The intermediate is $O(g)$. It is neither an original reactant nor a final product but is formed in the first step of the mechanism and consumed in the second.

Practice Exercise

Consider the following two-step reaction mechanism:

$$A(g) + B(g) \longrightarrow X(g) + Y(g)$$
$$X(g) + C(g) \longrightarrow Y(g) + Z(g)$$

Which of the following statements about this mechanism is or are true?
(i) Both of the steps in this mechanism are bimolecular.
(ii) The overall reaction is $A(g) + B(g) + C(g) \longrightarrow Y(g) + Z(g)$.
(iii) The substance $X(g)$ is an intermediate in this mechanism.
(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

Rate Laws for Elementary Reactions

In Section 14.3, we stressed that rate laws must be determined experimentally; they cannot be predicted from the coefficients of balanced chemical equations. We are now in a position to understand why this is so. Every reaction is made up of a series of one or more elementary steps, and the rate laws and relative speeds of these steps dictate the overall rate law for the reaction. Indeed, the rate law for a reaction can be determined from its mechanism, as we will see shortly, and compared with the experimental rate law. Thus, our next challenge in kinetics is to arrive at reaction mechanisms that lead to rate laws consistent with those observed experimentally. We start by examining the rate laws of elementary reactions.

Elementary reactions are significant in a very important way: *If a reaction is elementary, its rate law is based directly on its molecularity*. For example, consider the unimolecular reaction

$$A \longrightarrow \text{products}$$

As the number of A molecules increases, the number that reacts in a given time interval increases proportionally. Thus, the rate of a unimolecular process is first order:

$$\text{Rate} = k[A]$$

For bimolecular elementary steps, the rate law is second order, as in the reaction

$$A + B \longrightarrow \text{products} \qquad \text{Rate} = k[A][B]$$

The second-order rate law follows directly from collision theory. If we double the concentration of A, the number of collisions between the molecules of A and B doubles; likewise, if we double [B], the number of collisions between A and B doubles. Therefore, the rate law is first order in both [A] and [B] and second order overall.

The rate laws for all feasible elementary reactions are given in **Table 14.3**. Notice how each rate law follows directly from the molecularity of the reaction. It is important to remember, however, that we cannot tell by merely looking at a balanced, overall chemical equation whether the reaction involves one or several elementary steps.

The Rate-Determining Step for a Multistep Mechanism

As with the reaction in Sample Exercise 14.13, most reactions occur by mechanisms that involve two or more elementary reactions. Each step of the mechanism has its own rate constant and activation energy. Often one step is much slower than the others, and the overall rate of a reaction cannot exceed the rate of the slowest elementary step. Because

TABLE 14.3 Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate $= k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate $= k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate $= k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate $= k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate $= k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate $= k[A][B][C]$

Sample Exercise 14.13

Predicting the Rate Law for an Elementary Reaction

If the following reaction occurs in a single elementary reaction, predict its rate law:

$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$

SOLUTION

Analyze We are given the equation and asked for its rate law, assuming that it is an elementary process.

Plan Because we are assuming that the reaction occurs as a single elementary reaction, we are able to write the rate law using the coefficients for the reactants in the equation as the reaction orders.

Solve The reaction is bimolecular, involving one molecule of H_2 and one molecule of Br_2. Thus, the rate law is first order in each reactant and second order overall:

$$\text{Rate} = k[H_2][Br_2]$$

Comment Experimental studies of this reaction show that the reaction actually has a very different rate law:

$$\text{Rate} = k[H_2][Br_2]^{1/2}$$

Because the experimental rate law differs from the one obtained by assuming a single elementary reaction, we can conclude that the mechanism cannot occur by a single elementary step. It must, therefore, involve two or more elementary steps.

Practice Exercise

Consider the following reaction: $2\,A + B \longrightarrow X + 2\,Y$. You are told that the first step in the mechanism of this reaction has the following rate law: Rate $= k[A][B]$. Which of the following could be the first step in the reaction mechanism (note that substance Z is an intermediate)?

(a) $A + A \longrightarrow Y + Z$
(b) $A \longrightarrow X + Z$
(c) $A + A + B \longrightarrow X + Y + Y$
(d) $B \longrightarrow X + Y$
(e) $A + B \longrightarrow X + Z$

the slow step limits the overall reaction rate, it is called the **rate-determining step** (or *rate-limiting step*).

To understand the concept of the rate-determining step for a reaction, consider a toll road with two toll plazas (**Figure 14.20**). Cars enter the toll road at point 1 and pass through toll plaza A. They then pass an intermediate point 2 before passing through toll plaza B and arriving at point 3. We can envision this trip along the toll road as occurring in two elementary steps:

Step 1:	Point 1 ⟶ Point 2	(through toll plaza A)
Step 2:	Point 2 ⟶ Point 3	(through toll plaza B)
Overall:	Point 1 ⟶ Point 3	(through both toll plazas)

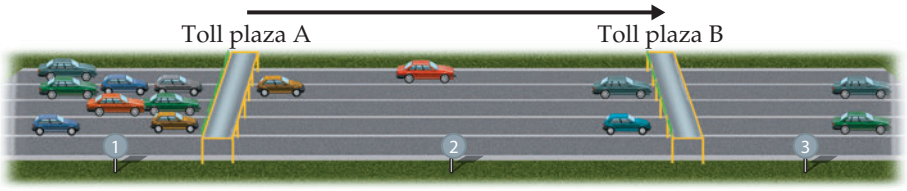
Now suppose that one or more gates at toll plaza A are malfunctioning, so that traffic backs up behind the gates, as depicted in Figure 14.20(a). The rate at which cars can get to point 3 is limited by the rate at which they can get through the traffic jam at plaza A. Thus, step 1 is the rate-determining step of the journey along the toll road. If, however, all gates at A are functioning but one or more at B are not, traffic flows quickly through A but gets backed up at B, as depicted in Figure 14.20(b). In this case, step 2 is the rate-determining step.

In the same way, *the slowest step in a multistep reaction determines the overall rate*. By analogy to Figure 14.20(a), the rate of a fast step following the rate-determining step does not speed up the overall rate. If the slow step is not the first one, as is the case in Figure 14.20(b), the faster preceding steps produce intermediate products that accumulate before being consumed in the slow step. In either case, *the rate-determining step governs the rate law for the overall reaction*.

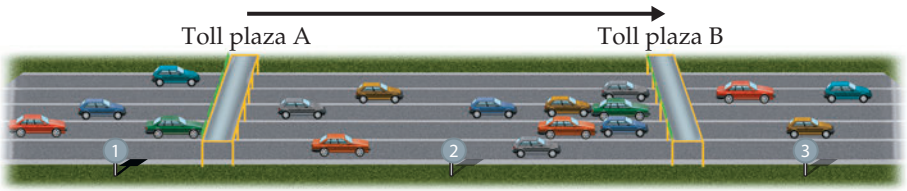
Mechanisms with a Slow Initial Step

We can most easily see the relationship between the slow step in a mechanism and the rate law for the overall reaction by considering an example in which the first step in a multistep mechanism is the rate-determining step. Consider the reaction of NO_2 and CO to produce NO and CO_2 (Equation 14.25). Below 225 °C, it is found experimentally that the rate law for this reaction is second order in NO_2 and zero order in CO: Rate $= k[NO_2]^2$.

Go Figure In scenario (a), would increasing the rate at which cars pass through Toll plaza B increase the rate at which cars go from point 1 to point 3?



(a) Cars slowed at toll plaza A, rate-determining step is passage through A



(b) Cars slowed at toll plaza B, rate-determining step is passage through B

▲ **Figure 14.20** **Rate-determining steps in traffic flow on a toll road.**

Can we propose a reaction mechanism consistent with this rate law? Consider the two-step mechanism:*

$$\text{Step 1: } NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) \quad \text{(slow)}$$
$$\text{Step 2: } NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) \quad \text{(fast)}$$
$$\text{Overall: } NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Step 2 is much faster than step 1; that is, $k_2 \gg k_1$, telling us that the intermediate $NO_3(g)$ is slowly produced in step 1 and immediately consumed in step 2.

Because step 1 is slow and step 2 is fast, step 1 is the rate-determining step. Thus, the rate of the overall reaction depends on the rate of step 1, and the rate law of the overall reaction equals the rate law of step 1. Step 1 is a bimolecular process that has the rate law

$$\text{Rate} = k_1[NO_2]^2$$

Thus, the rate law predicted by this mechanism agrees with the one observed experimentally. The reactant CO is absent from the rate law because it reacts in a step that follows the rate-determining step.

A scientist would not, at this point, say that we have "proved" that this mechanism is correct. All we can say is that the rate law predicted by the mechanism is *consistent with experiment*. We can often envision a different sequence of steps that leads to the same rate law. If, however, the predicted rate law of the proposed mechanism disagrees with experiment, we know for certain that the mechanism cannot be correct.

Sample Exercise 14.14

Determining the Rate Law for a Multistep Mechanism

The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$N_2O(g) \longrightarrow N_2(g) + O(g) \quad \text{(slow)}$$
$$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) \quad \text{(fast)}$$

(**a**) Write the equation for the overall reaction. (**b**) Write the rate law for the overall reaction.

SOLUTION

Analyze Given a multistep mechanism with the relative speeds of the steps, we are asked to write the overall reaction and the rate law for that overall reaction.

Plan (**a**) Find the overall reaction by adding the elementary steps and eliminating the intermediates. (**b**) The rate law for the overall reaction will be that of the slow, rate-determining step.

Solve

(**a**) Adding the two elementary reactions gives

$$2\,N_2O(g) + O(g) \longrightarrow 2\,N_2(g) + O_2(g) + O(g)$$

Omitting the intermediate, $O(g)$, which occurs on both sides of the equation, gives the overall reaction:

$$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$$

(**b**) The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

$$\text{Rate} = k[N_2O]$$

Practice Exercise

An alternative two-step reaction mechanism has been proposed for the reaction $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$, which was discussed on page 692:

Step 1:

$$NO_2(g) + NO_2(g) \longrightarrow N_2O_4(g) \quad \text{(slow)}$$

Step 2:

$$N_2O_4(g) + CO(g) \longrightarrow NO(g) + CO_2(g) + NO_2(g) \quad \text{(fast)}$$

Which experiment would allow you to distinguish between the two proposed mechanisms?
(**a**) Run trials with different initial concentrations of $NO_2(g)$ and measure the initial reaction rates. (**b**) Run trials with different initial concentrations of $CO(g)$ and measure the initial reaction rates. (**c**) Conduct experiments to identify the reaction intermediate(s). (**d**) It is not possible to distinguish between the two proposed reaction mechanisms.

*Note the rate constants k_1 and k_2 written above the reaction arrows. The subscript on each rate constant identifies the elementary step involved. Thus, k_1 is the rate constant for step 1, and k_2 is the rate constant for step 2. A negative subscript refers to the rate constant for the reverse of an elementary step. For example, k_{-1} is the rate constant for the reverse of the first step.

Mechanisms with a Fast Initial Step

It is possible, but not particularly straightforward, to derive the rate law for a mechanism in which an intermediate is a reactant in the rate-determining step. This situation arises in multistep mechanisms when the first step is fast and therefore *not* the rate-determining step. Let's consider one example: the gas-phase reaction of nitric oxide (NO) with bromine (Br_2):

$$2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g) \qquad [14.26]$$

The experimentally determined rate law for this reaction is second order in NO and first order in Br_2:

$$\text{Rate} = k[NO]^2[Br_2] \qquad [14.27]$$

We seek a reaction mechanism that is consistent with this rate law. One possibility is that the reaction occurs in a single termolecular step:

$$NO(g) + NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g) \quad \text{Rate} = k[NO]^2[Br_2] \qquad [14.28]$$

As noted in Practice Exercise 2 of Exercise 14.13, this does not seem likely because termolecular processes are so rare.

Let's consider an alternative mechanism that does not involve a termolecular step:

$$\text{Step 1:} \quad NO(g) + Br_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2(g) \quad \text{(fast)}$$

$$\text{Step 2:} \quad NOBr_2(g) + NO(g) \xrightarrow{k_2} 2\,NOBr(g) \quad \text{(slow)} \qquad [14.29]$$

In this mechanism, step 1 involves two processes: a forward reaction and its reverse.

Because step 2 is the rate-determining step, the rate law for that step governs the rate of the overall reaction:

$$\text{Rate} = k_2[NOBr_2][NO] \qquad [14.30]$$

Note that $NOBr_2$ is an intermediate generated in the forward reaction of step 1. Intermediates are usually unstable and have a low, unknown concentration. Thus, the rate law of Equation 14.30 depends on the unknown concentration of an intermediate, which isn't desirable. We want instead to express the rate law for a reaction in terms of the reactants, or the products if necessary, of the reaction.

With the aid of some assumptions, we can express the concentration of the intermediate $NOBr_2$ in terms of the concentrations of the starting reactants NO and Br_2. We first assume that $NOBr_2$ is unstable and does not accumulate to any significant extent in the reaction mixture. Once formed, $NOBr_2$ can be consumed either by reacting with NO to form NOBr or by falling back apart into NO and Br_2. The first of these possibilities is step 2 of our alternative mechanism, a slow process. The second is the reverse of step 1, a unimolecular process:

$$NOBr_2(g) \xrightarrow{k_{-1}} NO(g) + Br_2(g)$$

Because step 2 is slow, we assume that most of the $NOBr_2$ falls apart according to this reaction. Thus, we have both the forward and reverse reactions of step 1 occurring much faster than step 2. Because they occur rapidly relative to step 2, the forward and reverse reactions of step 1 establish an equilibrium. As in any other dynamic equilibrium, the rate of the forward reaction equals that of the reverse reaction:

$$\underset{\text{Rate of forward reaction}}{k[NO][Br_2]} = \underset{\text{Rate of reverse reaction}}{k_{-1}[NOBr_2]}$$

Solving for $[NOBr_2]$, we have

$$[NOBr_2] = \frac{k_1}{k_{-1}}[NO][Br_2]$$

Substituting this relationship into Equation 14.30, we have

$$\text{Rate} = k_2\frac{k_1}{k_{-1}}[NO][Br_2][NO] = k[NO]^2[Br_2]$$

where the experimental rate constant k equals k_2k_1/k_{-1}. This expression is consistent with the experimental rate law (Equation 14.27). Thus, our alternative mechanism (Equation 14.29), which involves two steps but only unimolecular and bimolecular processes, is far more probable than the single-step termolecular mechanism of Equation 14.28.

In general, whenever a fast step precedes a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the fast step.

So far we have considered only three reaction mechanisms: one for a reaction that occurs in a single elementary step and two for simple multistep reactions where there is one rate-determining step. There are other more complex mechanisms, however. If you take a biochemistry class, for example, you will learn about cases in which the concentration of an intermediate cannot be neglected in deriving the rate law. Furthermore, some mechanisms require a large number of steps, sometimes 35 or more, to arrive at a rate law that agrees with experimental data!

Sample Exercise 14.15

Deriving the Rate Law for a Mechanism with a Fast Initial Step

Show that the following mechanism for Equation 14.26 also produces a rate law consistent with the experimentally observed one:

$$\text{Step 1:}\quad NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g) \quad \text{(fast, equilibrium)}$$

$$\text{Step 2:}\quad N_2O_2(g) + Br_2(g) \xrightarrow{k_2} 2\,NOBr(g) \quad \text{(slow)}$$

SOLUTION

Analyze We are given a mechanism with a fast initial step and asked to write the rate law for the overall reaction.

Plan The rate law of the slow elementary step in a mechanism determines the rate law for the overall reaction. Thus, we first write the rate law based on the molecularity of the slow step. In this case, the slow step involves the intermediate N_2O_2 as a reactant. Experimental rate laws, however, do not contain the concentrations of intermediates; instead they are expressed in terms of the concentrations of reactants, and in some cases products. Thus, we must relate the concentration of N_2O_2 to the concentration of NO by assuming that an equilibrium is established in the first step.

Solve The second step is rate determining, so the overall rate is

$$\text{Rate} = k_2[N_2O_2][Br_2]$$

We solve for the concentration of the intermediate N_2O_2 by assuming that an equilibrium is established in step 1; thus, the rates of the forward and reverse reactions in step 1 are equal:

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

Solving for the concentration of the intermediate, N_2O_2, gives

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

Substituting this expression into the rate expression gives

$$\text{Rate} = k_2\frac{k_1}{k_{-1}}[NO]^2[Br_2] = k[NO]^2[Br_2]$$

Thus, this mechanism also yields a rate law consistent with the experimental one. Remember: There may be more than one mechanism that leads to an observed experimental rate law!

Practice Exercise

Consider the following hypothetical reaction:
$2\,P + Q \longrightarrow 2\,R + S$. The following mechanism is proposed for this reaction:

$$P + P \rightleftharpoons T \quad \text{(fast)}$$
$$Q + T \longrightarrow R + U \quad \text{(slow)}$$
$$U \longrightarrow R + S \quad \text{(fast)}$$

Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?
(a) Rate $= k[P]^2$ **(b)** Rate $= k[P][Q]$ **(c)** Rate $= k[P]^2[Q]$
(d) Rate $= k[P][Q]^2$ **(e)** Rate $= k[U]$

Self-Assessment Exercise

14.33 For the reaction: $2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g)$ a two-step mechanism was proposed with Step 1 as the rate-determining step:

$NO_2 + F_2 \rightarrow NO_2F + F$ Step 1
$NO_2 + F \rightarrow NO_2F$ Step 2

What rate law is consistent with this mechanism?
(a) Rate $= k[NO_2][F_2]$
(b) Rate $= k[NO_2][F]$
(c) Rate $= k[NO_2]^2[F_2]$

Exercises

14.34 (**a**) Can an intermediate appear as a reactant in the first step of a reaction mechanism? (**b**) On a reaction energy profile diagram, is an intermediate represented as a peak or a valley? (**c**) If a molecule like Cl_2 falls apart in an elementary reaction, what is the molecularity of the reaction?

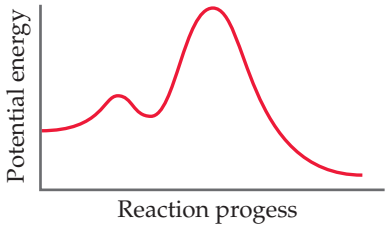
14.35 What is the molecularity of each of the following elementary reactions? Write the rate law for each.

(**a**) $2\,NO(g) \longrightarrow N_2O_2(g)$

(**b**) $H_2C(CH_2)CH_2(g) \longrightarrow CH_2{=}CH{-}CH_3(g)$

(**c**) $SO_3(g) \longrightarrow SO_2(g) + O(g)$

14.36 Consider the following energy profile.



(**a**) How many elementary reactions are in the reaction mechanism? (**b**) How many intermediates are formed in the reaction? (**c**) Which step is rate limiting? (**d**) For the overall reaction, is ΔE positive, negative, or zero?

14.37 The decomposition of hydrogen peroxide is catalyzed by iodide ion. The catalyzed reaction is thought to proceed by a two-step mechanism:

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + IO^-(aq) \quad \text{(slow)}$$
$$IO^-(aq) + H_2O_2(aq) \longrightarrow H_2O(l) + O_2(g) + I^-(aq) \quad \text{(fast)}$$

(**a**) Write the chemical equation for the overall process. (**b**) Identify the intermediate, if any, in the mechanism. (**c**) Assuming that the first step of the mechanism is rate determining, predict the rate law for the overall process.

14.38 You have studied the gas-phase oxidation of HBr by O_2:

$$4\,HBr(g) + O_2(g) \longrightarrow 2\,H_2O(g) + 2\,Br_2(g)$$

You find the reaction to be first order with respect to HBr and first order with respect to O_2. You propose the following mechanism:

$$HBr(g) + O_2(g) \longrightarrow HOOBr(g)$$
$$HOOBr(g) + HBr(g) \longrightarrow 2\,HOBr(g)$$
$$HOBr(g) + HBr(g) \longrightarrow H_2O(g) + Br_2(g)$$

(**a**) Confirm that the elementary reactions add to give the overall reaction. (**b**) Based on the experimentally determined rate law, which step is rate determining? (**c**) What are the intermediates in this mechanism? (**d**) If you are unable to detect HOBr or HOOBr among the products, does this disprove your mechanism?

Answers to Self-Assessment Exercises

14.33 (a)

14.7 | Catalysis



We have seen that the rate of a reaction is very dependent on the fraction of reacting molecules that have above a minimum amount of energy, the activation energy, and the rate increases rapidly as the temperature of the reaction increases. This allows us to perform quite slow reactions simply by heating them. But what about a situation wherein

we cannot change the temperature? A healthy person maintains a body temperature of 37 ± 0.5 °C, yet there is a myriad of very different chemical reactions that would be vanishingly slow under normal laboratory conditions at that temperature. The body employs a vast number of catalysts to facilitate these reactions while maintaining a constant temperature of 37 °C. Occasionally a person may not produce sufficient amount of a catalyst and supplementation may be needed; for example a diabetic may require insulin injections in order to metabolize blood sugars.

By the end of this section, you should be able to

- Explain the principles underlying catalysis.

A **catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself. Most reactions in the body, the atmosphere, and the oceans occur with the help of catalysts. Much industrial chemical research is devoted to the search for more effective catalysts for reactions of commercial importance. Extensive research efforts also are devoted to finding means of inhibiting or removing certain catalysts that promote undesirable reactions, such as those that corrode metals, age our bodies, and cause tooth decay.

Homogeneous Catalysis

A catalyst that is present in the same phase as the reactants in a reaction mixture is called a **homogeneous catalyst**. Examples abound both in solution and in the gas phase. Consider, for example, the decomposition of aqueous hydrogen peroxide, $H_2O_2(aq)$, into water and oxygen:

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g) \qquad [14.31]$$

In the absence of a catalyst, this reaction occurs extremely slowly. Many substances are capable of catalyzing the reaction, however, including bromide ion, which reacts with hydrogen peroxide in acidic solution, forming aqueous bromine and water (**Figure 14.21**).

$$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l) \qquad [14.32]$$

If this were the complete reaction, bromide ion would not be a catalyst because it undergoes chemical change during the reaction. However, hydrogen peroxide also reacts with the $Br_2(aq)$ generated in Equation 14.32:

$$Br_2(aq) + H_2O_2(aq) \longrightarrow 2\,Br^-(aq) + 2\,H^+(aq) + O_2(g) \qquad [14.33]$$

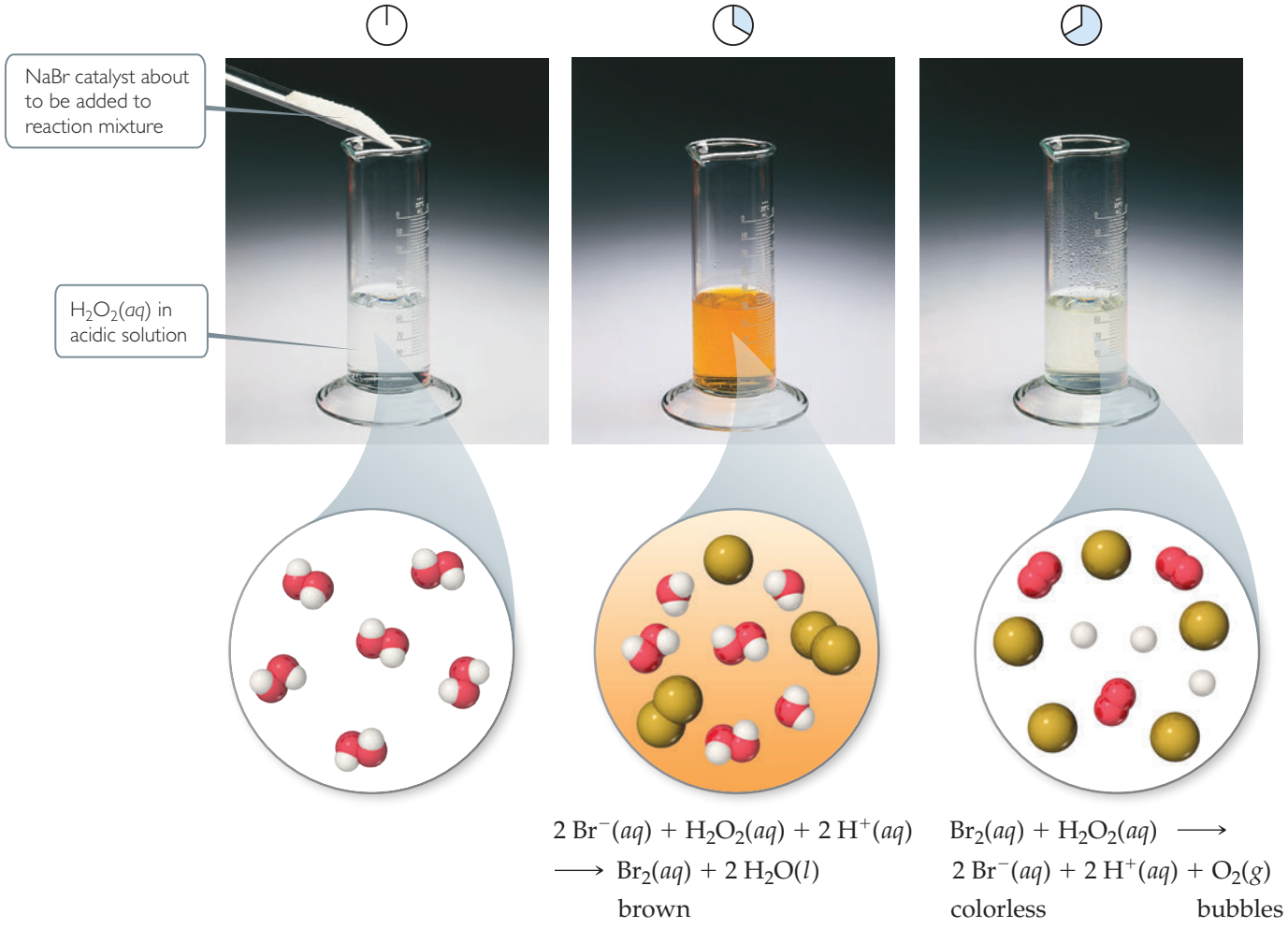
The sum of Equations 14.32 and 14.33 is just Equation 14.31, a result that you can check for yourself.

When the H_2O_2 has been completely decomposed, we are left with a colorless solution of $Br^-(aq)$, which means that this ion is indeed a catalyst of the reaction because it speeds up the reaction without itself undergoing any net change. In contrast, Br_2 is an intermediate because it is first formed (Equation 14.32) and then consumed (Equation 14.33). The color change we see in Figure 14.22 illustrates that the presence of intermediates can in some cases be readily detected. Neither the catalyst nor the intermediate appears in the equation for the overall reaction. Notice, however, that *the catalyst is present at the start of the reaction, whereas the intermediate is formed during the course of the reaction.*

How does a catalyst work? If we think about the general form of rate laws (Equation 14.7, rate $= k[A]^m[B]^n$), we conclude that the catalyst must affect the numerical value of k, the rate constant. On the basis of the Arrhenius equation (Equation 14.21, $k = Ae^{-E_a/RT}$), k is determined by the activation energy (E_a) and the frequency factor (A). A catalyst may affect the rate of reaction by altering the value of either E_a or A. We can envision this happening in two ways: The catalyst could provide a new mechanism for the reaction that has an E_a value lower than the E_a value for the uncatalyzed reaction, or the catalyst could assist in the orientation of reactants and so increase A. The most dramatic catalytic effects come from lowering E_a. As a general rule, *a catalyst provides a different mechanism for the chemical reaction of lower overall activation energy*.

In the decomposition of hydrogen peroxide, for example, two successive reactions of H_2O_2, first with bromide and then with bromine, take place. Because these two reactions

Go Figure Which species is responsible for the brownish color in the middle cylinder: H_2O_2, Br_2, Na^+, Br^-, or O_2? Is the brown substance a catalyst or an intermediate?



▲ **Figure 14.21 Homogeneous catalysis.** Effect of catalyst on the speed of hydrogen peroxide decomposition to water and oxygen gas.

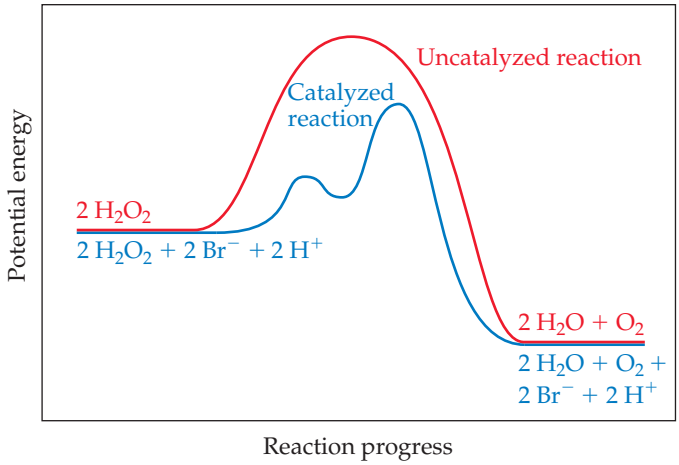
together serve as a catalytic pathway for hydrogen peroxide decomposition, *both* of them must have significantly lower activation energies than the uncatalyzed decomposition (**Figure 14.22**).

Heterogeneous Catalysis

A **heterogeneous catalyst** is one that exists in a phase different from the phase of the reactant molecules, usually as a solid in contact with either gaseous reactants or reactants in a liquid solution. Many industrially important reactions are catalyzed by the surfaces of solids. For example, raw petroleum is transformed into smaller hydrocarbon molecules by using what are called "cracking" catalysts. Heterogeneous catalysts are often composed of metals or metal oxides.

The initial step in heterogeneous catalysis is usually **adsorption** of reactants. (Adsorption refers to the binding of molecules to a surface, whereas absorption refers to the uptake of molecules into the interior of a substance.) Adsorption occurs because the atoms or ions at the surface of a solid are extremely reactive. Because the catalyzed reaction occurs on the surface, special methods are often used to prepare catalysts so that they have very large surface areas. Unlike their counterparts in the interior of the substance, surface atoms and ions have unused bonding capacity that can be used to bond molecules from the gas or solution phase to the surface of the solid.

Go Figure How many steps are there in the catalyzed reaction?



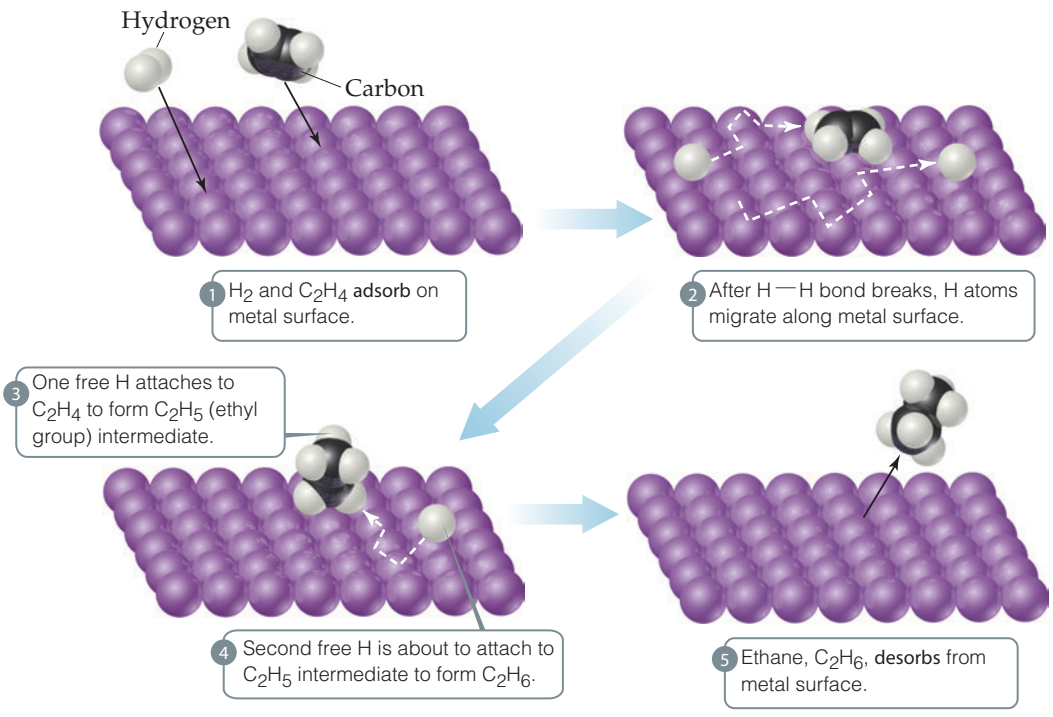
▲ **Figure 14.22** **Energy profiles for the uncatalyzed and bromide-catalyzed decomposition of H_2O_2.**

The reaction of hydrogen gas with ethene gas to form ethane gas provides an example of heterogeneous catalysis:

$$\underset{\text{Ethene}}{C_2H_4(g)} + H_2(g) \longrightarrow \underset{\text{Ethane}}{C_2H_6(g)} \qquad \Delta H^\circ = -137 \text{ kJ/mol} \qquad [14.34]$$

Even though this reaction is exothermic, it occurs very slowly in the absence of a catalyst. In the presence of a finely powdered metal, however, such as nickel, palladium, or platinum, the reaction occurs easily at room temperature via the mechanism diagrammed in **Figure 14.23**. Both ethene and hydrogen are adsorbed on the metal surface. Upon adsorption, the H—H bond of H_2 breaks, leaving two H atoms initially bonded to the metal surface but relatively free to move. When a hydrogen encounters an adsorbed ethene molecule, it can form a σ bond to one of the carbon atoms, effectively destroying the C—C π bond and leaving an *ethyl group* (C_2H_5) bonded to the surface via a metal-to-carbon σ bond. This σ bond is relatively weak, so when the other carbon atom also encounters a hydrogen atom, a sixth C—H σ bond is readily formed, and an ethane molecule (C_2H_6) is released from the metal surface.

▶ **Figure 14.23** **Heterogeneous catalysis.** Mechanism for reaction of ethene with hydrogen on a catalytic surface.



CHEMISTRY PUT TO WORK Catalytic Converters

Heterogeneous catalysis plays a major role in the fight against urban air pollution. Two components of automobile exhausts that help form photochemical smog are nitrogen oxides and unburned hydrocarbons. In addition, automobile exhaust may contain considerable quantities of carbon monoxide. Even with the most careful attention to engine design, it is impossible under normal driving conditions to reduce the quantity of these pollutants to an acceptable level in the exhaust gases. It is therefore necessary to remove them from the exhaust before they are vented to the air. This removal is accomplished in the *catalytic converter*.

The catalytic converter, which is part of an automobile's exhaust system, must perform two functions: (1) oxidation of CO and unburned hydrocarbons (C_xH_y) to carbon dioxide and water, and (2) reduction of nitrogen oxides to nitrogen gas:

$$CO, C_xH_y \xrightarrow{O_2} CO_2 + H_2O$$
$$NO, NO_2 \longrightarrow N_2 + O_2$$

These two functions require different catalysts, so the development of a successful catalyst system is a difficult challenge. The catalysts must be effective over a wide range of operating temperatures. They must continue to be active despite the fact that various components of the exhaust can block the active sites of the catalyst. And the catalysts must be sufficiently rugged to withstand exhaust gas turbulence and the mechanical shocks of driving under various conditions for thousands of miles.

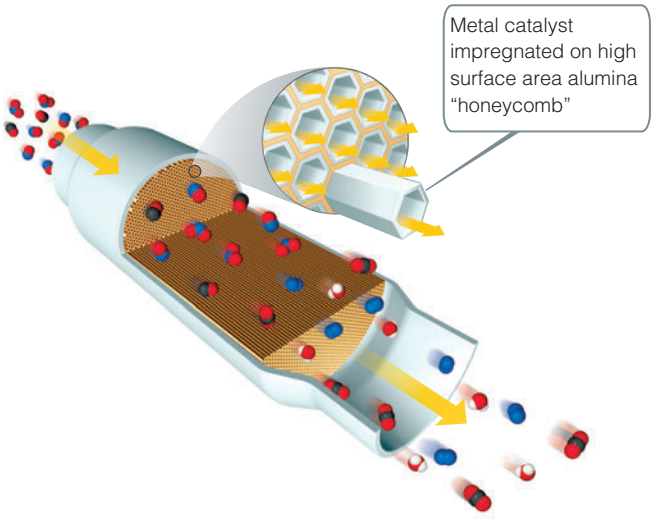
Catalysts that promote the combustion of CO and hydrocarbons are, in general, the transition-metal oxides and the noble metals. These materials are supported on a structure (Figure 14.24) that allows the best possible contact between the flowing exhaust gas and the catalyst surface. A honeycomb structure made from alumina (Al_2O_3) and impregnated with the catalyst that is employed. Such catalysts operate by first adsorbing oxygen gas present in the exhaust gas. This adsorption weakens the O—O bond in O_2, so that oxygen atoms are available for reaction with adsorbed CO to form CO_2. Hydrocarbon oxidation probably proceeds somewhat similarly, with the hydrocarbons first being adsorbed followed by rupture of a C—H bond.

Transition-metal oxides and noble metals are also the most effective catalysts for reduction of NO to N_2 and O_2. The catalysts that are most effective in one reaction, however, are usually much less effective in the other. It is therefore necessary to have two catalytic components.

Catalytic converters contain remarkably efficient heterogeneous catalysts. The automotive exhaust gases are in contact with the catalyst for only 100 to 400 ms, but in this very short time, 96% of the hydrocarbons and CO is converted to CO_2 and H_2O, and the emission of nitrogen oxides is reduced by 76%.

Although the exact combination of catalysts used varies from one catalytic converter to another, precious metals are an essential component of any catalytic converter. Platinum is very good at catalyzing the oxidation reactions and has good resistance to impurities such as lead, sulfur, and phosphorus that can poison or disable the catalyst. Palladium is a slightly less expensive alternative to platinum, but it is more sensitive to poisoning from impurities in the exhaust stream. Rhodium is the metal of choice for reduction of nitrogen oxides and has reasonable activity for the oxidation reactions. Unfortunately, it is even rarer and more expensive than platinum. Catalytic converters currently account for approximately 35% of the world's use of platinum, 65% of palladium, and 95% of rhodium. Deposits of these metals tend to be concentrated in South Africa and Russia.

Related Exercises: 14.31, 14.95, 14.43, 14.133



▲ **Figure 14.24** Cross section of a catalytic converter.

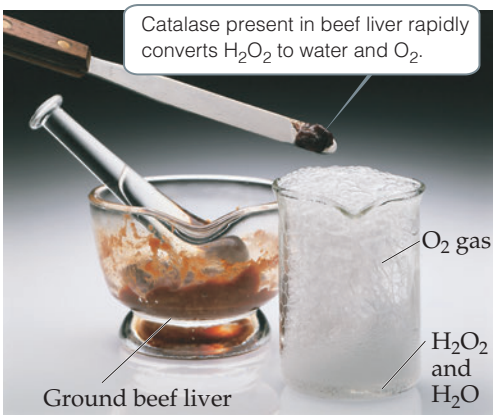
Enzymes

The human body is characterized by an extremely complex system of interrelated chemical reactions, all of which must occur at carefully controlled rates to maintain life. A large number of marvelously efficient biological catalysts known as **enzymes** are necessary for many of these reactions to occur at suitable rates. Most enzymes are large protein molecules with molecular weights ranging from about 10,000 to about 1 million u. They are very selective in the reactions they catalyze, and some are absolutely specific, operating for only one substance in only one reaction. The decomposition of hydrogen peroxide, for example, is an important biological process. Because hydrogen peroxide is strongly oxidizing, it can be physiologically harmful. For this reason, the blood and liver of mammals contain an enzyme, *catalase*, that catalyzes the decomposition of hydrogen peroxide into water and oxygen (Equation 14.31). Figure 14.25 shows the dramatic acceleration of this chemical reaction by the catalase in beef liver.

The reaction any given enzyme catalyzes takes place at a specific location in the enzyme called the **active site**. The substances that react at this site are called **substrates**. The **lock-and-key model** provides a simple explanation

Go Figure

Why is the reaction faster when the liver is ground up?



▲ **Figure 14.25** Enzymes speed up reactions.

for the specificity of an enzyme (**Figure 14.26**). The substrate is pictured as fitting neatly into the active site, much like a key fits into a lock.

Lysozyme is an enzyme that is important to the functioning of our immune system because it accelerates reactions that damage (or "lyse") bacterial cell walls. **Figure 14.27** shows a model of the enzyme lysozyme without and with a bound substrate molecule.

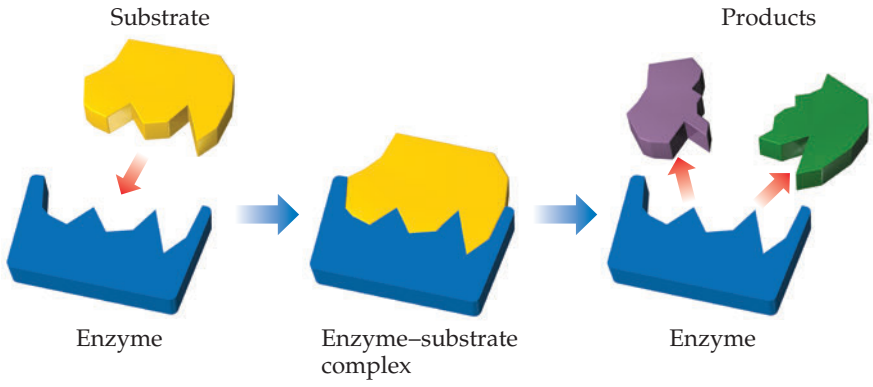
The combination of enzyme and substrate is called the *enzyme–substrate complex*. Although Figure 14.26 shows both the active site and its substrate as having a fixed shape, the active site is often fairly flexible and so may change shape as it binds the substrate. The binding between substrate and active site involves dipole–dipole attractions, hydrogen bonds, and dispersion forces.

As substrate molecules enter the active site, they are somehow activated so that they are capable of reacting rapidly. This activation process may occur, for example, by the withdrawal or donation of electron density from a particular bond or group of atoms in the enzyme's active site. In addition, the substrate may become distorted in the process of fitting into the active site and made more reactive. Once the reaction occurs, the products depart from the active site, allowing another substrate molecule to enter.

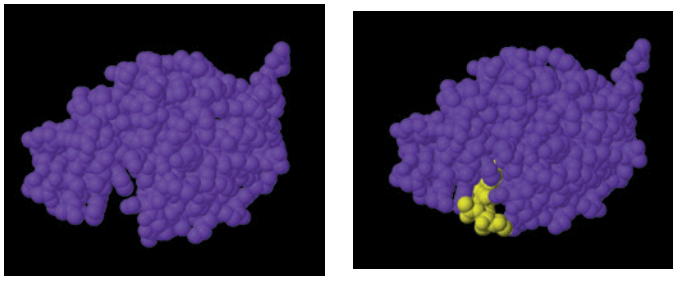
The activity of an enzyme is destroyed if some molecule other than the substrate specific to that enzyme binds to the active site and blocks entry of the substrate. Such substances are called *enzyme inhibitors*. Nerve poisons and certain toxic metal ions, such as lead and mercury, are believed to act in this way to inhibit enzyme activity. Some other poisons act by attaching elsewhere on the enzyme, thereby distorting the active site so that the substrate no longer fits.

Enzymes are enormously more efficient than nonbiochemical catalysts. The number of individual catalyzed reaction events occurring at a particular active site, called the *turnover number*, is generally in the range of 10^3 to 10^7 per second. Such large turnover numbers correspond to very low activation energies. Compared with a simple chemical catalyst, enzymes can increase the rate constant for a given reaction by a millionfold or more.

Go Figure Which molecules must bind more tightly to the active site, substrates or products?



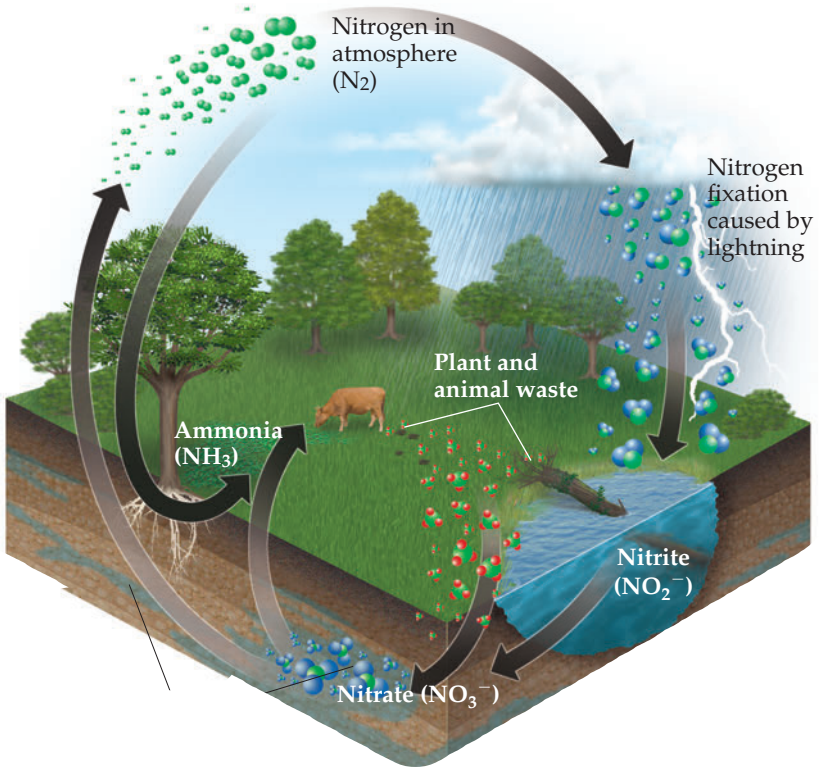
▲ **Figure 14.26 Lock-and-key model for enzyme action.**



▲ **Figure 14.27 Lysozyme was one of the first enzymes for which a structure–function relationship was described.** This model shows how the substrate (yellow) "fits" into the active site of the enzyme.

CHEMISTRY AND LIFE Nitrogen Fixation and Nitrogenase

Nitrogen is one of the most essential elements in living organisms, found in many compounds vital to life, including proteins, nucleic acids, vitamins, and hormones. Nitrogen is continually cycling through the biosphere in various forms, as shown in **Figure 14.28**. For example, certain microorganisms convert the nitrogen in animal waste and dead plants and animals into $N_2(g)$, which then returns to the atmosphere. For the food chain to be sustained, there must be a means of converting atmospheric $N_2(g)$ into a form plants can use. For this reason, if a chemist were asked to name the most important chemical reaction in the world, she might easily say *nitrogen fixation*, the process by which atmospheric $N_2(g)$ is converted into compounds suitable for plant use. Some fixed nitrogen results from the action of lightning on the atmosphere, and some is produced industrially using a process we will discuss in Chapter 15. About 60% of fixed nitrogen, however, is a consequence of the action of the remarkable and complex enzyme *nitrogenase*. This enzyme is *not* present in humans or other animals; rather, it is found in bacteria that live in the root nodules of certain plants, such as the legumes clover and alfalfa.



▲ **Figure 14.28** **Simplified picture of the nitrogen cycle.**

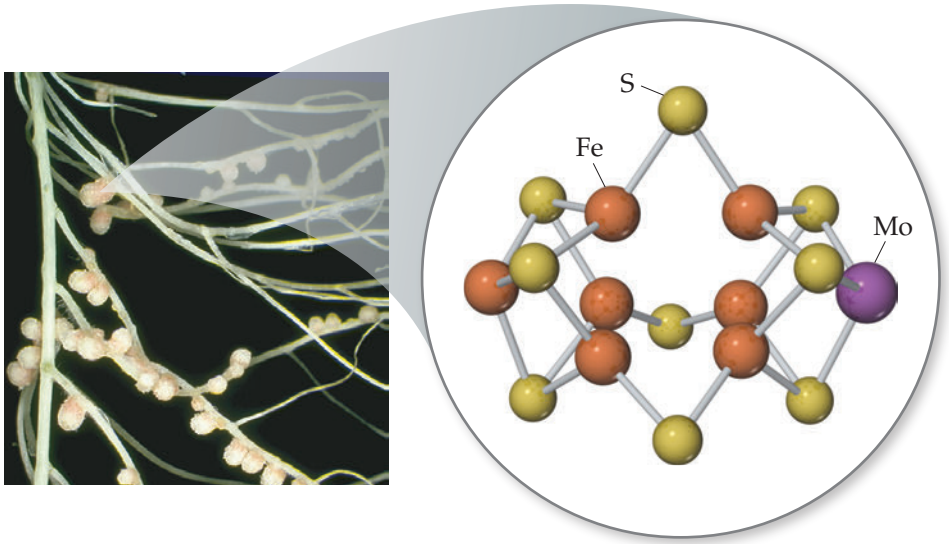
Nitrogenase converts N_2 into NH_3, a process that, in the absence of a catalyst, has a very large activation energy. This process is a *reduction* reaction in which the oxidation state of N is reduced from 0 in N_2 to −3 in NH_3. The mechanism by which nitrogenase reduces N_2 is not fully understood. Like many other enzymes, including catalase, the active site of nitrogenase contains transition-metal atoms; such enzymes are called *metalloenzymes*. Because transition metals can readily change oxidation state, metalloenzymes are especially useful for effecting transformations in which substrates are either oxidized or reduced.

It has been known for nearly 40 years that a portion of nitrogenase contains iron and molybdenum atoms. This portion, called the *FeMo-cofactor*, is thought to serve as the active site of the enzyme. The FeMo-cofactor of nitrogenase is a cluster of seven Fe atoms and one Mo atom, all linked by sulfur atoms (**Figure 14.29**).

It is one of the wonders of life that simple bacteria can contain beautifully complex and vitally important enzymes such as nitrogenase. Because of this enzyme, nitrogen is continually cycled between its comparatively inert role in the atmosphere and its critical role in living organisms. Without nitrogenase, life as we know it could not exist on Earth.

Related Exercises: 14.45, 14.124, 14.125

▶ **Figure 14.29** **The FeMo-cofactor of nitrogenase.** Nitrogenase is found in nodules in the roots of certain plants, such as the white clover roots shown at the left. The cofactor, which is thought to be the active site of the enzyme, contains seven Fe atoms and one Mo atom, linked by sulfur atoms. The molecules on the outside of the cofactor connect it to the rest of the protein.



Self-Assessment Exercise

14.39 True or false: catalysts increase the yield of a reaction.

(a) True

(b) False

Exercises

14.40 (**a**) Most commercial heterogeneous catalysts are extremely finely divided solid materials. Why is particle size important? (**b**) What role does adsorption play in the action of a heterogeneous catalyst?

14.41 In solution, chemical species as simple as H^+ and OH^- can serve as catalysts for reactions. Imagine you could measure the $[H^+]$ of a solution containing an acid-catalyzed reaction as it occurs. Assume the reactants and products themselves are neither acids nor bases. Sketch the $[H^+]$ concentration profile you would measure as a function of time for the reaction, assuming $t = 0$ is when you add a drop of acid to the reaction.

14.42 The addition of NO accelerates the decomposition of N_2O, possibly by the following mechanism:

$$NO(g) + N_2O(g) \longrightarrow N_2(g) + NO_2(g)$$
$$2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$$

(**a**) What is the chemical equation for the overall reaction? Show how the two steps can be added to give the overall equation. (**b**) Is NO serving as a catalyst or an intermediate in this reaction? (**c**) If experiments show that during the decomposition of N_2O, NO_2 does not accumulate in measurable quantities, does this rule out the proposed mechanism?

14.43 (**a**) If you were going to build a system to check the effectiveness of catalytic converters on cars, what substances would you want to look for in the car exhaust? (**b**) Car catalytic converters have to work at high temperatures, as hot exhaust gases stream through them. In what ways could this be an advantage? In what ways a disadvantage? (**c**) Why is the rate of flow of exhaust gases over a catalytic converter important?

14.44 Heterogeneous catalysts that perform hydrogenation reactions, as illustrated in Figure 14.23, are subject to "poisoning," which shuts down their catalytic ability. Compounds of sulfur are often poisons. Suggest a mechanism by which such compounds might act as poisons.

14.45 The enzyme urease catalyzes the reaction of urea, (NH_2CONH_2), with water to produce carbon dioxide and ammonia. In water, without the enzyme, the reaction proceeds with a first-order rate constant of $4.15 \times 10^{-5}\ s^{-1}$ at 100 °C. In the presence of the enzyme in water, the reaction proceeds with a rate constant of $3.4 \times 10^{4}\ s^{-1}$ at 21 °C. (**a**) Write out the balanced equation for the reaction catalyzed by urease. (**b**) If the rate of the catalyzed reaction were the same at 100 °C as it is at 21 °C, what would be the difference in the activation energy between the catalyzed and uncatalyzed reactions? (**c**) In actuality, what would you expect for the rate of the catalyzed reaction at 100 °C as compared to that at 21 °C? (**d**) On the basis of parts (c) and (d), what can you conclude about the difference in activation energies for the catalyzed and uncatalyzed reactions?

14.46 Suppose that a certain biologically important reaction is quite slow at physiological temperature (37 °C) in the absence of a catalyst. Assuming that the collision factor remains the same, by how much must an enzyme lower the activation energy of the reaction to achieve a 1×10^5 fold increase in the reaction rate?

Answers to Self-Assessment Exercises

14.39 (b)

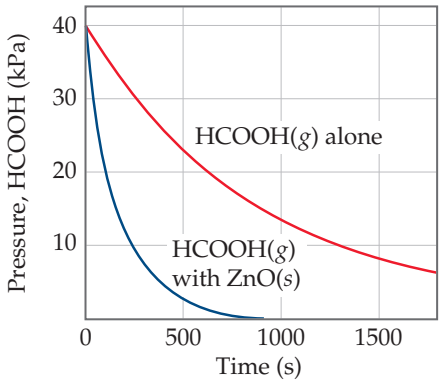
Sample Integrative Exercise

Putting Concepts Together

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:

$$HCOOH(g) \longrightarrow CO_2(g) + H_2(g)$$

The uncatalyzed decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in **Figure 14.30**. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.30.



▲ **Figure 14.30 Variation in pressure of HCOOH(*g*) as a function of time at 838 K.**

(**a**) Estimate the half-life and first-order rate constant for formic acid decomposition.

(**b**) What can you conclude from the effect of added ZnO on the decomposition of formic acid?

(**c**) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of *k*?

(**d**) The pressure of formic acid vapor at the start of the reaction is 40 kPa. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm^3, how many moles of gas occupy the reaction chamber at the end of the reaction?

(**e**) The standard heat of formation of formic acid vapor is $\Delta H_f^\circ = -378.6$ kJ/mol. Calculate ΔH° for the overall reaction. If the activation energy (E_a) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the reaction, and label E_a, ΔH°, and the transition state.

SOLUTION

(**a**) The initial pressure of HCOOH is 40 kPa. On the graph we move to the level at which the partial pressure of HCOOH is 20 kPa, half the initial value. This corresponds to a time of about 6.60×10^2 s, which is therefore the half-life. The first-order rate constant is given by Equation 14.17: $k = 0.693/t_{1/2} = 0.693/660\text{ s} = 1.05 \times 10^{-3}\text{ s}^{-1}$.

(**b**) The reaction proceeds much more rapidly in the presence of solid ZnO, so the surface of the oxide must be acting as a catalyst for the decomposition of the acid. This is an example of heterogeneous catalysis.

(**c**) If we had graphed the concentration of formic acid in units of moles per liter, we would still have determined that the half-life for decomposition is 660 s, and we would have computed the same value for k. Because the units for k are s^{-1}, the value for k is independent of the units used for concentration.

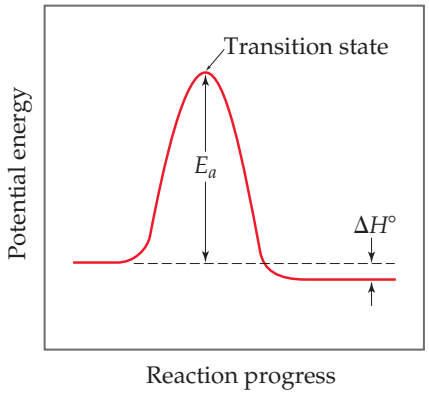
(**d**) According to the stoichiometry of the reaction, two moles of product are formed for each mole of reactant. When reaction is completed, therefore, the pressure will be 80 kPa, just twice the initial pressure, assuming ideal-gas behavior. (Because we are working at quite high temperature and fairly low gas pressure, assuming ideal-gas behavior is reasonable.) The number of moles of gas present can be calculated using the ideal-gas equation:

$$n = \frac{PV}{RT} = \frac{(80\text{ kPa})(0.436\text{ L})}{(8.314\text{ m}^3\text{ Pa/mol K})(838\text{ K})} = 5.00 \times 10^{-3}\text{ mol}$$

(**e**) We first calculate the overall change in energy, ΔH°, as in

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(CO_2(g)) + \Delta H_f^\circ(H_2(g)) - \Delta H_f^\circ(HCOOH(g)) \\ &= -393.5\text{ kJ/mol} + 0 - (-378.6\text{ kJ/mol}) \\ &= -14.9\text{ kJ/mol}\end{aligned}$$

From this and the given value for E_a, we can draw an approximate energy profile for the reaction, in analogy to Figure 14.16.



Chapter Summary and Key Terms

INTRODUCTION TO KINETICS (INTRODUCTION AND SECTION 14.1)

Chemical kinetics is the area of chemistry in which **reaction rates** are studied. Factors that affect reaction rate are the physical state of the reactants; concentration; temperature; and the presence of catalysts.

REACTION RATES (SECTION 14.2)

Reaction rates are usually expressed as changes in concentration per unit time: Typically, for reactions in solution, rates are given in units of molarity per second (M/s). For most reactions, a plot of molarity versus time shows that the rate slows down as the reaction proceeds. The **instantaneous rate** is the slope of a line drawn tangent to the concentration-versus-time curve at a specific time. Rates can be written in terms of the appearance of products or the disappearance of reactants; the stoichiometry of the reaction dictates the relationship between rates of appearance and disappearance.

RATES AND CONCENTRATION (SECTION 14.3)

The quantitative relationship between rate and concentration is expressed by a **rate law**, which usually has the following form:

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots$$

The constant k in the rate law is called the **rate constant**; the exponents m, n, and so forth are called **reaction orders** for the reactants. The sum of the reaction orders gives the **overall reaction order**. Reaction orders must be determined experimentally. The units of the rate constant depend on the overall reaction order. For a reaction in which the overall reaction order is 1, k has units of s^{-1}; for one in which the overall reaction order is 2, k has units of $M^{-1}\,s^{-1}$.

Spectroscopy is one technique that can be used to monitor the course of a reaction. According to Beer's law, the absorption of electromagnetic radiation by a substance at a particular wavelength is directly proportional to its concentration.

CONCENTRATION AND TIME (SECTION 14.4)

Rate laws can be used to determine the concentrations of reactants or products at any time during a reaction. In a **first-order reaction** the rate is proportional to the concentration of a single reactant raised to the first power: Rate $= k[A]$. In such cases the integrated form of the rate law is $\ln[A]_t = -kt + \ln[A]_0$, where $[A]_t$ is the concentration of reactant A at time t, k is the rate constant, and $[A]_0$ is the initial concentration of A. Thus, for a first-order reaction, a graph of ln[A] versus time yields a straight line of slope $-k$.

A **second-order reaction** is one for which the overall reaction order is 2. If a second-order rate law depends on the concentration of only one reactant, then rate $= k[A]^2$, and the time dependence of [A] is given by the integrated form of the rate law: $1/[A]_t = 1/[A]_0 + kt$. In this case, a graph of $1/[A]_t$ versus time yields a straight line. A **zero-order reaction** is one for which the overall reaction order is 0. Rate $= k$ if the reaction is zero order.

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to drop to one-half of its original value. For a first-order reaction, the half-life depends only on the rate constant and not on the initial concentration: $t_{1/2} = 0.693/k$. The half-life of a second-order reaction depends on both the rate constant and the initial concentration of A: $t_{1/2} = 1/(k[A]_0)$.

THE EFFECT OF TEMPERATURE ON RATES (SECTION 14.5) The **collision model**, which assumes that reactions occur as a result of collisions between molecules, helps explain why the magnitudes of rate constants increase with increasing temperature. The greater the kinetic energy of the colliding molecules, the greater is the energy of collision. The minimum energy required for a reaction to occur is called the **activation energy**, E_a. A collision with energy E_a or greater can cause the atoms of the colliding molecules to reach the **activated complex** (or **transition state**), which is the highest energy arrangement in the pathway from reactants to products. Even if a collision is energetic enough, it may not lead to reaction; the reactants must also be correctly oriented relative to one another in order for a collision to be effective.

Because the kinetic energy of molecules depends on temperature, the rate constant of a reaction is very dependent on temperature. The relationship between k and temperature is given by the **Arrhenius equation**: $k = Ae^{-E_a/RT}$. The term A is called the **frequency factor**; it relates to the number of collisions that are favorably oriented for reaction. The Arrhenius equation is often used in logarithmic form: $\ln k = \ln A - E_a/RT$. Thus, a graph of $\ln k$ versus $1/T$ yields a straight line with slope $-E_a/R$.

REACTION MECHANISMS (SECTION 14.6) A **reaction mechanism** details the individual steps that occur in the course of a reaction. Each of these steps, called **elementary reactions**, has a well-defined rate law that depends on the number of molecules (the **molecularity**) of the step. Elementary reactions are defined as either **unimolecular**, **bimolecular**, or **termolecular**, depending on whether one, two, or three reactant molecules are involved, respectively. Termolecular elementary reactions are very rare. Unimolecular, bimolecular, and termolecular reactions follow rate laws that are first order overall, second order overall, and third order overall, respectively.

Many reactions occur by a multistep mechanism, involving two or more elementary reactions, or steps. An **intermediate** is produced in one elementary step and is consumed in a later elementary step, therefore it does not appear in the overall equation for the reaction. When a mechanism has several elementary steps, the overall rate is limited by the slowest elementary step, called the **rate-determining step**. A fast elementary step that follows the rate-determining step will have no effect on the rate law of the reaction. A fast step that precedes the rate-determining step often creates an equilibrium that involves an intermediate. For a mechanism to be valid, the rate law predicted by the mechanism must be the same as that observed experimentally.

CATALYSTS (SECTION 14.7) A **catalyst** is a substance that increases the rate of a reaction without undergoing a net chemical change itself. It does so by providing a different mechanism for the reaction, one that has a lower activation energy. A **homogeneous catalyst** is one that is in the same phase as the reactants. A **heterogeneous catalyst** has a different phase from the reactants. Finely divided metals are often used as heterogeneous catalysts for solution- and gas-phase reactions. Reacting molecules can undergo binding, or **adsorption**, at the surface of the catalyst. The adsorption of a reactant at specific sites on the surface makes bond breaking easier, lowering the activation energy. Catalysis in living organisms is achieved by **enzymes**, large protein molecules that usually catalyze a very specific reaction. The specific reactant molecules involved in an enzymatic reaction are called **substrates**. The site of the enzyme where the catalysis occurs is called the **active site**. In the **lock-and-key model** for enzyme catalysis, substrate molecules bind very specifically to the active site of the enzyme, after which they can undergo reaction.

Learning Outcomes After studying this chapter, you should be able to:

- List the factors that affect the rate of chemical reactions. (Section 14.1) *Related Exercises: 14.2, 14.63*
- Determine the rate of a reaction by measuring the concentration of a reactant or product as a function of time. (Section 14.2) *Related Exercises: 14.5, 14.6, 14.64, 14.65*
- Relate the rate of formation of products and the rate of disappearance of reactants given the balanced chemical equation for the reaction. (Section 14.2) *Related Exercises: 14.7, 14.8, 14.66, 14.67*
- Explain the form and meaning of a rate law, including the ideas of reaction order and rate constant. (Section 14.3) *Related Exercises: 14.11, 14.13, 14.68, 14.69*
- Determine the rate law and rate constant for a reaction from a series of experiments given the measured rates for various concentrations of reactants. (Section 14.3) *Related Exercises: 14.14, 14.15, 14.71, 14.72*
- Apply the integrated form of a rate law to determine the concentration of a reactant at a given time. (Section 14.4) *Related Exercises: 14.21, 14.75, 14.76*
- Apply the relationship between the rate constant of a first-order reaction and its half-life. (Section 14.4) *Related Exercises: 14.20, 14.75, 14.109, 14.110*
- Determine the order of a reaction from a table of reactant concentration as a function of time. (Section 14.4) *Related Exercises: 14.23, 14.24, 14.78, 14.79*
- Explain how the activation energy affects a rate and be able to use the Arrhenius equation. (Section 14.5) *Related Exercises: 14.31, 14.32, 14.84, 14.85*
- Predict a rate law for a reaction having a multistep mechanism given the individual steps in the mechanism. (Section 14.6) *Related Exercises: 14.37, 14.38, 14.90, 14.91*
- Explain the principles underlying catalysis. (Section 14.7) *Related Exercises: 14.40, 14.92–14.94*

Key Equations

- $\text{Rate} = -\frac{1}{a}\frac{\Delta[\text{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\text{D}]}{\Delta t}$ [14.4]

  Definition of reaction rate in terms of the components of the balanced chemical equation $a\,\text{A} + b\,\text{B} \longrightarrow c\,\text{C} + d\,\text{D}$

- $\text{Rate} = k[\text{A}]^m[\text{B}]^n$ [14.7]

  General form of a rate law for the reaction $\text{A} + \text{B} \longrightarrow$ products

- $\ln[\text{A}]_t - \ln[\text{A}]_0 = -kt \quad \text{or} \quad \ln\frac{[\text{A}]_t}{[\text{A}]_0} = -kt$ [14.12]

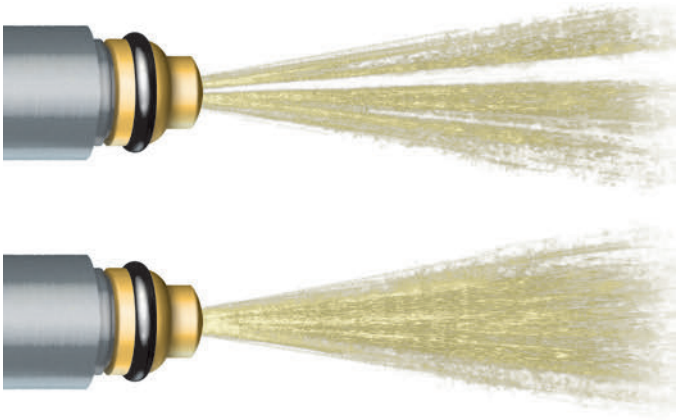
  The integrated form of a first-order rate law for the reaction $\text{A} \longrightarrow$ products

- $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ [14.14] The integrated form of a second-order rate law for the reaction A ⟶ products
- $[A]_t = -kt + [A]_0$ [14.16] The integrated form of a zero-order rate law for the reaction A ⟶ products
- $t_{1/2} = \frac{0.693}{k}$ [14.17] Relating the half-life and rate constant for a first-order reaction
- $k = Ae^{-E_a/RT}$ [14.21] The Arrhenius equation, which expresses how the rate constant depends on temperature
- $\ln k = -\frac{E_a}{RT} + \ln A$ [14.22] Logarithmic form of the Arrhenius equation

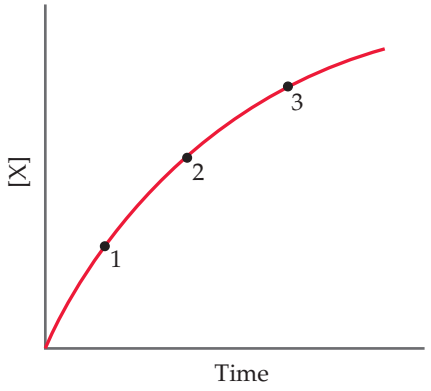
Exercises

Visualizing Concepts

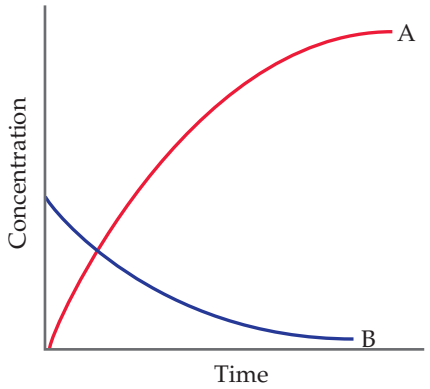
14.47 An automotive fuel injector dispenses a fine spray of gasoline into the automobile cylinder, as shown in the bottom drawing here. When an injector gets clogged, as shown in the top drawing, the spray is not as fine or even and the performance of the car declines. How is this observation related to chemical kinetics? [Section 14.1]



14.48 Consider the following graph of the concentration of a substance X over time. Is each of the following statements true or false? (**a**) X is a product of the reaction. (**b**) The rate of the reaction remains the same as time progresses. (**c**) The average rate between points 1 and 2 is greater than the average rate between points 1 and 3. (**d**) As time progresses, the curve will eventually turn downward toward the *x*-axis. [Section 14.2]



14.49 You study the rate of a reaction, measuring both the concentration of the reactant and the concentration of the product as a function of time, and obtain the following results:



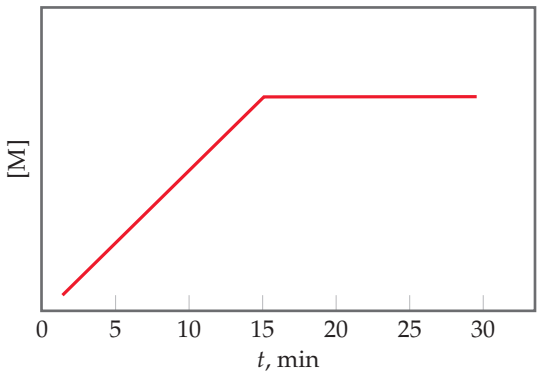
(**a**) Which chemical equation is consistent with these data:

(**i**) A ⟶ B, (**ii**) B ⟶ A, (**iii**) A ⟶ 2 B,

(**iv**) B ⟶ 2 A?

(**b**) Write equivalent expressions for the rate of the reaction in terms of the appearance or disappearance of the two substances. [Section 14.2]

14.50 Suppose that for the reaction K + L ⟶ M, you monitor the production of M over time, and then plot the following graph from your data:

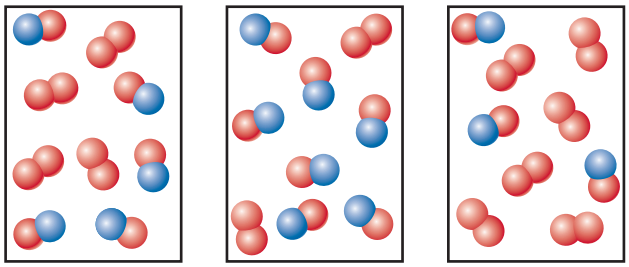


(**a**) From $t = 0$ to $t = 15$ min, what can you tell about the reaction rate? (**b**) How does the reaction change at $t = 15$ min? (**c**) Suppose the reaction as plotted here were started with 0.30 mol K and 0.40 mol L. After 20 min, an additional 0.10 mol K are added to the reaction mixture. Which of the following correctly describes how the plot would look from $t = 20$ min to $t = 30$ min? (i) [M] would remain at the same constant value it has at $t = 20$ min, (ii) [M] decreases and reaches 0 at $t = 25$ min, or (iii) [M] would increase with the same slope as $t = 0$ to 15 min, until $t = 25$ min at which point the plot becomes horizontal again.

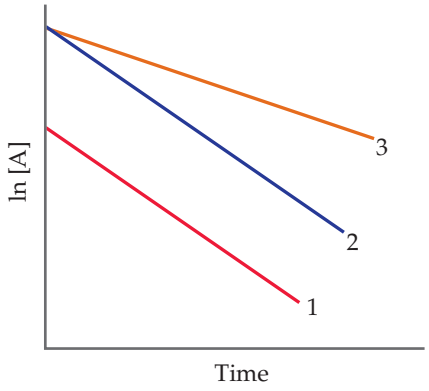
14.51 The following diagrams represent mixtures of NO(g) and $O_2(g)$. These two substances react as follows:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

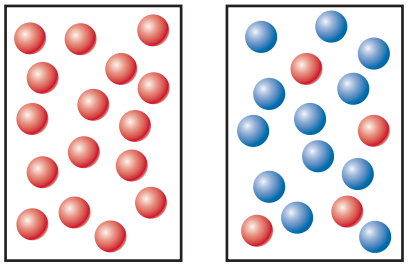
It has been determined experimentally that the rate is second order in NO and first order in O_2. Based on this fact, which of the following mixtures will have the fastest initial rate? [Section 14.3]



14.52 A friend studies a first-order reaction and obtains the following three graphs for experiments done at two different temperatures. (**a**) Which two graphs represent experiments done at the same temperature? What accounts for the difference in these two graphs? In what way are they the same? (**b**) Which two graphs represent experiments done with the same starting concentration but at different temperatures? Which graph probably represents the lower temperature? How do you know? [Section 14.4]

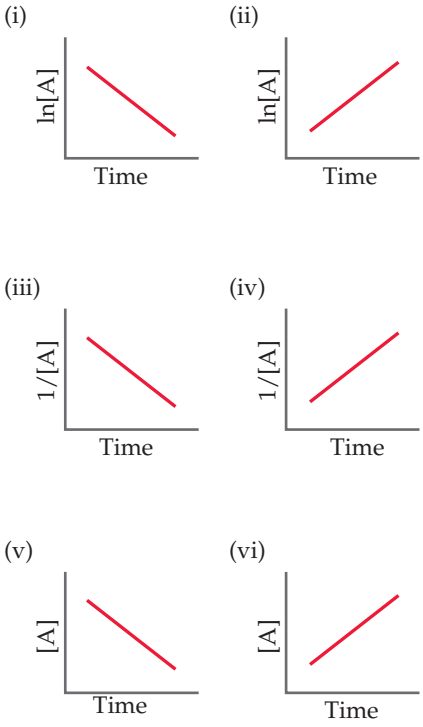


14.53 (**a**) Given the following diagrams at $t = 0$ min and $t = 30$ min, what is the half-life of the reaction if it follows first-order kinetics?

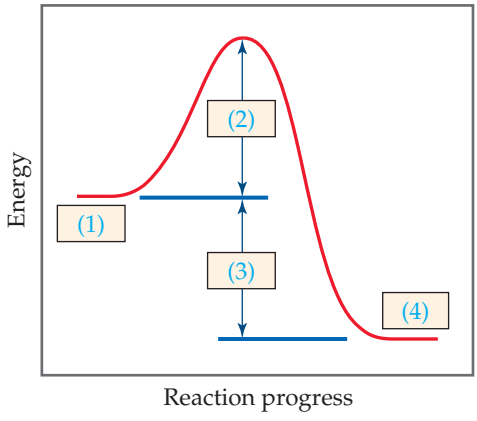


(**b**) After four half-life periods for a first-order reaction, what fraction of reactant remains? [Section 14.4]

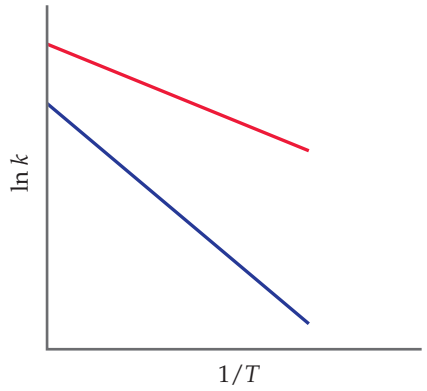
14.54 Which of the following linear plots do you expect for a reaction A $\longrightarrow$ products if the kinetics are (**a**) zero order, (**b**) first order, or (**c**) second order? [Section 14.4]



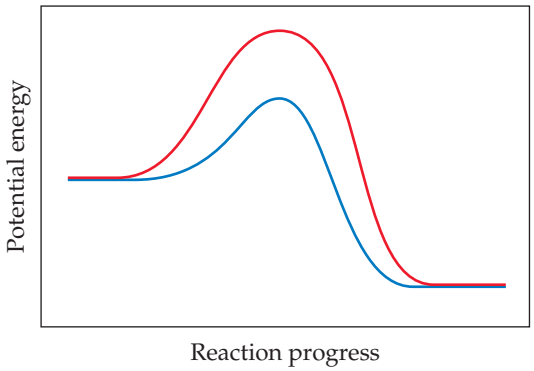
14.55 The following diagram shows a reaction profile. Label the components indicated by the boxes. [Section 14.5]



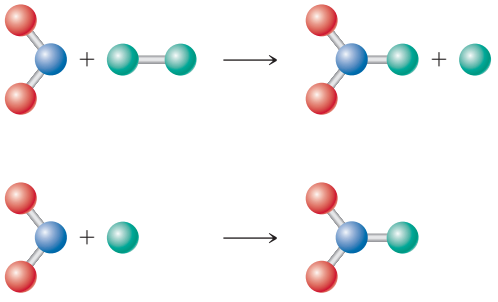
14.56 The accompanying graph shows plots of ln k versus $1/T$ for two different reactions. The plots have been extrapolated to the y-intercepts. Which reaction (red or blue) has (**a**) the larger value for E_a, and (**b**) the larger value for the frequency factor, A? [Section 14.5]



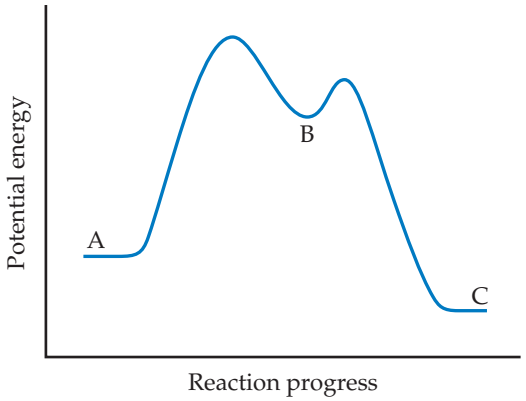
14.57 The following graph shows two different reaction pathways for the same overall reaction at the same temperature. Is each of the following statements true or false? (**a**) The rate is faster for the red path than for the blue path. (**b**) For both paths, the rate of the reverse reaction is slower than the rate of the forward reaction. (**c**) The energy change ΔE is the same for both paths. [Section 14.6]



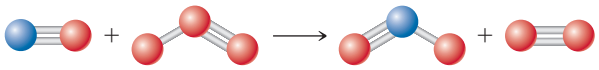
14.58 Consider the diagram that follows, which represents two steps in an overall reaction. The red spheres are oxygen, the blue ones nitrogen, and the green ones fluorine. (**a**) Write the chemical equation for each step in the reaction. (**b**) Write the equation for the overall reaction. (**c**) Identify the intermediate in the mechanism. (**d**) Write the rate law for the overall reaction if the first step is the slow, rate-determining step. [Section 14.6]



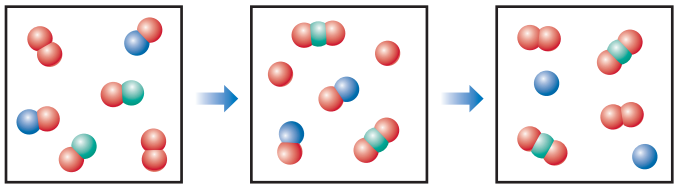
14.59 Based on the following reaction profile, how many intermediates are formed in the reaction A ⟶ C? How many transition states are there? Which step, A ⟶ B or B ⟶ C, is the faster? For the reaction A ⟶ C, is ΔE positive, negative, or zero? [Section 14.6]



14.60 Draw a possible transition state for the bimolecular reaction depicted here. (The blue spheres are nitrogen atoms, and the red ones are oxygen atoms.) Use dashed lines to represent the bonds that are in the process of being broken or made in the transition state. [Section 14.6]



14.61 The following diagram represents an imaginary two-step mechanism. Let the red spheres represent element A, the green ones element B, and the blue ones element C. (**a**) Write the equation for the net reaction that is occurring. (**b**) Identify the intermediate. (**c**) Identify the catalyst. [Sections 14.6 and 14.7]



14.62 Draw a graph showing the reaction pathway for an overall exothermic reaction with two intermediates that are produced at different rates. On your graph indicate the reactants, products, intermediates, transition states, and activation energies. [Sections 14.6 and 14.7]

Reaction Rates (Sections 14.1 and 14.2)

14.63 (**a**) What are the units usually used to express the rates of reactions occurring in solution? (**b**) As the temperature increases, does the reaction rate increase or decrease? (**c**) As a reaction proceeds, does the instantaneous reaction rate increase or decrease?

14.64 Consider the following hypothetical aqueous reaction: A(aq) ⟶ B(aq). A flask is charged with 0.065 mol of A in a total volume of 100.0 mL. The following data are collected:

Time (min)	0	10	20	30	40
Moles of A	0.065	0.051	0.042	0.036	0.031

(**a**) Calculate the number of moles of B at each time in the table, assuming that there are no molecules of B at time zero and that A cleanly converts to B with no intermediates. (**b**) Calculate the average rate of disappearance of A for each 10 min interval in units of M/s. (**c**) Between $t = 0$ min and $t = 30$ min, what is the average rate of appearance of B in units of M/s? Assume that the volume of the solution is constant.

14.65 The isomerization of methyl isonitrile (CH_3NC) to acetonitrile (CH_3CN) was studied in the gas phase at 215 °C, and the following data were obtained:

Time (s)	$[CH_3NC]$ (M)
0	0.0165
2000	0.0110
5000	0.00591
8000	0.00314
12,000	0.00137
15,000	0.00074

(**a**) Calculate the average rate of reaction, in M/s, for the time interval between each measurement. (**b**) Calculate the average rate of reaction over the entire time of the data from $t = 0$ to $t = 15{,}000$ s. (**c**) Which is greater, the average rate between $t = 2000$ and $t = 12{,}000$ s, or between $t = 8000$ and $t = 15{,}000$ s? (**d**) Graph $[CH_3NC]$ versus time and determine the instantaneous rates in M/s at $t = 5000$ s and $t = 8000$ s.

14.66 For each of the following gas-phase reactions, indicate how the rate of disappearance of each reactant is related to the rate of appearance of each product:

(**a**) $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$

(**b**) $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$

(**c**) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$

(**d**) $N_2O_4(g) \longrightarrow 2\,NO_2(g)$

14.67 (**a**) Consider the combustion of hydrogen, $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$. If hydrogen is burning at a rate of 0.5 mol/s, what is the rate of consumption of oxygen? What is the rate of formation of water vapor? (**b**) The reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$ is carried out in a closed vessel. If the partial pressure of NO is decreasing at the rate of 60 kPa/min, what is the rate of change of the total pressure of the vessel?

Rate Laws (Section 14.3)

14.68 A reaction A + B ⟶ C obeys the following rate law: Rate $= k[A]^3$. (**a**) If [B] is doubled, how will the rate change? Will the rate constant change? (**b**) What are the reaction orders for A and B? What is the overall reaction order? (**c**) What are the units of the rate constant?

14.69 Consider the following reaction:

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

(**a**) The rate law for this reaction is first order in H_2 and second order in NO. Write the rate law. (**b**) If the rate constant for this reaction at 1000 K is $6.0 \times 10^4\,M^{-2}\,s^{-1}$, what is the reaction rate when $[NO] = 0.035\,M$ and $[H_2] = 0.015\,M$? (**c**) What is the reaction rate at 1000 K when the concentration of NO is increased to 0.10 M, while the concentration of H_2 is 0.010 M? (**d**) What is the reaction rate at 1000 K if [NO] is decreased to 0.010 M and $[H_2]$ is increased to 0.030 M?

14.70 Consider the following reaction:

$$C_2H_5Cl(aq) + OH^-(aq) \longrightarrow C_2H_5OH(aq) + Cl^-(aq)$$

The rate law for this reaction is first order in C_2H_5Cl and first order in OH^-. When $[C_2H_5Cl] = 4.0 \times 10^{-3}\,M$ and $[OH^-] = 2.5 \times 10^{-2}\,M$, the reaction rate at 310 K is $5.20 \times 10^{-2}\,M$/s. (**a**) What is the value of the rate constant? (**b**) What are the units of the rate constant? (**c**) What would happen to the rate if the concentration of OH^- were cut in half? (**d**) What would happen to the rate if the concentration of both reactants were cut in half?

14.71 The iodide ion reacts with hypochlorite ion (the active ingredient in chlorine bleaches) in the following way: $OCl^- + I^- \longrightarrow OI^- + Cl^-$. This rapid reaction gives the following rate data:

$[OCl^-]$ (M)	$[I^-]$ (M)	Initial Rate (M/s)
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{-4}
3.0×10^{-3}	1.5×10^{-3}	2.72×10^{-4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{-4}

(**a**) Write the rate law for this reaction. (**b**) Calculate the rate constant with proper units. (**c**) Calculate the rate when $[OCl^-] = 2.0 \times 10^{-3}\,M$ and $[I^-] = 5.0 \times 10^{-4}\,M$.

14.72 The following data were measured for the reaction $BF_3(g) + NH_3(g) \longrightarrow F_3BNH_3(g)$:

Experiment	$[BF_3]$ (M)	$[NH_3]$ (M)	Initial Rate (M/s)
1	0.250	0.250	0.2130
2	0.250	0.125	0.1065
3	0.200	0.100	0.0682
4	0.350	0.100	0.1193
5	0.175	0.100	0.0596

(**a**) What is the rate law for the reaction? (**b**) What is the overall order of the reaction? (**c**) Calculate the rate constant with proper units? (**d**) What is the rate when $[BF_3] = 0.100\,M$ and $[NH_3] = 0.500\,M$?

14.73 Consider the gas-phase reaction between nitric oxide and bromine at 273 °C: $2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$. The following data for the initial rate of appearance of NOBr were obtained:

Experiment	[NO] (M)	$[Br_2]$ (M)	Initial Rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

(**a**) Determine the rate law. (**b**) Calculate the average value of the rate constant for the appearance of NOBr from the four data sets. (**c**) How is the rate of appearance of NOBr related to the rate of disappearance of Br_2? (**d**) What is the rate of disappearance of Br_2 when $[NO] = 0.075\,M$ and $[Br_2] = 0.25\,M$?

Change of Concentration with Time (Section 14.4)

14.74 (**a**) Develop an equation for the half-life of a zero-order reaction. (**b**) Does the half-life of a zero-order reaction increase, decrease, or remain the same as the reaction proceeds?

14.75 Consider the reaction $2\,C_4H_6(g) \longrightarrow C_8H_{12}(g)$, the rate constant at 500 K is $1.4 \times 10^{-2}\,M^{-1}\,s^{-1}$ and the initial concentration of A is 0.020 *M*. (**a**) What is the order of the reaction? (**b**) What is the half-life for this reaction? (**c**) How much $C_4H_6(g)$ will remain after 1 hour at the same temperature?

14.76 The first-order rate constant for the decomposition of N_2O_5, $2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$, at 70 °C is $6.82 \times 10^{-3}\,s^{-1}$. Suppose we start with 0.0250 mol of $N_2O_5(g)$ in a volume of 2.0 L. (**a**) How many moles of N_2O_5 will remain after 5.0 min? (**b**) How many minutes will it take for the quantity of N_2O_5 to drop to 0.010 mol? **(c)** What is the half-life of N_2O_5 at 70 °C ?

14.77 The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is first order in SO_2Cl_2. Using the following kinetic data, determine the magnitude and units of the first-order rate constant:

Time (s)	Pressure SO_2Cl_2 (kPa)
0	101.3 kPa
2500	95.95 kPa
5000	90.69 kPa
7500	85.92 kPa
10,000	81.36 kPa

14.78 Consider the data in Exercise 14.64. (**a**) By using appropriate graphs, determine the reaction order with respect to A. (**b**) How long will it take to consume 90% of A initially present in the flask?

14.79 The gas-phase decomposition of NO_2, $2\,NO_2(g) \longrightarrow 2\,NO(g) + O_2(g)$, is studied at 383 °C, giving the following data:

Time (s)	$[NO_2]$ (*M*)
0.0	0.100
5.0	0.017
10.0	0.0090
15.0	0.0062
20.0	0.0047

(**a**) Is the reaction first order or second order with respect to the concentration of NO_2? (**b**) What is the rate constant? (**c**) Predict the reaction rates at the beginning of the reaction for initial concentrations of 0.200 *M*, 0.100 *M*, and 0.050 *M* NO_2.

Temperature and Rate (Section 14.5)

14.80 (**a**) In which of the following reactions would you expect the orientation factor to be more important in leading to reaction: $O_3 + O \longrightarrow 2O_2$ or $NO + NO_3 \longrightarrow 2NO_2$? (**b**) What is related to the orientation factor? Which, smaller or larger ratio of effectively oriented collisions to all possible collisions, would lead to a smaller orientation factor?

14.81 Calculate the fraction of molecules in a sample of nitrogen gas at 300 K that has an energy of 10.0 kJ or greater.

14.82 The gas-phase reaction $Cl(g) + HBr(g) \longrightarrow HCl(g) + Br(g)$ has an overall energy change of −66 kJ. The activation energy for the reaction is 7 kJ. (**a**) Sketch the energy profile for the reaction, and label E_a and ΔE. (**b**) What is the activation energy for the reverse reaction?

14.83 Indicate whether each statement is true or false.

(**a**) If you compare two reactions with similar collision factors, the one with the larger activation energy will be faster.

(**b**) A reaction that has a small rate constant must have a small frequency factor.

(**c**) Increasing the reaction temperature increases the fraction of successful collisions between reactants.

14.84 Based on their activation energies and energy changes and assuming that all collision factors are the same, rank the following reactions from slowest to fastest.

(**a**) $E_a = 75$ kJ/mol; $\Delta E = -20$ kJ/mol

(**b**) $E_a = 100$ kJ/mol; $\Delta E = +30$ kJ/mol

(**c**) $E_a = 85$ kJ/mol; $\Delta E = -50$ kJ/mol

14.85 (**a**) A certain first-order reaction has a rate constant of $2.75 \times 10^{-2}\,s^{-1}$ at 20 °C. What is the value of *k* at 60 °C if $E_a = 75.5$ kJ/mol ? (**b**) Another first-order reaction also has a rate constant of $2.75 \times 10^{-2}\,s^{-1}$ at 20 °C. What is the value of *k* at 60 °C if $E_a = 125$ kJ/mol ? (**c**) What assumptions do you need to make in order to calculate answers for parts (a) and (b)?

14.86 The rate of the reaction

$$CH_3COOC_2H_5(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + C_2H_5OH(aq)$$

was measured at several temperatures, and the following data were collected:

Temperature (°C)	$k\,(M^{-1}\,s^{-1})$
15	0.0521
25	0.101
35	0.184
45	0.332

Calculate the value of E_a by constructing an appropriate graph.

Reaction Mechanisms (Section 14.6)

14.87 (**a**) What is meant by the term *elementary reaction*? (**b**) What is the difference between a *unimolecular* and a *bimolecular* elementary reaction? (**c**) What is a *reaction mechanism*? (**d**) What is meant by the term *rate-determining step*?

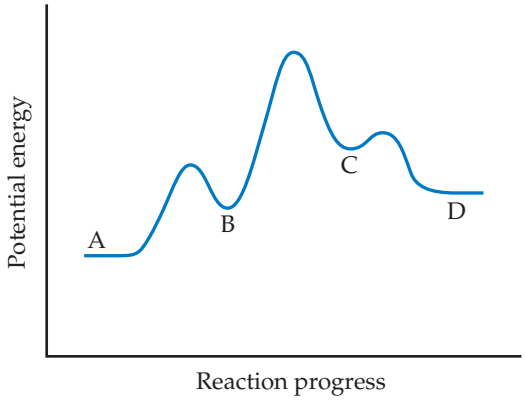
14.88 What is the molecularity of each of the following elementary reactions? Write the rate law for each.

(**a**) $H_2O(l) + CN^-(aq) \longrightarrow HCN(aq)$

(**b**) $CH_3Cl(solv) + OH^-(solv) \longrightarrow CH_3OH(solv) + Cl^-(solv)$

(**c**) $N_2O_4(g) \rightarrow 2\,NO_2$

14.89 (**a**) Based on the following reaction profile, how many intermediates are formed in the reaction A ⟶ D? (**b**) How many transition states are there? (**c**) Which step is the fastest? (**d**) For the reaction A ⟶ D, is ΔE positive, negative, or zero?

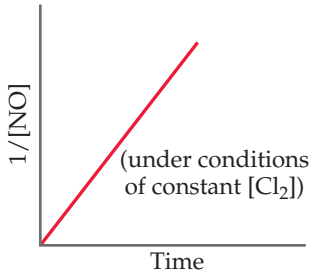


14.90 The following mechanism has been proposed for the gas-phase reaction of H_2 with ICl:

$$H_2(g) + ICl(g) \longrightarrow HI(g) + HCl(g)$$
$$HI(g) + ICl(g) \longrightarrow I_2(g) + HCl(g)$$

(**a**) Write the balanced equation for the overall reaction. (**b**) Identify any intermediates in the mechanism. (**c**) If the first step is slow and the second one is fast, which rate law do you expect to be observed for the overall reaction?

14.91 The reaction $2\,NO(g) + Cl_2(g) \longrightarrow 2\,NOCl(g)$ was performed and the following data were obtained under conditions of constant $[Cl_2]$:



(**a**) Is the following mechanism consistent with the data?

$$NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g) \quad \text{(fast)}$$
$$NOCl_2(g) + NO(g) \longrightarrow 2\,NOCl(g) \quad \text{(slow)}$$

(**b**) Does the linear plot guarantee that the overall rate law is second order?

Catalysis (Section 14.7)

14.92 (**a**) What is a catalyst? (**b**) What is the difference between a homogeneous and a heterogeneous catalyst? (**c**) Do catalysts affect the overall enthalpy change for a reaction, the activation energy, or both?

14.93 In Figure 14.21, we saw that $Br^-(aq)$ catalyzes the decomposition of $H_2O_2(aq)$ into $H_2O(l)$ and $O_2(g)$. Suppose that some $KBr(s)$ is added to an aqueous solution of hydrogen peroxide. Make a sketch of $[Br^-(aq)]$ versus time from the addition of the solid to the end of the reaction.

14.94 The oxidation of SO_2 to SO_3 is accelerated by NO_2. The reaction proceeds according to:

$$NO_2(g) + SO_2(g) \longrightarrow NO(g) + SO_3(g)$$
$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

(**a**) Show that, with appropriate coefficients, the two reactions can be summed to give the overall oxidation of SO_2 by O_2 to give SO_3. (**b**) Do we consider NO_2 a catalyst or an intermediate in this reaction? (**c**) Would you classify NO as a catalyst or as an intermediate? (**d**) Is this an example of homogeneous catalysis or heterogeneous catalysis?

14.95 Many metallic catalysts, particularly the precious-metal ones, are often deposited as very thin films on a substance of high surface area per unit mass, such as alumina (Al_2O_3) or silica (SiO_2). (**a**) Why is this an effective way of utilizing the catalyst material compared to having powdered metals? (**b**) How does the surface area affect the rate of reaction?

14.96 When D_2 reacts with ethene (C_2H_4) in the presence of a finely divided catalyst, ethane with two deuteriums, $CH_2D—CH_2D$, is formed. (Deuterium, D, is an isotope of hydrogen of mass 2.) Very little ethane forms in which two deuteriums are bound to one carbon (for example, $CH_3—CHD_2$). Use the sequence of steps involved in the reaction (Figure 14.23) to explain why this is so.

14.97 A certain enzyme catalyzes a biochemical reaction. In water, without the enzyme, the reaction proceeds with a rate constant of $6.50 \times 10^{-4}\,min^{-1}$ at 37 °C. In the presence of the enzyme in water, the reaction proceeds with a rate constant of $1.67 \times 10^{4}\,min^{-1}$ at 37 °C. Assuming the collision factor is the same for both situations, calculate the difference in activation energies for the uncatalyzed versus enzyme-catalyzed reaction.

14.98 The activation energy of an uncatalyzed reaction is 95 kJ/mol. The addition of a catalyst lowers the activation energy to 55 kJ/mol. Assuming that the collision factor remains the same, by what factor will the catalyst increase the rate of the reaction at (**a**) 25 °C, (**b**) 125 °C?

Additional Exercises

14.99 Consider the reaction $2\,A \longrightarrow B$. Is each of the following statements true or false? (**a**) The rate law for the reaction must be, Rate $= k[A]^2$. (**b**) If the reaction is an elementary reaction, the rate law is second order. (**c**) If the reaction is an elementary reaction, the rate law of the reverse reaction is first order. (**d**) The activation energy for the reverse reaction must be smaller than that for the forward reaction.

14.100 Hydrogen sulfide (H_2S) is a common and troublesome pollutant in industrial wastewaters. One way to remove H_2S is to treat the water with chlorine, in which case the following reaction occurs:

$$H_2S(aq) + Cl_2(aq) \longrightarrow S(s) + 2\,H^+(aq) + 2\,Cl^-(aq)$$

The rate of this reaction is first order in each reactant. The rate constant for the disappearance of H_2S at 30 °C is $4.0 \times 10^{-2}\,M^{-1}\,s^{-1}$. If at a given time the concentration of H_2S is $2.5 \times 10^{-4}\,M$ and that of Cl_2 is $2.0 \times 10^{-2}\,M$, what is the rate of formation of H^+?

14.101 The reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ is second order in NO and first order in O_2. When $[NO] = 0.040\,M$, and $[O_2] = 0.035\,M$, the observed rate of disappearance of NO is $9.3 \times 10^{-5}\,M/s$. (**a**) What is the rate of disappearance of O_2 at this moment? (**b**) What is the value of the rate constant? (**c**) What are the units of the rate constant? (**d**) What would happen to the rate if the concentration of NO were increased by a factor of 1.8?

14.102 You perform a series of experiments for the reaction $A \longrightarrow 2B$ and find that the rate law has the form, rate $= k[A]^x$. Determine the value of x in each of the following cases: (**a**) The rate increases by a factor of 6.25, when $[A]_0$ is increased by a factor of 2.5. (**b**) There is no rate change when $[A]_0$ is increased by a factor of 4. (**c**) The rate decreases by a factor of 1/2, when $[A]_0$ is cut in half.

14.103 Consider the following reaction between mercury(II) chloride and oxalate ion:

$$2\,HgCl_2(aq) + C_2O_4^{2-}(aq) \longrightarrow 2\,Cl^-(aq) + 2\,CO_2(g) + Hg_2Cl_2(s)$$

The initial rate of this reaction was determined for several concentrations of $HgCl_2$ and $C_2O_4^{2-}$, and the following rate data were obtained for the rate of disappearance of $C_2O_4^{2-}$:

Experiment	$[HgCl_2]$ (M)	$[C_2O_4^{2-}]$ (M)	Rate (M/s)
1	0.164	0.15	3.2×10^{-5}
2	0.164	0.45	2.9×10^{-4}
3	0.082	0.45	1.4×10^{-4}
4	0.246	0.15	4.8×10^{-5}

(**a**) What is the rate law for this reaction? (**b**) What is the value of the rate constant with proper units? (**c**) What is the reaction rate when the initial concentration of $HgCl_2$ is 0.100 M and that of $C_2O_4^{2-}$ is 0.25 M if the temperature is the same as that used to obtain the data shown?

14.104 The following kinetic data are collected for the initial rates of a reaction 2 X + Z ⟶ products:

Experiment	$[X]_0$(M)	$[Z]_0$(M)	Rate (M/s)
1	0.25	0.25	4.0×10^{1}
2	0.50	0.50	3.2×10^{2}
3	0.50	0.75	7.2×10^{2}

(**a**) What is the rate law for this reaction? (**b**) What is the value of the rate constant with proper units? (**c**) What is the reaction rate when the initial concentration of X is 0.75 M and that of Z is 1.25 M?

14.105 The dimerization of C_2F_4 to C_4F_8 has a rate constant $k = 0.045\ M^{-1}s^{-1}$ at 450 K. (**a**) Based on the unit of k, what is the reaction order in C_2F_4? (**b**) If the initial concentration of C_2F_4 is 0.100 M, how long would it take for the concentration to decrease to 0.020 M at 450 K?

14.106 Consider two reactions. Reaction (1) has a half-life that gets longer as the reaction proceeds. Reaction (2) has a half-life that gets shorter as the reaction proceeds. What can you conclude about the rate laws of these reactions from these observations?

14.107 For a first order reaction A ⟶ B + C, if the half-life of A at 25 °C is 3.05×10^4 s, what is the rate constant k at this temperature? What percentage of A will not have reacted after one day?

14.108 (**a**) The reaction $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$ is first order with in $C_{12}H_{22}O_{11}(aq)$ and zero-order in H_2O. At 300 K the rate constant equals $3.30 \times 10^{-2}\ min^{-1}$. Calculate the half-life at this temperature. (**b**) If the activation energy for this reaction is 80.0 kJ/mol, at what temperature would the reaction rate be doubled?

14.109 Cobalt-60 is used in radiation therapy to treat cancer. It has a first-order rate constant for radioactive decay of $k = 1.31 \times 10^{-1}\ yr^{-1}$. Another radioactive isotope, iron-59, which is used as a tracer in the study of iron metabolism, has a rate constant of $k = 1.55 \times 10^{-2}\ day^{-1}$. (**a**) What are the half-lives of these two isotopes? (**b**) Which one decays at a faster rate? (**c**) How much of a 1.00 mg sample of each isotope remains after three half-lives? How much of a 1.00 mg sample of each isotope remains after five days?

14.110 Urea (NH_2CONH_2) is the end product in protein metabolism in animals. The decomposition of urea in 0.1 M HCl occurs according to the reaction

$$NH_2CONH_2(aq) + H^+(aq) + 2\,H_2O(l) \longrightarrow 2\,NH_4^+(aq) + HCO_3^-(aq)$$

The reaction is first order in urea and first order overall. When $[NH_2CONH_2] = 0.200\ M$, the rate at 61.05 °C is $8.56 \times 10^{-5}\ M$/s. (**a**) What is the rate constant, k? (**b**) What is the concentration of urea in this solution after 4.00×10^3 s if the starting concentration is 0.500 M? (**c**) What is the half-life for this reaction at 61.05 °C ?

14.111 The rate of a first-order reaction is followed by spectroscopy, monitoring the absorbance of a colored reactant at 520 nm. The reaction occurs in a 1.00 cm sample cell, and the only colored species in the reaction has an extinction coefficient of $5.60 \times 10^3\ M^{-1}\ cm^{-1}$ at 520 nm. (**a**) Calculate the initial concentration of the colored reactant if the absorbance is 0.605 at the beginning of the reaction. (**b**) The absorbance falls to 0.250 at 30.0 min. Calculate the rate constant in units of s^{-1}. (**c**) Calculate the half-life of the reaction. (**d**) How long does it take for the absorbance to fall to 0.100?

14.112 A colored dye compound decomposes to give a colorless product. The original dye absorbs at 608 nm and has an extinction coefficient of $4.7 \times 10^4\ M^{-1}cm^{-1}$ at that wavelength. You perform the decomposition reaction in a 1-cm cuvette in a spectrometer and obtain the following data:

Time (min)	Absorbance at 608 nm
0	1.254
30	0.941
60	0.752
90	0.672
120	0.545

From these data, determine the rate law for the reaction "dye ⟶ product" and determine the rate constant.

14.113 Cyclopentadiene (C_5H_6) reacts with itself to form dicyclopentadiene ($C_{10}H_{12}$). A 0.0400 M solution of C_5H_6 was monitored as a function of time as the reaction $2\,C_5H_6 \longrightarrow C_{10}H_{12}$ proceeded. The following data were collected:

Time (s)	$[C_5H_6]$ (M)
0.0	0.0400
50.0	0.0300
100.0	0.0240
150.0	0.0200
200.0	0.0174

Plot $[C_5H_6]$ versus time, $\ln[C_5H_6]$ versus time, and $1/[C_5H_6]$ versus time. (**a**) What is the order of the reaction? (**b**) What is the value of the rate constant?

14.114 The first-order rate constant for reaction of a particular organic compound with water varies with temperature as follows:

Temperature (K)	Rate Constant (s^{-1})
300	3.2×10^{-11}
320	1.0×10^{-9}
340	3.0×10^{-8}
355	2.4×10^{-7}

From these data, calculate the activation energy in units of kJ/mol.

14.115 At 25 °C, raw milk sours in 6.0 h but takes 60 h to sour in a refrigerator at 5 °C. Estimate the activation energy in kJ/mol for the reaction that leads to the souring of milk.

14.116 The following mechanism has been proposed for the reaction of NO with H_2 to form N_2O and H_2O:

$$NO(g) + NO(g) \longrightarrow N_2O_2(g)$$
$$N_2O_2(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$$

(**a**) Show that the elementary reactions of the proposed mechanism add to provide a balanced equation for the reaction. (**b**) Write a rate law for each elementary reaction in the mechanism. (**c**) Identify any intermediates in the mechanism. (**d**) The observed rate law is rate $= k[NO]^2[H_2]$. If the proposed mechanism is correct, what can we conclude about the relative speeds of the first and second reactions?

14.117 Ozone in the upper atmosphere can be destroyed by the following two-step mechanism:

$$Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2(g)$$
$$ClO(g) + O(g) \longrightarrow Cl(g) + O_2(g)$$

(**a**) What is the overall equation for this process? (**b**) What is the catalyst in the reaction? (**c**) What is the intermediate in the reaction?

14.118 The gas-phase decomposition of ozone is thought to occur by the following two-step mechanism.

Step 1: $O_3(g) \rightleftharpoons O_2(g) + O(g)$ (fast)

Step 2: $O(g) + O_3(g) \longrightarrow 2\,O_2(g)$ (slow)

(**a**) Write the balanced equation for the overall reaction. (**b**) Derive the rate law that is consistent with this mechanism. (*Hint*: The product appears in the rate law.) (**c**) Is O a catalyst or an intermediate? (**d**) If instead the reaction occurred in a single step, would the rate law change? If so, what would it be?

14.119 The following mechanism has been proposed for the gas-phase reaction of chloroform ($CHCl_3$) and chlorine:

Step 1: $Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Cl(g)$ (fast)

Step 2: $Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g)$ (slow)

Step 3: $Cl(g) + CCl_3(g) \xrightarrow{k_3} CCl_4$ (fast)

(**a**) What is the overall reaction? (**b**) What are the intermediates in the mechanism? (**c**) What is the molecularity of each of the elementary reactions? (**d**) What is the rate-determining step? (**e**) What is the rate law predicted by this mechanism? (*Hint:* The overall reaction order is not an integer.)

14.120 Consider the hypothetical reaction $2\,A + B \longrightarrow 2\,C + D$. The following two-step mechanism is proposed for the reaction:

Step 1: $A + B \longrightarrow C + X$

Step 2: $A + X \longrightarrow C + D$

X is an unstable intermediate. (**a**) What is the predicted rate law expression if Step 1 is rate determining? (**b**) What is the predicted rate law expression if Step 2 is rate determining? (**c**) Your result for part (b) might be considered surprising for which of the following reasons: (**i**) The concentration of a product is in the rate law. (**ii**) There is a negative reaction order in the rate law. (**iii**) Both reasons (i) and (ii). (**iv**) Neither reasons (i) nor (ii).

14.121 In a hydrocarbon solution, the gold compound $(CH_3)_3AuPH_3$ decomposes into ethane (C_2H_6) and a different gold compound, $(CH_3)AuPH_3$. The following mechanism has been proposed for the decomposition of $(CH_3)_3AuPH_3$:

Step 1: $(CH_3)_3\,AuPH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3Au + PH_3$ (fast)

Step 2: $(CH_3)_3\,Au \xrightarrow{k_2} C_2H_6 + (CH_3)Au$ (slow)

Step 3: $(CH_3)Au + PH_3 \xrightarrow{k_3} (CH_3)AuPH_3$ (fast)

(**a**) What is the overall reaction? (**b**) What are the intermediates in the mechanism? (**c**) What is the molecularity of each of the elementary steps? (**d**) What is the rate-determining step? (**e**) What is the rate law predicted by this mechanism? (**f**) What would be the effect on the reaction rate of adding PH_3 to the solution of $(CH_3)_3AuPH_3$?

14.122 Platinum nanoparticles of diameter ~2 nm are important catalysts in carbon monoxide oxidation to carbon dioxide. Platinum crystallizes in a face-centered cubic arrangement with an edge length of 392.4 pm. (**a**) Estimate how many platinum atoms would fit into a 2.0-nm sphere; the volume of a sphere is $(4/3)\pi r^3$. Recall that $1\,pm = 1 \times 10^{-12}\,m$ and $1\,nm = 1 \times 10^{-9}\,m$. (**b**) Estimate how many platinum atoms are on the surface of a 2.0-nm Pt sphere, using the surface area of a sphere ($4\pi r^2$) and assuming that the "footprint" of one Pt atom can be estimated from its atomic diameter of 280 pm (**c**) Using your results from (a) and (b), calculate the percentage of Pt atoms that are on the surface of a 2.0-nm nanoparticle. (**d**) Repeat these calculations for a 5.0-nm platinum nanoparticle. (**e**) Which size of nanoparticle would you expect to be more catalytically active and why?

14.123 The human body is characterized by an extremely complex system of interrelated chemical reactions. A large number of enzymes are necessary for many of these reactions to occur at suitable rates. Enzymes are very selective in the reactions they catalyze, and some are absolutely specific. Use the lock-and-key model to account for the specificity of an enzyme.

14.124 Suppose that, in the absence of a catalyst, a certain biochemical reaction occurs x times per second at normal body temperature (37 °C). In order to be physiologically useful, the reaction needs to occur 5000 times faster than when it is uncatalyzed. By how many kJ/mol must an enzyme lower the activation energy of the reaction to make it useful?

14.125 Enzymes are often described as following the two-step mechanism:

$$E + S \rightleftharpoons ES \quad \text{(fast)}$$
$$ES \longrightarrow E + P \quad \text{(slow)}$$

where E = enzyme, S = substrate,

ES = enzyme–substrate complex, and P = product.

(**a**) If an enzyme follows this mechanism, what rate law is expected for the reaction? (**b**) Molecules that can bind to the active site of an enzyme but are not converted into product are called *enzyme inhibitors*. Write an additional elementary step to add into the preceding mechanism to account for the reaction of E with I, an inhibitor.

Integrative Exercises

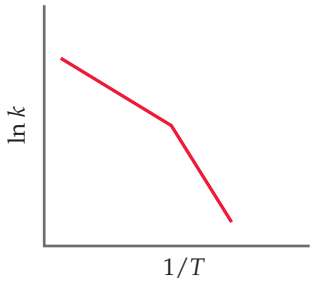
14.126 The rate of the reaction $4\,PH_3(g) \rightarrow P_4(g) + 6\,H_2(g)$ was studied by charging $PH_3(g)$ into a constant-volume reaction vessel and measuring the total pressure.

Time (s)	0	30	60	90	120
$\mathbf{P_{total}}$ **(kPa)**	13.3	18.5	20.9	22.1	22.8

Determine the reaction order and also the rate constant for the reaction.

14.127 The reaction between ethyl iodide and hydroxide ion in ethanol (C_2H_5OH) solution, $C_2H_5I(alc) + OH^-(alc) \longrightarrow C_2H_5OH(l) + I^-(alc)$ has an activation energy of 86.8 kJ/mol and a frequency factor of $2.1 \times 10^{11} M^{-1}s^{-1}$. (**a**) Predict the rate constant for the reaction at 30 °C. (**b**) A solution of KOH in ethanol is made up by dissolving 0.500 g KOH in ethanol to form 500 mL of solution. Similarly, 1.500 g of C_2H_5I is dissolved in ethanol to form 500 mL of solution. Equal volumes of the two solutions are mixed. Assuming the reaction is first order in each reactant, what is the initial rate at 30 °C? (**c**) Which reagent in the reaction is limiting, assuming the reaction proceeds to completion? (**d**) Assuming the frequency factor and activation energy do not change as a function of temperature, calculate the rate constant for the reaction at 40 °C.

14.128 You obtain kinetic data for a reaction at a set of different temperatures. You plot $\ln k$ versus $1/T$ and obtain the following graph:



Suggest a molecular-level interpretation of these unusual data.

14.129 The gas-phase reaction of NO with F_2 to form NOF and F has an activation energy of $E_a = 6.3$ kJ/mol. and a frequency factor of $A = 6.0 \times 10^8\, M^{-1}\,s^{-1}$. The reaction is believed to be bimolecular:

$$NO(g) + F_2(g) \longrightarrow NOF(g) + F(g)$$

(**a**) Calculate the rate constant at 100 °C. (**b**) Draw the Lewis structures for the NO and the NOF molecules, given that the chemical formula for NOF is misleading because the nitrogen atom is actually the central atom in the molecule. (**c**) Predict the shape for the NOF molecule. (**d**) Draw a possible transition state for the formation of NOF, using dashed lines to indicate the weak bonds that are beginning to form. (**e**) Suggest a reason for the low activation energy for the reaction.

14.130 The mechanism for the oxidation of HBr by O_2 to form $2\,H_2O$ and Br_2 is shown in Exercise 14.38. (**a**) Calculate the overall standard enthalpy change for the reaction process. (**b**) HBr does not react with O_2 at a measurable rate at room temperature under ordinary conditions. What can you infer from this about the magnitude of the activation energy for the rate-determining step? (**c**) Draw a plausible Lewis structure for the intermediate HOOBr. To what familiar compound of hydrogen and oxygen does it appear similar?

14.131 The rates of many atmospheric reactions are accelerated by the absorption of light by one of the reactants. For example, consider the reaction between methane and chlorine to produce methyl chloride and hydrogen chloride:

$$\text{Reaction 1: } CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$$

This reaction is very slow in the absence of light. However, $Cl_2(g)$ can absorb light to form Cl atoms:

$$\text{Reaction 2: } Cl_2(g) + h\nu \longrightarrow 2\,Cl(g)$$

Once the Cl atoms are generated, they can catalyze the reaction of CH_4 and Cl_2, according to the following proposed mechanism:

$$\text{Reaction 3: } CH_4(g) + Cl(g) \longrightarrow CH_3(g) + HCl(g)$$
$$\text{Reaction 4: } CH_3(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + Cl(g)$$

The enthalpy changes and activation energies for these two reactions are tabulated as follows:

Reaction	$\Delta H°$ (kJ/mol)	E_a (kJ/mol)
3	+4	17
4	−109	4

(**a**) By using the bond enthalpy for Cl_2 (Table 8.4), determine the longest wavelength of light that is energetic enough to cause reaction 2 to occur. In which portion of the electromagnetic spectrum is this light found? (**b**) By using the data tabulated here, sketch a quantitative energy profile for the catalyzed reaction represented by reactions 3 and 4. (**c**) By using bond enthalpies, estimate where the reactants, $CH_4(g) + Cl_2(g)$, should be placed on your diagram in part (b). Use this result to estimate the value of E_a for the reaction $CH_4(g) + Cl_2(g) \longrightarrow CH_3(g) + HCl(g) + Cl(g)$. (**d**) The species $Cl(g)$ and $CH_3(g)$ in reactions 3 and 4 are radicals, that is, atoms or molecules with unpaired electrons. Draw a Lewis structure of CH_3, and verify that it is a radical. (**e**) The sequence of reactions 3 and 4 comprises a radical chain mechanism. Why do you think this is called a "chain reaction"? Propose a reaction that will terminate the chain reaction.

14.132 Many primary amines, RNH_2, where R is a carbon-containing fragment such as CH_3, CH_3CH_2, and so on, undergo reactions where the transition state is tetrahedral. (a) Draw a hybrid orbital picture to visualize the bonding at the nitrogen in a primary amine (just use a C atom for "R"). (b) What kind of reactant with a primary amine can produce a tetrahedral intermediate?

14.133 The NO_x waste stream from automobile exhaust includes species such as NO and NO_2. Catalysts that convert these species to N_2 are desirable to reduce air pollution. (**a**) Draw the Lewis dot and VSEPR structures of NO, NO_2, and N_2. (**b**) Using a resource such as Table 8.3, look up the energies of the bonds in these molecules. In what region of the electromagnetic spectrum are these energies? (**c**) Design a spectroscopic experiment to monitor the conversion of NO_x into N_2, describing what wavelengths of light need to be monitored as a function of time.

14.134 As shown in Figure 14.23, the first step in the heterogeneous hydrogenation of ethene is adsorption of the ethene molecule on a metal surface. One proposed

explanation for the "sticking" of ethene to a metal surface is the interaction of the electrons in the C—C π bond with vacant orbitals on the metal surface. (**a**) If this notion is correct, would ethane be expected to adsorb to a metal surface, and, if so, how strongly would ethane bind compared to ethene? (**b**) Based on its Lewis structure, would you expect ammonia to adsorb to a metal surface using a similar explanation as for ethene?

Design an Experiment

Let's explore the chemical kinetics of our favorite hypothetical reaction: $a\,A + b\,B \longrightarrow c\,C + d\,D$. We shall assume that all the substances are soluble in water and that we carry out the reaction in aqueous solution. Substances A and C both absorb visible light, and the absorption maxima are 510 nm for A and for 640 nm for C. Substances B and D are colorless. You are provided with pure samples of all four substances and you know their chemical formulas. You are also provided appropriate instrumentation to obtain visible absorption spectra (see the Closer Look box on using spectroscopic methods in Section 14.3). Let's design an experiment to ascertain the kinetics of our reaction. (**a**) What experiments could you design to determine the rate law and the rate constant for the reaction at room temperature? Would you need to know the values of the stoichiometric constants a and c in order to find the rate law? (**b**) Design an experiment to determine the activation energy for the reaction. What challenges might you face in actually carrying out this experiment? (**c**) You now want to test whether a particular water-soluble substance Q is a homogeneous catalyst for the reaction. What experiments can you carry out to test this notion? (**d**) If Q does indeed catalyze the reaction, what follow-up experiments might you undertake to learn more about the reaction profile for the reaction?

15

CHEMICAL EQUILIBRIUM

WHAT'S AHEAD

15.1 The Concept of Equilibrium
15.2 The Equilibrium Constant
15.3 Understanding and Working with Equilibrium Constants
15.4 Calculating Equilibrium Constants
15.5 Le Châtelier's Principle

15.1 The Concept of Equilibrium



To be in equilibrium is to be in a state of balance. A tug of war in which the two sides pull with equal force so that the rope does not move is an example of a *static* equilibrium, one in which an object is at rest. Equilibria can also be *dynamic*, whereby a forward process and the reverse process take place at the same rate so that no net change occurs. Team sports that allow player substitutions (rugby, water polo, and soccer for example) are examples of *dynamic* equilibria. The number of players 'in play' is always constant, but they are not always the same players because of the substitutions that are allowed,

We have already encountered several examples of dynamic equilibrium involving physical changes of matter, including vapor pressure, the formation of saturated solutions, and Henry's law. Consider vapor pressure as an illustrative example. In a closed container, the pressure of a vapor above a liquid stops changing when the rate at which molecules escaping from the liquid into the gas phase equals the rate at which molecules from the gas phase are captured by and reenter the liquid.

Just like evaporation and condensation, or dissolution and crystallization, chemical reactions can run in the forward and reverse directions. If the reverse reaction is sufficiently slow, we can neglect it altogether, as we have done in reactions we've encountered up to this point, but there are many important examples where we must consider the rates of both forward and reverse reactions.

Chemical equilibrium *occurs when the forward and reverse reactions proceed at equal rates.*

When a reaction is at equilibrium, the rate at which the products form from the reactants equals the rate at which the reactants form from the products. As a result, concentrations cease to change, and the reaction appears to stop before it reaches completion.

In this and the next two chapters, we will explore chemical equilibrium in detail. Later, in Chapter 19, we will learn how to relate chemical equilibria to thermodynamics. Here, we learn how to express the equilibrium state of a reaction in quantitative terms and study the factors that determine the relative concentrations of reactants and products in equilibrium mixtures.

At the end of this section, you should be able to

- Explain what is meant by chemical equilibrium and how it relates to reaction rates

Let's examine a simple chemical reaction to see how it reaches an *equilibrium state*—a mixture of reactants and products whose concentrations no longer change with time. We begin with N_2O_4, a colorless substance that dissociates to form brown NO_2. **Figure 15.1** shows a sample of frozen N_2O_4 inside a sealed tube. The solid N_2O_4 becomes a gas as it is warmed above its boiling point (21.2 °C), and the gas turns darker as the colorless N_2O_4 gas dissociates into brown NO_2 gas. Eventually, even though there is still N_2O_4 in the tube, the color stops getting darker because the system reaches equilibrium. We are left with an *equilibrium mixture* of N_2O_4 and NO_2 in which the concentrations of the gases no longer change as time passes. Because the reaction is in a closed system, no gases escape, and the equilibrium mixture can be maintained.

The equilibrium mixture results because the reaction is *reversible*: N_2O_4 can form NO_2, and NO_2 can form N_2O_4. Dynamic equilibrium is represented by writing the equation for the reaction with two half arrows pointing in opposite directions:

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\ NO_2(g)} \qquad [15.1]$$

We can analyze this equilibrium using our knowledge of kinetics. Let's call the decomposition of N_2O_4 the forward reaction and the formation of N_2O_4 the reverse reaction. In this case, both the forward reaction and the reverse reaction are *elementary reactions*. As we learned in Section 14.6, the rate laws for elementary reactions can be written from their chemical equations:

$$\textit{Forward reaction}: N_2O_4(g) \longrightarrow 2\ NO_2(g) \qquad \text{Rate}_f = k_f[N_2O_4] \qquad [15.2]$$

$$\textit{Reverse reaction}: 2\ NO_2(g) \longrightarrow N_2O_4(g) \qquad \text{Rate}_r = k_r[NO_2]^2 \qquad [15.3]$$

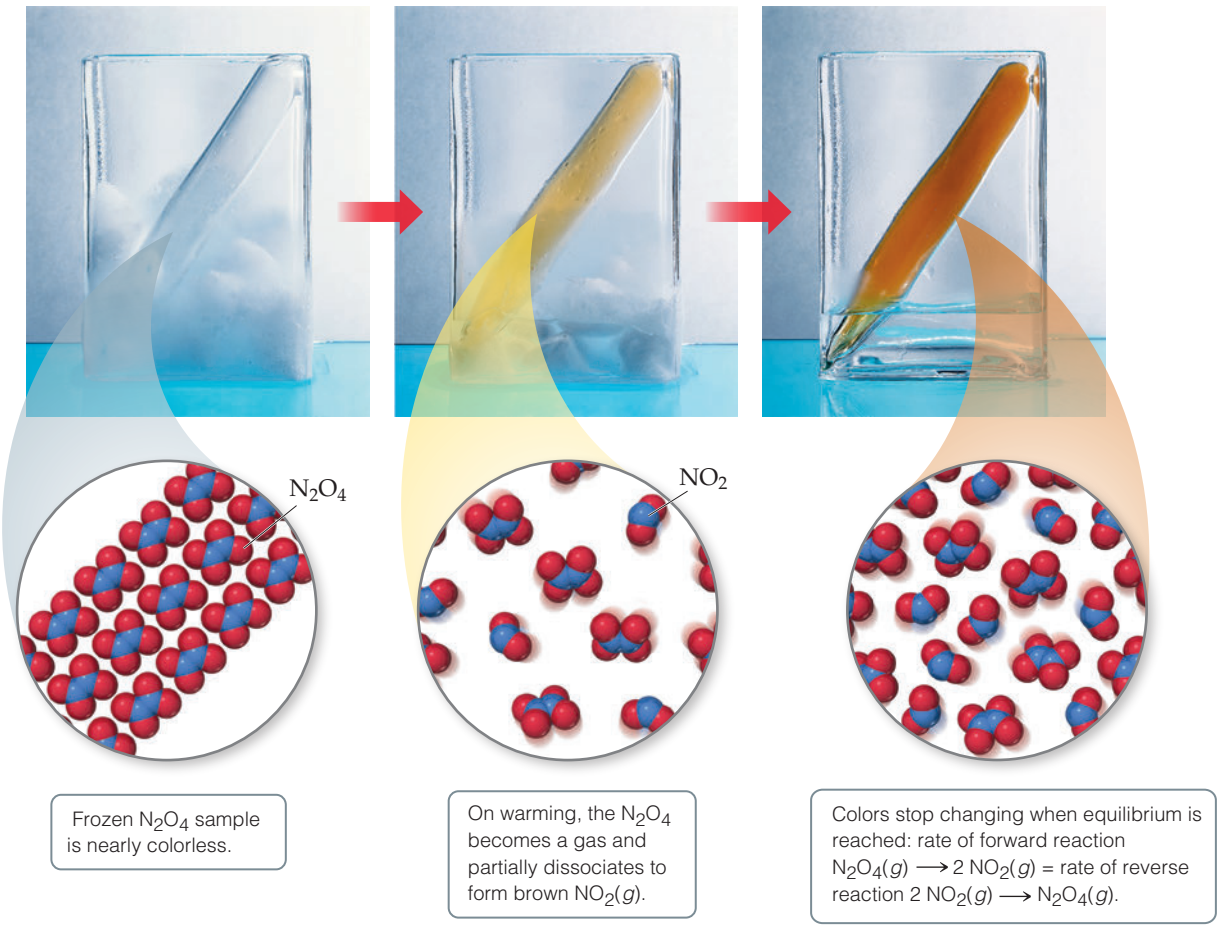
At equilibrium, the rate at which NO_2 forms in the forward reaction equals the rate at which N_2O_4 forms in the reverse reaction:

$$\underset{\text{Forward reaction}}{k_f[N_2O_4]} = \underset{\text{Reverse reaction}}{k_r[NO_2]^2} \qquad [15.4]$$

Rearranging this equation gives

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant} \qquad [15.5]$$

Go Figure If you were to let the tube on the right sit overnight and then take another picture, would the brown color look darker, lighter, or the same?



▲ **Figure 15.1** **The equilibrium between NO_2 and N_2O_4.**

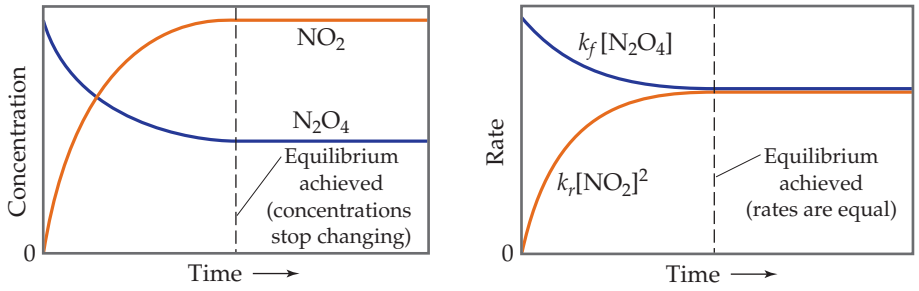
From Equation 15.5, we see that the quotient of two rate constants is another constant, which as we will learn is called the equilibrium constant. We also see that, at equilibrium, the ratio of the concentration terms equals this same constant. It makes no difference whether we start with N_2O_4 or with NO_2, or even with some mixture of the two. At equilibrium, at a given temperature, the ratio equals a specific value. Thus, there is an important constraint on the proportions of N_2O_4 and NO_2 at equilibrium.

Once equilibrium is established, the concentrations of N_2O_4 and NO_2 no longer change, as shown in **Figure 15.2**(**a**). However, the fact that the composition of the equilibrium mixture remains constant with time does not mean that N_2O_4 and NO_2 stop reacting. On the contrary, the equilibrium is *dynamic*—which means some N_2O_4 is always converting to NO_2 and some NO_2 is always converting to N_2O_4. At equilibrium, however, the two processes occur at the same rate, as shown in Figure 15.2(**b**).

We learn several important lessons about equilibrium from this example:

- At equilibrium, the concentrations of reactants and products no longer change with time.
- For equilibrium to occur, neither reactants nor products can escape from the system.
- At equilibrium, a particular ratio of concentration terms equals a constant.

Go Figure Why does the rate of the forward reaction slow down as the reaction proceeds?



▲ **Figure 15.2 Achieving chemical equilibrium in the $N_2O_4(g) \longrightarrow 2\,NO_2(g)$ reaction.** Equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.

Self-Assessment Exercise

15.1 Which of the following variables are equal when the $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ reaction reaches equilibrium?

(a) k_f and k_r
(b) the forward and reverse reaction rates
(c) the concentrations of $[N_2O_4]$ and $[NO_2]$

Exercise

15.2 Suppose that the gas-phase reactions $A \longrightarrow B$ and $B \longrightarrow A$ are both elementary processes with rate constants of $2.5 \times 10^{-2}\,min^{-1}$ and $2.5 \times 10^{-1}\,min^{-1}$, respectively. (**a**) What is the value of the equilibrium constant for the equilibrium $A(g) \rightleftharpoons B(g)$? (**b**) Which is greater at equilibrium, the partial pressure of A or the partial pressure of B?

Answers to Self-Assessment Exercise

15.1 (b)

15.2 The Equilibrium Constant



Imagine yourself as a research chemist synthesizing a compound in the laboratory. Before you start a synthesis you need to consider the stoichiometry of the reaction you are undertaking to determine how much of each chemical you need, what solvent would be appropriate to use as well as the rate at which the reaction occurs and whether you will need to employ heat or add a catalyst. In addition, you might have to consider if the reaction is an equilibrium and how that will affect the yield of your desired product.

In this section, we see that equilibria can be quantified. By the end of this section, you should be able to

- Write the equilibrium expression for any reaction
- Convert K_c to K_p and vice versa.

A reaction in which reactants convert to products and products convert to reactants in the same reaction vessel naturally leads to an equilibrium, regardless of how complicated the reaction is and regardless of the nature of the kinetic processes for the forward and reverse reactions. Consider the synthesis of ammonia from nitrogen and hydrogen:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \qquad [15.6]$$

This reaction is the basis for the **Haber process**, which is critical for the production of fertilizers and therefore critical to the world's food supply. In the Haber process, N_2 and H_2 react at high pressure and temperature in the presence of a catalyst to form ammonia. In a closed system, however, the reaction does not lead to complete consumption of the N_2 and H_2. Rather, at some point the reaction appears to stop, with all three components of the reaction mixture present at the same time.

How the concentrations of H_2, N_2, and NH_3 vary with time is shown in **Figure 15.3**. Notice that an equilibrium mixture is obtained regardless of whether we begin with N_2 and H_2 or with NH_3. *The equilibrium condition is reached from either direction.*

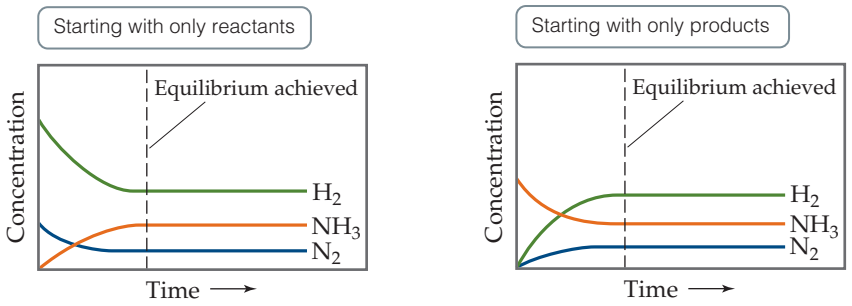
An expression similar to Equation 15.5 governs the concentrations of N_2, H_2, and NH_3 at equilibrium. If we were to systematically change the relative amounts of the three gases in the starting mixture and then analyze each equilibrium mixture, we could determine the relationship among the equilibrium concentrations.

Chemists carried out studies of this kind on other chemical systems in the nineteenth century before Haber's work. In 1864, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) postulated their **law of mass action**, which expresses, for any reaction, the relationship between the concentrations of the reactants and products present at equilibrium. Suppose we have the general equilibrium equation

$$a\,A + b\,B \rightleftharpoons d\,D + e\,E \qquad [15.7]$$

where A, B, D, and E are the chemical species involved and a, b, d, and e are their coefficients in the balanced chemical equation. According to the law of mass action, the equilibrium condition is described by the expression

Go Figure Is the rate of disappearance of H_2 related to the rate of disappearance of N_2? If so, how they are related?



▲ **Figure 15.3** **The same equilibrium is reached whether we start with only reactants (N_2 and H_2) or with only product (NH_3).**

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \quad \begin{matrix} \longleftarrow \text{ products} \\ \longleftarrow \text{ reactants} \end{matrix} \qquad [15.8]$$

We call this relationship the **equilibrium-constant expression** (or merely the *equilibrium expression*) for the reaction. The constant K_c, the **equilibrium constant**, is the numerical value obtained when we substitute molar equilibrium concentrations into the equilibrium expression. The subscript c on the K indicates that concentrations expressed in molarity are used to evaluate the constant.

The numerator of the equilibrium expression is the product of the concentrations of all substances on the product side of the equilibrium equation, each raised to a power equal to its coefficient in the balanced equation. The denominator is similarly derived from the reactant side of the equilibrium equation. Thus, for the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, the equilibrium expression is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad [15.9]$$

Once we know the balanced chemical equation for a reaction that reaches equilibrium, we can write the equilibrium expression even if we do not know the reaction mechanism.

The equilibrium expression depends only on the stoichiometry of the reaction, not on its mechanism.

In this way equilibrium expressions are different from rate laws.

The value of the equilibrium constant at any given temperature does not depend on the initial amounts of reactants and products. It also does not matter whether other substances are present, as long as they do not react with a reactant or a product. The value of K_c depends only on the particular reaction and on the temperature.

CHEMISTRY PUT TO WORK The Haber Process

The quantity of food required to feed the ever-increasing human population far exceeds that provided by nitrogen-fixing plants. Therefore, human agriculture requires substantial amounts of ammonia-based fertilizers for croplands. Of all the chemical reactions that humans have learned to control for their own purposes, the synthesis of ammonia from hydrogen and atmospheric nitrogen is one of the most important.

In 1912, the German chemist Fritz Haber (1868–1934) developed the Haber process (Equation 15.6). The process is sometimes also called the *Haber–Bosch process* to honor Karl Bosch, the engineer who developed the industrial process on a large scale (**Figure 15.4**). The engineering needed to implement the Haber process requires the use of temperatures (approximately 500 °C) and pressures (20 to 60 MPa) that were difficult to achieve at that time.

The Haber process provides a historically interesting example of the complex impact of chemistry on our lives. At the start of World War I, in 1914, Germany depended on nitrate deposits in Chile for the nitrogen-containing compounds needed to manufacture explosives. During the war, the Allied naval blockade of South America cut off this supply. However, by using the Haber reaction to fix nitrogen from air, Germany was able to continue to produce explosives. Experts have estimated that World War I would have ended perhaps a year earlier had it not been for the Haber process.

From these unhappy beginnings as a major factor in international warfare, the Haber process has become the world's principal source of fixed nitrogen. The same process that prolonged World War I has enabled the manufacture of fertilizers that have increased crop yields, thereby saving millions of people from starvation. About 180 million tonnes of ammonia are manufactured annually worldwide, mostly by the Haber process. The ammonia can be applied directly to the soil, or it can be converted into ammonium salts that are also used as fertilizers.

Haber was a patriotic German who gave enthusiastic support to his nation's war effort. He served as chief of Germany's Chemical Warfare Service during World War I and developed the use of chlorine as a poison-gas weapon. Consequently, the decision to award him the Nobel Prize in Chemistry in 1918 was the subject of considerable controversy and criticism. The ultimate irony, however, came in 1933 when Haber was expelled from Germany because he was Jewish.

Related Exercises: 15.21, 15.85



▲ **Figure 15.4** **A high-pressure steel reactor used in the Haber process is on display at Karlsruhe Institute of Technology in Germany where the Haber process was developed.**

Sample Exercise 15.1

Writing Equilibrium Expressions

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$

SOLUTION

Analyze We are given three equations and are asked to write an equilibrium expression for each.

Plan Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each concentration term is raised to the power of its coefficient in the balanced chemical equation.

Solve

(a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$ (b) $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$ (c) $K_c = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

Practice Exercise

For the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, which of the following is the correct equilibrium expression?

(a) $K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$ (b) $K_c = \dfrac{2[SO_2][O_2]}{2[SO_3]}$

(c) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ (d) $K_c = \dfrac{2[SO_3]}{2[SO_2][O_2]}$

Evaluating K_c

We can illustrate how the law of mass action was discovered empirically and demonstrate that the equilibrium constant is independent of starting concentrations by examining a series of experiments involving dinitrogen tetroxide and nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad [15.10]$$

We start with several sealed tubes containing different concentrations of NO_2 and N_2O_4. The tubes are kept at 100 °C until equilibrium is reached. We then analyze the mixtures and determine the equilibrium concentrations of NO_2 and N_2O_4, which are shown in Table 15.1.

To evaluate K_c, we insert the equilibrium concentrations into the equilibrium-constant expression. For example, using Experiment 1 data, $[NO_2] = 0.0172\,M$ and $[N_2O_4] = 0.00140\,M$, we find

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.0172]^2}{0.00140} = 0.211$$

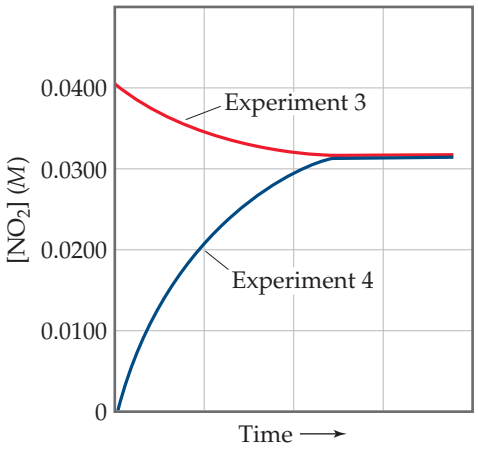
Proceeding in the same way, the values of K_c for the other samples are calculated. Note from Table 15.1 that the value for K_c is constant (within the limits of experimental error), even though the initial concentrations vary, as do the final concentrations.

TABLE 15.1 Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

Go Figure

In which experiment, 3 or 4, does the concentration of N_2O_4 decrease to reach equilibrium?



▲ **Figure 15.5 The same equilibrium mixture is produced regardless of the initial NO_2 concentration.** The concentration of NO_2 either increases or decreases until equilibrium is reached.

Furthermore, Experiment 4 shows that equilibrium can be achieved beginning with N_2O_4 rather than with NO_2. That is, equilibrium can be approached from either direction. **Figure 15.5** shows how Experiments 3 and 4 result in the same equilibrium mixture even though the two experiments start with very different NO_2 concentrations.

Notice that no units are given for K_c either in Table 15.1 or in the calculation we just did using Experiment 1 data. It is common practice to write equilibrium constants without units for reasons that we address later in this section.

Equilibrium Constants in Terms of Pressure, K_p

When the reactants and products in a chemical reaction are gases, we can formulate the equilibrium expression in terms of partial pressures. When partial pressures in atmospheres are used in the expression, we denote the equilibrium constant K_p (where the subscript p stands for pressure). For the general reaction in Equation 15.7, we have

$$K_p = \frac{(P_D)^d (P_E)^e}{(P_A)^a (P_B)^b} \qquad [15.11]$$

where P_A is the partial pressure of A, P_B is the partial pressure of B, and so forth. For example, for our N_2O_4/NO_2 reaction, we have

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

For a given reaction, the numerical value of K_c is generally different from the numerical value of K_p. We must therefore take care to indicate, via subscript c or p, which constant we are using. It is possible, however, to calculate one from the other using the ideal-gas equation:

$$PV = nRT, \text{ so } P = \frac{n}{V}RT \qquad [15.12]$$

The usual units for n/V are mol/L, which equals molarity, M. For substance A in our generic reaction, we therefore see that

$$P_A = \frac{n_A}{V}RT = [A]RT \qquad [15.13]$$

When we substitute Equation 15.13 and like expressions for the other gaseous components of the reaction into Equation 15.11, we obtain a general expression relating K_p and K_c:

$$K_p = \frac{([D]RT)^d ([E]RT)^e}{([A]RT)^a ([B]RT)^b} = \left(\frac{[D]^d[E]^e}{[A]^a[B]^b}\right)\frac{(RT)^{d+e}}{(RT)^{a+b}} \qquad [15.14]$$

Notice that the term in brackets is equal to K_c, so we can simplify the expression:

$$K_p = K_c(RT)^{(d+e)-(a+b)} = K_c(RT)^{\Delta n} \qquad [15.15]$$

The quantity Δn is the change in the number of moles of gas in the balanced chemical equation. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants:

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \qquad [15.16]$$

For example, in the $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ reaction, there are 2 mol of product NO_2 and 1 mol of reactant N_2O_4. Therefore, $\Delta n = 2 - 1 = 1$, and $K_p = K_c(RT)$, for this reaction. In our derivation gas pressures are expressed as kilopascals and concentrations in moles per liter, thus the appropriate form of the gas constant is $R = 8.314$ L kPa/mol K. Note that K_p has the partial pressures expressed in bar. A standard atmosphere is now defined as 1 bar or 100 kPa which is taken into account in the conversion.

Sample Exercise 15.2

Converting between K_c and K_p

For the Haber process,

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

SOLUTION

Analyze We are given K_c for a reaction and asked to calculate K_p.

Plan The relationship between K_c and K_p is given by Equation 15.15. To apply that equation, we must determine Δn by comparing the number of moles of product with the number of moles of reactants (Equation 15.16).

Solve With 2 mol of gaseous products ($2\,NH_3$) and 4 mol of gaseous reactants ($1\,N_2 + 3\,H_2$), $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on *products minus reactants*.) The temperature is $273 + 300 = 573$ K. The value for the ideal-gas constant, R, is 8.314 L kPa/mol K. Remember we need to convert to a standard atmosphere which is 100 kPa. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(8.314 \times 573)^{-2}$$

$$= \frac{(9.60)}{(8.314 \times 573)^2} = 4.23 \times 10^{-10}$$

Practice Exercise

For which of the following reactions is the ratio K_p/K_c largest at 300 K?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(c) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$
(d) $C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$

Equilibrium Constants and Units

You may wonder why equilibrium constants are reported without units. The equilibrium constant is related to the kinetics of a reaction as well as to the thermodynamics. (We explore this latter connection in Chapter 19.) Equilibrium constants derived from thermodynamic measurements are defined in terms of *activities* rather than concentrations or partial pressures.

The activity of any substance in an *ideal* mixture is the ratio of the concentration or pressure of the substance either to a reference concentration (1 M) or to a reference pressure (100 kPa). For example, if the concentration of a substance in an equilibrium mixture is 0.010 M, its activity is $0.010\,M/1\,M = 0.010$. The units of such ratios always cancel and, consequently, activities have no units. Furthermore, the numerical value of the activity equals the concentration. For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

In real systems, activities are also ratios that have no units. Even though these activities may not be exactly numerically equal to concentrations, we will assume those differences are small enough that we can neglect them. All we need to know at this point is that activities have no units. As a result, the *thermodynamic equilibrium constants* derived from them also have no units. It is therefore common practice to write all types of equilibrium constants without units, a practice that we adhere to in this text. In more advanced chemistry courses, you may make more rigorous distinctions between concentrations and activities.

Self-Assessment Exercises

15.3 What is the equilibrium expression for the reaction: $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$?

(a) $K = \dfrac{[H_2][I_2]}{[HI]}$

(b) $K = \dfrac{[H_2][I_2]}{[HI]^2}$

(c) $K = [HI]^2$

15.4 For the equilibrium $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$ $K_c = 0.022$ at 490 °C. What is the value of K_p?

(a) $K_p = 0.022$
(b) $K_p = 0.14$
(c) $K_p = 46$

Exercises

15.5 Write the expressions for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

(**a**) $O_2(g) \rightleftharpoons 2\,O(g)$

(**b**) $Si(s) + 2\,Cl_2(g) \rightleftharpoons SiCl_4(g)$

(**c**) $H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$

(**d**) $O_2(g) + 2\,CO(g) \rightleftharpoons 2\,CO_2(g)$

(**e**) $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$

(**f**) $Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ce^{3+}(aq)$

(**g**) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

15.6 Which of the following reactions lies to the right, favoring the formation of products, and which lies to the left, favoring formation of reactants?

(**a**) $H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 1300 K $K_c = 0.57$

(**b**) $2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$ at 900 K $K_p = 0.0572$

15.7 Which of the following statements are true and which are false? (**a**) For the reaction $2\,A(g) + B(g) \rightleftharpoons A_2B(g)$ K_c and K_p are numerically the same. (**b**) It is possible to distinguish K_c from K_p by comparing the units used to express the equilibrium constant. (**c**) For the equilibrium in (a), the value of K_c increases with increasing pressure.

15.8 Calculate K_c at 900 K for $2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$ if $K_p = 0.0572$ at this temperature.

Answers to Self-Assessment Exercises

15.3 (b) **15.4** (b)

15.3 Understanding and Working with Equilibrium Constants



When we have solved a problem involving some calculation, we have emphasized the importance of taking a moment to appraise the answer we get to see if it 'looks about right'. In this way, we can avoid errors, for example, adding an extra zero to a number in some part of the calculation by mistake. Another important skill you will develop is a feel for quantities. Our experience has taught us that a weather forecast of 40 °C tells us that it is going to be a hot day. With a little practice, we will be able to view the numbers we use in chemistry and get a feel for what they represent. For instance, does a particular ΔH value represent a large or small amount of energy? If I hold a golf ball–sized sample of something with a density of 10 g/mL will it feel heavy? How does an equilibrium constant of 1000 relate to the yield of product I may hope to get from the reaction? We start

this section by exploring the magnitude of K. By the end of this section, you should be able to

- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture.
- Manipulate the equilibrium constant to reflect changes in the chemical equation.
- Write the equilibrium expression for a heterogeneous reaction.

Before doing calculations with equilibrium constants, it is valuable to understand what the magnitude of an equilibrium constant can tell us about the relative concentrations of reactants and products in an equilibrium mixture. It is also useful to consider how the magnitude of any equilibrium constant depends on how the chemical equation is expressed.

The Magnitude of Equilibrium Constants

The magnitude of the equilibrium constant for a reaction gives us important information about the composition of the equilibrium mixture. For example, consider the experimental data for the reaction of carbon monoxide gas and chlorine gas at 100 °C to form phosgene ($COCl_2$), a toxic gas used in the manufacture of certain polymers and insecticides:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_c = \frac{[COCl_2]}{[CO][Cl_2]} = 4.56 \times 10^9$$

For the equilibrium constant to be so large, the numerator of the equilibrium expression must be approximately a billion (10^9) times larger than the denominator. Thus, the equilibrium concentration of $COCl_2$ must be much greater than that of CO or Cl_2, and in fact, this is just what we find experimentally. We say that this equilibrium *lies to the right* (that is, toward the product side). Likewise, a very small equilibrium constant indicates that the equilibrium mixture contains mostly reactants. We then say that the equilibrium *lies to the left*. In general,

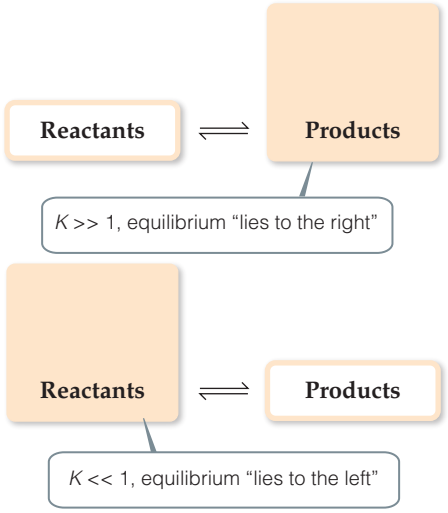
If $K \gg 1$ (large K): Equilibrium lies to right, products predominate

If $K \ll 1$ (small K): Equilibrium lies to left, reactants predominate

These situations are summarized in **Figure 15.6**. *Remember, it is forward and reverse reaction rates, not reactant and product concentrations, that are equal at equilibrium.*

Go Figure

What would this figure look like for a reaction in which $K \approx 1$?

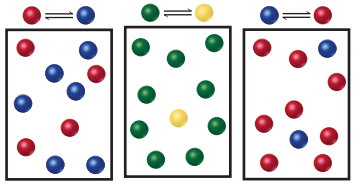


▲ **Figure 15.6 Relationship between magnitude of *K* and composition of an equilibrium mixture.**

Sample Exercise 15.3

Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three systems at equilibrium, all in the same-size containers. (**a**) Without doing any calculations, rank the systems in order of increasing K_c. (**b**) If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate K_c for each system.



SOLUTION

Analyze We are asked to judge the relative magnitudes of three equilibrium constants and then to calculate them.

Plan (**a**) The more product present at equilibrium, relative to reactant, the larger the equilibrium constant. (**b**) The equilibrium constant is given by Equation 15.8.

Solve

(**a**) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Therefore, the equilibrium constant varies in the order (ii) < (i) < (iii), from smallest (most reactants) to largest (most products).

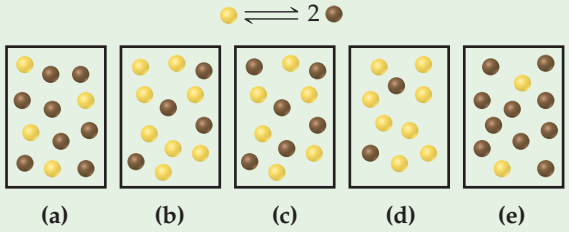
(**b**) In (i), we have 0.60 mol/L product and 0.40 mol/L reactant, giving $K_c = 0.60/0.40 = 1.5$. (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii), we have 0.10 mol/L product and 0.90 mol/L reactant, giving $K_c = 0.10/0.90 = 0.11$ (or 1 sphere/9 spheres = 0.11). In (iii), we have 0.80 mol/L product and 0.20 mol/L reactant, giving $K_c = 0.80/0.20 = 4.0$ (or 8 spheres/2 spheres = 4.0). These calculations verify the order in (a).

Continued

Comment Imagine a drawing that represents a reaction with a very small or very large value of K_c. For example, what would the drawing look like if $K_c = 1 \times 10^{-5}$? In that case, there would need to be 100,000 reactant molecules for only 1 product molecule. But then, that would be impractical to draw.

Practice Exercise

The equilibrium constant for the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ at 2 °C is $K_c = 2.0$. If each yellow sphere represents 1 mol of N_2O_4 and each brown sphere 1 mol of NO_2 which of the following 1.0 L containers represents the equilibrium mixture at 2 °C?



The Direction of the Chemical Equation and *K*

We have seen that we can represent the N_2O_4/NO_2 equilibrium as

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \quad (\text{at } 100\,^\circ\text{C}) \qquad [15.17]$$

We could equally well consider this equilibrium in terms of the reverse reaction:

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

The equilibrium expression is then

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100\,^\circ\text{C}) \qquad [15.18]$$

Equation 15.18 is the reciprocal of the expression in Equation 15.17. *The equilibrium expression for a reaction written in one direction is the reciprocal of the expression for the reaction written in the reverse direction*. Consequently, the numerical value of the equilibrium constant for the reaction written in one direction is the reciprocal of that for the reverse reaction. Both expressions are equally valid, but it is meaningless to say that the equilibrium constant for the equilibrium between NO_2 and N_2O_4 is "0.212" or "4.72" unless we indicate how the equilibrium reaction is written and specify the temperature. Therefore, whenever you are using an equilibrium constant, you should always write the associated balanced chemical equation.

Relating Chemical Equation Stoichiometry and Equilibrium Constants

There are many ways to write a balanced chemical equation for a given reaction. For example, if we multiply Equation 15.1, $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ by 2, we have

$$2\,N_2O_4(g) \rightleftharpoons 4\,NO_2(g)$$

This chemical equation is balanced and might be written this way in some contexts. Therefore, the equilibrium expression for this equation is

$$K_c = \frac{[NO_2]^4}{[N_2O_4]^2}$$

which is the square of the equilibrium expression given in Equation 15.10 for the reaction as written in Equation 15.1: $[NO_2]^2/[N_2O_4]$. Because the new equilibrium expression equals the original expression squared, the new equilibrium constant K_c equals the original constant squared: $0.212^2 = 0.0449$ (at 100 °C). Once again, it is important to remember that you must relate each equilibrium constant you work with to a *specific* balanced chemical equation. *The concentrations of the substances in the equilibrium mixture*

will be the same no matter how you write the chemical equation, but the value of K_c you calculate depends on how you write the reaction.

It is also possible to calculate the equilibrium constant for a reaction if we know the equilibrium constants for other reactions that add up to give us the one we want, similar to the manner in which the reaction enthalpy of an unknown reaction can be determined from known reaction enthalpies using Hess's law. For example, consider the following two reactions, their equilibrium expressions, and their equilibrium constants at 100 °C:

1. $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g) \quad K_{c1} = \dfrac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$

2. $Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_{c2} = \dfrac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$

The net sum of these two equations is:

3. $2\,NOBr(g) + Cl_2(g) \rightleftharpoons 2\,NO(g) + 2\,BrCl(g)$

You can prove algebraically that the equilibrium expression for the net reaction is the product of the expressions for individual reactions:

$$K_{c3} = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{[BrCl]^2}{[Br_2][Cl_2]}$$

Thus,

$$K_{c3} = (K_{c1})(K_{c2}) = (0.014)(7.2) = 0.10$$

To summarize:

1. The equilibrium constant of a reaction in the *reverse* direction is the *inverse* (or *reciprocal*) of the equilibrium constant of the reaction in the forward direction:

$$A + B \rightleftharpoons C + D \quad K_1$$
$$C + D \rightleftharpoons A + B \quad K = 1/K_1$$

2. The equilibrium constant of a reaction that has been *multiplied* by a number is equal to the original equilibrium constant raised to a *power* equal to that number.

$$A + B \rightleftharpoons C + D \quad K_1$$
$$n\,A + n\,B \rightleftharpoons n\,C + n\,D \quad K = K_1^n$$

3. The equilibrium constant for a net reaction made up by adding *two or more reactions* is the *product* of the equilibrium constants for the individual reactions:

$$\begin{array}{l} A + B \rightleftharpoons C + D \quad K_1 \\ C + F \rightleftharpoons G + A \quad K_2 \\ \hline B + F \rightleftharpoons D + G \quad K_3 = (K_1)(K_2) \end{array}$$

Sample Exercise 15.4

Combining Equilibrium Expressions

Given the reactions

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \quad K_c = 6.8 \times 10^{-4}$$
$$H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4^{2-}(aq) \quad K_c = 3.8 \times 10^{-6}$$

determine the value of K_c for the reaction

$$2\,HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

SOLUTION

Analyze We are given two equilibrium equations and the corresponding equilibrium constants and are asked to determine the equilibrium constant for a third equation, which is related to the first two.

Plan We cannot simply add the first two equations to get the third. Instead, we need to determine how to manipulate these equations to come up with equations that we can add to give us the desired equation.

Continued

Solve

If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$$

Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives

$$2\,H^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$$

Now, we have two equations that sum to give the net equation, and we can multiply the individual K_c values to get the desired equilibrium constant.

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad K_c = 4.6 \times 10^{-7}$$
$$2\,H^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad K_c = 2.5 \times 10^5$$
$$2\,HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq) \qquad K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12$$

Practice Exercise

Given the equilibrium constants for the following two reactions in aqueous solution at 25 °C,

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq) \qquad K_c = 4.5 \times 10^{-4}$$
$$H_2SO_3(aq) \rightleftharpoons 2\,H^+(aq) + SO_3^-(aq) \qquad K_c = 1.1 \times 10^{-9}$$

what is the value of K_c for the reaction?

$$2\,HNO_2(aq) + SO_3^{2-}(aq) \rightleftharpoons H_2SO_3(aq) + 2\,NO_2^-(aq)$$

(a) 4.9×10^{-13} **(b)** 4.1×10^5 **(c)** 8.2×10^5 **(d)** 1.8×10^2 **(e)** 5.4×10^{-3}

Heterogeneous Equilibria

Many equilibria involve substances that are all in the same phase. Such equilibria are called **homogeneous equilibria**. The equilibrium between $N_2O_4(g)$ and $NO_2(g)$ shown in Figure 15.1 is one such example. In some cases, however, the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**. An example occurs when solid lead(II) chloride dissolves in water to form a saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \qquad [15.19]$$

This system consists of a solid in equilibrium with two aqueous species. If we want to write the equilibrium expression for this process, we encounter a problem we have not encountered previously: How do we express the concentration of a solid? If we were to carry out experiments starting with varying amounts of products and reactants, we would find that the equilibrium expression for the reaction of Equation 15.19 is

$$K_c = [Pb^{2+}][Cl^-]^2 \qquad [15.20]$$

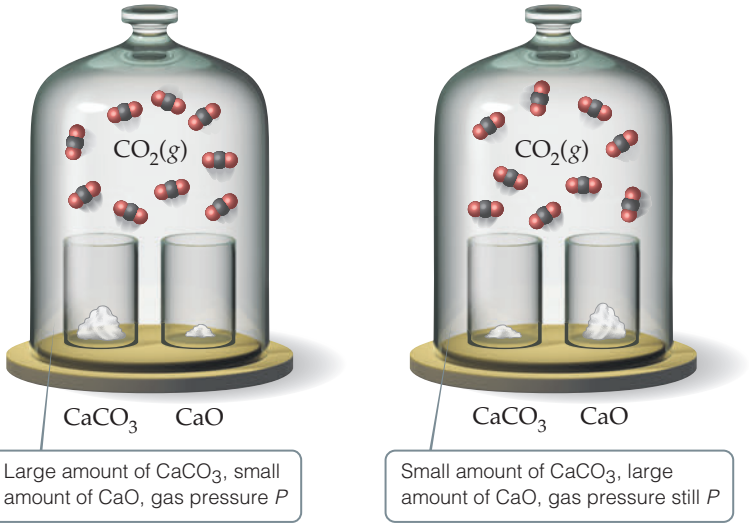
Thus, our problem of how to express the concentration of a solid is not relevant in the end because $PbCl_2(s)$ does not show up in the equilibrium expression. More generally, we can state that *whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium expression*.

The fact that pure solids and pure liquids are excluded from equilibrium expressions can be explained in two ways. First, the concentration of a pure solid or liquid has a constant value. If the mass of a solid is doubled, its volume also doubles. Thus, its concentration, which relates to the ratio of mass to volume, stays the same. Because equilibrium expressions include terms only for reactants and products whose concentrations can change during a chemical reaction, the concentrations of pure solids and pure liquids are omitted.

The omission can also be rationalized in a second way. Recall from Section 15.2 that what is substituted into a thermodynamic equilibrium expression is the activity of each substance, which is a ratio of the concentration to a reference value. For a pure substance,

Go Figure If some of the $CO_2(g)$ were released from the bell jar on the left, the seal then restored and the system allowed to return to equilibrium, would the amount of $CaCO_3(s)$ increase, decrease, or remain the same?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$



▲ **Figure 15.7** **At a given temperature, the equilibrium pressure of CO_2 in the bell jars is the same no matter how much of each solid is present.**

the reference value is the concentration of the pure substance, so that the activity of any pure solid or liquid is always 1.

Decomposition of calcium carbonate is another example of a heterogeneous reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Omitting the concentrations of the solids from the equilibrium expression gives

$$K_c = [CO_2] \quad \text{and} \quad K_p = P_{CO_2}$$

These equations tell us that at a given temperature, an equilibrium among $CaCO_3$, CaO, and CO_2 always leads to the same CO_2 partial pressure as long as all three components are present. As shown in **Figure 15.7**, we have the same CO_2 pressure regardless of the relative amounts of CaO and $CaCO_3$.

Sample Exercise 15.5

Writing Equilibrium Expressions for Heterogeneous Reactions

Write the equilibrium expression K_c for

(**a**) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

(**b**) $SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g)$

SOLUTION

Analyze We are given two chemical equations, both for heterogeneous equilibria, and asked to write the corresponding equilibrium expressions.

Plan We use the law of mass action, remembering to omit any pure solids and pure liquids from the expressions.

Solve

(**a**) The equilibrium expression is

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

Because H_2O appears in the reaction as a liquid, its concentration does not appear in the equilibrium expression.

Continued

(**b**) The equilibrium expression is

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

Because SnO_2 and Sn are pure solids, their concentrations do not appear in the equilibrium expression.

Practice Exercise

Consider the equilibrium that is established in a saturated solution of silver chloride, $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$. If solid AgCl is added to this solution, what will happen to the concentration of Ag^+ and Cl^- ions in solution? (**a**) $[Ag^+]$ and $[Cl^-]$ will both increase (**b**) $[Ag^+]$ and $[Cl^-]$ will both decrease (**c**) $[Ag^+]$ will increase and $[Cl^-]$ will decrease (**d**) $[Ag^+]$ will decrease and $[Cl^-]$ will increase (**e**) neither $[Ag^+]$ nor $[Cl^-]$ will change

Sample Exercise 15.6

Analyzing a Heterogeneous Equilibrium

Each of these mixtures was placed in a closed container and allowed to stand:

(**a**) $CaCO_3(s)$

(**b**) $CaO(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p

(**c**) $CaCO_3(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p

(**d**) $CaCO_3(s)$ and $CaO(s)$

Determine whether or not each mixture can attain the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

SOLUTION

Analyze We are asked which of several combinations of species can establish an equilibrium between calcium carbonate and its decomposition products, calcium oxide and carbon dioxide.

Plan For equilibrium to be achieved, it must be possible for both the forward process and the reverse process to occur. For the forward process to occur, some calcium carbonate must be present. For the reverse process to occur, both calcium oxide and carbon dioxide must be present. In both cases, either the necessary compounds may be present initially or they may be formed by reaction of the other species.

Solve Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. (**a**) $CaCO_3$ simply decomposes, forming $CaO(s)$ and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained. There must be enough $CaCO_3$, however, to allow the CO_2 pressure to reach equilibrium. (**b**) CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value. (**c**) Because there is no CaO present, equilibrium cannot be attained; there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some CO_2 to react with CaO). (**d**) The situation is essentially the same as in (a): $CaCO_3$ decomposes until equilibrium is attained. The presence of CaO initially makes no difference.

Practice Exercise

If 8.0 g of $NH_4HS(s)$ is placed in a sealed vessel with a volume of 1.0 L and heated to 200 °C the reaction $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ will occur. When the system comes to equilibrium, some $NH_4HS(s)$ is still present. Which of the following changes will lead to a reduction in the amount of $NH_4HS(s)$ that is present, assuming in all cases that equilibrium is re-established following the change? (**a**) Adding more $NH_3(g)$ to the vessel (**b**) Adding more $H_2S(g)$ to the vessel (**c**) Adding more $NH_4HS(s)$ to the vessel (**d**) Increasing the volume of the vessel (**e**) Decreasing the volume of the vessel

When a solvent is a reactant or product in an equilibrium, its concentration is omitted from the equilibrium expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance. Applying this guideline to an equilibrium involving water as a solvent,

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3^-(aq) \qquad [15.21]$$

gives an equilibrium expression that does not contain $[H_2O]$:

$$K_c = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} \qquad [15.22]$$

Self-Assessment Exercises

15.9 For the reaction $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ $K_c = 855$ at 1000 K. Do the reactants or the product dominate the equilibrium mixture?

(a) The reactants

(b) The product

15.10 For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the equilibrium constant $K_c = 0.0059$ at 300 K. What is the equilibrium constant for the reverse reaction $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$, at 300 K?

(a) $K_c = 0.0059$
(b) $K_c = -0.0059$
(c) $K_c = 169$

15.11 Write the equilibrium constant expression for the reaction $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

(a) $K = [Ag^+][Cl^-]$

(b) $K = \dfrac{[Ag^+][Cl^-]}{[AgCl]}$

Exercises

15.12 Consider the following equilibrium:

$$2\,H_2(g) + S_2(g) \rightleftharpoons 2\,H_2S(g) \quad K_c = 1.08 \times 10^7 \text{at } 700\,^\circ\text{C}$$

(**a**) Calculate K_p. (**b**) Does the equilibrium mixture contain mostly H_2 and S_2 or mostly H_2S? (**c**) Calculate the value of K_c if you rewrote the equation $H_2(g) + \frac{1}{2}S_2(g) \rightleftharpoons H_2S(g)$.

15.13 Consider the following equilibrium, for which $K_p = 7.62$ at 480 °C:

$$2\,Cl_2(g) + 2\,H_2O(g) \rightleftharpoons 4\,HCl(g) + O_2(g)$$

(**a**) What is the value of K_p for the reaction $4\,HCl(g) + O_2(g) \rightleftharpoons 2\,Cl_2(g) + 2\,H_2O(g)$?

(**b**) What is the value of K_p for the reaction $Cl_2(g) + H_2O(g) \rightleftharpoons 2\,HCl(g) + \frac{1}{2}\,O_2(g)$?

15.14 Consider the equilibrium

$$N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$$

Calculate the equilibrium constant K_p for this reaction, given the following information (at 298 K):

$$2\,NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g) \quad K_c = 2.0$$
$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g) \quad K_c = 2.1 \times 10^{30}$$

15.15 Consider the equilibrium $Na_2O(s) + SO_2(g) \rightleftharpoons Na_2SO_3(s)$. (**a**) Write the equilibrium expression for this reaction in terms of partial pressures. (**b**) All the compounds in this reaction are soluble in water. Rewrite the equilibrium expression in terms of molarities for the aqueous reaction.

Answers to Self-Assessment Exercises

15.9 (b) **15.10** (c) **15.11** (a)

15.4 | Calculating Equilibrium Constants



In this section, we are performing calculations using equilibrium expressions and the associated constants. In some cases, they may seem complicated but having a clear working method allows us to follow a logical procedure to get to the desired answer. By the end of this section, you should be able to

- Perform calculations of different sorts involving equilibrium expressions

If we can measure the equilibrium concentrations of all the reactants and products in a chemical reaction, as we did with the data in Table 15.1, calculating the value of the equilibrium constant is straightforward. We simply insert all the equilibrium concentrations into the equilibrium expression for the reaction.

Sample Exercise 15.7

Calculating *K* When All Equilibrium Concentrations Are Known

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 bar H_2, 2.46 bar N_2, and 0.166 bar NH_3. From these data, calculate the equilibrium constant K_p for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

SOLUTION

Analyze We are given a balanced equation and equilibrium partial pressures and are asked to calculate the value of the equilibrium constant.

Plan Using the balanced equation, we write the equilibrium-constant expression. We then substitute the equilibrium partial pressures into the expression and solve for K_p.

Solve

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{0.166^2}{(249.3)(747.8)^3} = 2.71 \times 10^{-9}$$

Practice Exercise

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[CH_3COOH] = 1.65 \times 10^{-2}\,M$; $[H^+] = 5.44 \times 10^{-4}\,M$; and $[CH_3COO^-] = 5.44 \times 10^{-4}\,M$. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Often, we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the initial concentrations and the equilibrium concentration of at least one species, however, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the others. The following steps outline the procedure:

How to Determine Concentrations of Unknown Species in an Equilibrium Mixture

1. Tabulate all known initial and equilibrium concentrations of the species that appear in the equilibrium expression.
2. For those species for which initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to calculate the changes in concentration for all other species in the equilibrium expression.
4. Use initial concentrations from step 1 and changes in concentration from step 3 to calculate any equilibrium concentrations not tabulated in step 1.
5. Determine the value of the equilibrium constant.

The best way to illustrate this procedure is by example, as we do in Sample Exercise 15.8.

Sample Exercise 15.8

Calculating *K* from Initial and Equilibrium Concentrations

A reaction vessel containing 1.000×10^{-3} *M* H_2 gas and 2.000×10^{-3} *M* I_2 gas is heated to 448 °C where the following reaction takes place

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

What is the value of the equilibrium constant K_c if once the system comes to equilibrium at 448 °C the concentration of HI is 1.87×10^{-3} *M*?

SOLUTION

Analyze We are given the initial concentrations of H_2 and I_2 and the equilibrium concentration of HI. We are asked to calculate the equilibrium constant K_c for $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$.

Plan We construct a table to find equilibrium concentrations of all species and then use the equilibrium concentrations to calculate the equilibrium constant.

Solve

(1) We tabulate the initial and equilibrium concentrations of as many species as we can. We also provide space in our table for listing the changes in concentrations. As shown, it is convenient to use the chemical equation as the heading for the table.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			1.87×10^{-3}

(2) We calculate the change in HI concentration, which is the difference between the equilibrium and initial values:

$$\text{Change in } [HI] = 1.87 \times 10^{-3}\,M - 0 = 1.87 \times 10^{-3}\,M$$

(3) We use the coefficients in the balanced equation to relate the change in [HI] to the changes in $[H_2]$ and $[I_2]$:

$$\left(1.87 \times 10^{-3}\,\frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1\text{ mol } H_2}{2\text{ mol HI}}\right) = 0.935 \times 10^{-3}\,\frac{\text{mol } H_2}{\text{L}}$$

$$\left(1.87 \times 10^{-3}\,\frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1\text{ mol } I_2}{2\text{ mol HI}}\right) = 0.935 \times 10^{-3}\,\frac{\text{mol } I_2}{\text{L}}$$

(4) We calculate the equilibrium concentrations of H_2 and I_2, using initial concentrations and changes in concentration. The equilibrium concentration equals the initial concentration minus that consumed:

$$[H_2] = (1.000 \times 10^{-3}\,M) - (0.935 \times 10^{-3}\,M) = 0.065 \times 10^{-3}\,M$$

$$[I_2] = (2.000 \times 10^{-3}\,M) - (0.935 \times 10^{-3}\,M) = 1.065 \times 10^{-3}\,M$$

(5) Our table now is complete (with equilibrium concentrations in blue for emphasis):

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
Equilibrium concentration (*M*)	0.065×10^{-3}	1.065×10^{-3}	1.87×10^{-3}

Notice that the entries for the changes are negative when a reactant is consumed and positive when a product is formed.

Finally, we use the equilibrium-constant expression to calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

Comment The same method can be applied to gaseous equilibrium problems to calculate K_p, in which case partial pressures are used as table entries in place of molar concentrations. Your instructor may refer to this kind of table as an ICE chart, where ICE stands for *I*nitial – *C*hange – *E*quilibrium.

Practice Exercise

In Section 15.1, we discussed the equilibrium between $N_2O_4(g)$ and $NO_2(g)$. Let's return to that equation in a quantitative example. When 9.2 g of frozen N_2O_4 is added to a 0.50 L reaction vessel that is heated to 400 K and allowed to come to equilibrium, the concentration of N_2O_4 is determined to be 0.057 M. Given this information, what is the value of K_c for the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ at 400 K? (**a**) 0.23 (**b**) 0.36 (**c**) 0.13 (**d**) 1.4 (**e**) 2.5

Applications of Equilibrium Constants

We have seen that the magnitude of K indicates the extent to which a reaction proceeds.

- If K is very large, the equilibrium mixture contains mostly substances on the product side of the equation for the reaction.
- If K is very small (that is, much less than 1), the equilibrium mixture contains mostly substances on the reactant side of the equation.

The equilibrium constant also allows us to (1) predict the direction in which a reaction mixture achieves equilibrium and (2) calculate equilibrium concentrations of reactants and products.

Predicting the Direction of Reaction

For the formation of NH_3 from N_2 and H_2 (Equation 15.6), $K_c = 0.105$ at 472 °C. Suppose we place 2.00 mol of H_2, 1.00 mol of N_2, and 2.00 mol of NH_3 in a 1.00 L container at 472 °C. How will the mixture react to reach equilibrium? Will N_2 and H_2 react to form more NH_3, or will NH_3 decompose to N_2 and H_2?

To answer this question, we substitute the starting concentrations of N_2, H_2, and NH_3 into the equilibrium expression and compare its value to the equilibrium constant:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas} \quad K_c = 0.105 \qquad [15.23]$$

To reach equilibrium, the quotient $[NH_3]^2/[N_2][H_2]^3$ must decrease from the starting value of 0.500 to the equilibrium value of 0.105. Because the system is closed, this change can happen only if $[NH_3]$ decreases and $[N_2]$ and $[H_2]$ increase. Thus, the reaction proceeds toward equilibrium by forming N_2 and H_2 from NH_3; that is, the reaction as written in Equation 15.6 proceeds from right to left.

This approach can be formalized by defining a quantity called the reaction quotient.

*The **reaction quotient**, Q, is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium expression.*

Therefore, for the general reaction

$$a\,A + b\,B \rightleftharpoons d\,D + e\,E$$

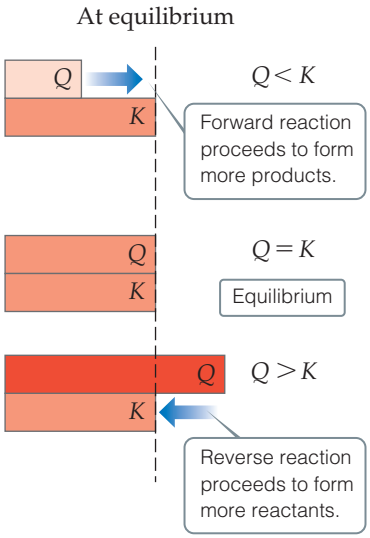
the reaction quotient in terms of molar concentrations is

$$Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \qquad [15.24]$$

A related quantity Q_p can be written for any reaction that involves gases by using partial pressures instead of concentrations.

Although we use what looks like the equilibrium expression to calculate the reaction quotient, the concentrations we use may or may not be the equilibrium concentrations. For example, when we substituted the starting concentrations into the equilibrium expression of Equation 15.23, we obtained $Q_c = 0.500$ whereas $K_c = 0.105$. The equilibrium constant has only one value at each temperature. The reaction quotient, however, varies as the reaction proceeds.

Of what use is Q? One practical thing we can do with Q is tell whether our reaction really is at equilibrium, which is an especially valuable option when a reaction is very slow. We can take samples of our reaction mixture as the reaction proceeds, separate the components, and measure their concentrations. Then we insert these numbers into Equation 15.24 for our reaction. To determine whether we are at equilibrium, or in which direction the reaction proceeds to achieve equilibrium, we compare the values of Q_c and K_c or Q_p and K_p. There are three possible scenarios (**Figure 15.8**), which can be summarized as follows:



▲ **Figure 15.8** **Predicting the direction of a reaction by comparing *Q* and *K* at a given temperature.**

How to Use Q to Analyze Reaction Progress

- $Q < K$: The concentration of products is too small and that of reactants too large. The reaction achieves equilibrium by forming more products; it proceeds from left to right.
- $Q = K$: The reaction quotient equals the equilibrium constant only if the system is at equilibrium.
- $Q > K$: The concentration of products is too large and that of reactants too small. The reaction achieves equilibrium by forming more reactants; it proceeds from right to left.

Sample Exercise 15.9

Predicting the Direction of Approach to Equilibrium

At 448 °C, the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} mol of I_2 in a 2.00 L container.

SOLUTION

Analyze We are given a volume and initial molar amounts of the species in a reaction and asked to determine in which direction the reaction must proceed to achieve equilibrium.

Plan We can determine the starting concentration of each species in the reaction mixture. We can then substitute the starting concentrations into the equilibrium expression to calculate the reaction quotient, Q_c. Comparing the magnitudes of the equilibrium constant, which is given, and the reaction quotient will tell us in which direction the reaction will proceed.

Solve

The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.0 \times 10^{-2}\,M$$
$$[H_2] = 1.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 5.0 \times 10^{-3}\,M$$
$$[I_2] = 3.0 \times 10^{-2}\,\text{mol}/2.00\,\text{L} = 1.5 \times 10^{-2}\,M$$

The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H_2 and I_2 must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.

Practice Exercise

Which of the following statements accurately describes what would happen to the direction of the reaction described in this sample exercise, if the size of the container were different from 2.00 L? (**a**) The reaction would proceed in the opposite direction (from right to left) if the container volume were reduced sufficiently. (**b**) The reaction would proceed in the opposite direction if the container volume were expanded sufficiently. (**c**) The direction of this reaction does not depend on the volume of the container.

Calculating Equilibrium Concentrations

Chemists frequently need to calculate the amounts of reactants and products present at equilibrium in a reaction for which they know the equilibrium constant. The approach in solving problems of this type is similar to the one we used for evaluating equilibrium constants: We tabulate initial concentrations or partial pressures, changes in those concentrations or pressures, and final equilibrium concentrations or partial pressures. Usually, we end up using the equilibrium expression to derive an equation that must be solved for an unknown quantity, as demonstrated in Sample Exercise 15.10.

Sample Exercise 15.10

Calculating Equilibrium Concentrations

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 1.41 \times 10^{-9}$, at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 94.03 bar and that of N_2 is 43.77 bar. What is the partial pressure of NH_3 in this equilibrium mixture?

Continued

SOLUTION

Analyze We are given an equilibrium constant, K_p, and the equilibrium partial pressures of two of the three substances in the equation (N_2 and H_2), and we are asked to calculate the equilibrium partial pressure for the third substance (NH_3).

Plan We can set K_p equal to the equilibrium expression and substitute in the partial pressures that we know. Then we can solve for the only unknown in the equation.

Solve

We tabulate the equilibrium pressures:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Equilibrium pressure bar 43.77 bar 94.03 bar x

Because we do not know the equilibrium pressure of NH_3, we represent it with x. At equilibrium, the pressures must satisfy the equilibrium expression:

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(43.77)(94.03)^3} = 1.41 \times 10^{-9}$$

We now rearrange the equation to solve for x:

$$x^2 = (1.41 \times 10^{-9})(43.77)(94.03)^3 = 5.14 \times 10^{-2}$$

$$x = \sqrt{5.14 \times 10^{-2}} = 0.227 \text{ bar} = P_{NH_3}$$

Check We can always check our answer by using it to recalculate the value of the equilibrium constant:

$$K_p = \frac{(0.227)^2}{(43.77)(94.03)^3} = 1.41 \times 10^{-9}$$

Practice Exercise

At 500 K, the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ has $K_p = 50.4$. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 87.14 kPa and that of PCl_3 is 34.46 kPa. What is the partial pressure of Cl_2 in the equilibrium mixture?

In many situations, we know the value of the equilibrium constant and the initial amounts of all species. We must then solve for the equilibrium amounts. Solving this type of problem usually entails treating the change in concentration as a variable. The stoichiometry of the reaction gives us the relationship between the changes in the amounts of all the reactants and products, as illustrated in Sample Exercise 15.11. The calculations frequently involve the quadratic formula, as you will see in this exercise.

Sample Exercise 15.11

Calculating Equilibrium Concentrations from Initial Concentrations

A 1.000 L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448 °C. The value of the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

at 448 °C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

SOLUTION

Analyze We are given the volume of a container, an equilibrium constant, and starting amounts of reactants in the container and are asked to calculate the equilibrium concentrations of all species.

Plan In this case, we are not given any of the equilibrium concentrations. We must develop some relationships that relate the initial concentrations to those at equilibrium. The procedure is similar in many regards to that outlined in Sample Exercise 15.8, where we calculated an equilibrium constant using initial concentrations.

Solve

(**1**) We note the initial concentrations of H_2 and I_2:

$$[H_2] = 1.000\,M \quad \text{and} \quad [I_2] = 2.000\,M$$

(**2**) We construct a table in which we tabulate the initial concentrations:

	$H_2(g)$ +	$I_2(g)$ ⇌	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)			
Equilibrium concentration (M)			

(3) We use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H_2 and I_2 concentrations will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H_2 by x. The balanced chemical equation tells us that for each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:

	$H_2(g)$	+ $I_2(g)$ ⇌	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)			

(4) We use initial concentrations and changes in concentrations, as dictated by stoichiometry, to express the equilibrium concentrations. With all our entries, our table now looks like this:

	$H_2(g)$	+ $I_2(g)$ ⇌	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)	$1.000 - x$	$2.000 - x$	$2x$

(5) We substitute the equilibrium concentrations into the equilibrium expression and solve for x:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

If you have an equation-solving calculator, you can solve this equation directly for x. If not, expand this expression to obtain a quadratic equation in x:

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$
$$46.5x^2 - 151.5x + 101.0 = 0$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for x:

$$x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

When we substitute $x = 2.323$ into the expressions for the equilibrium concentrations, we find *negative* concentrations of H_2 and I_2. Because a negative concentration is not chemically meaningful, we reject this solution. We then use $x = 0.935$ to find the equilibrium concentrations:

$$[H_2] = 1.000 - x = 0.065\,M$$
$$[I_2] = 2.000 - x = 1.065\,M$$
$$[HI] = 2x = 1.87\,M$$

Check We can check our solution by putting these numbers into the equilibrium expression to assure that we correctly calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

Comment Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions to the equation will give you a value that leads to negative concentrations and thus is not chemically meaningful. Reject this solution to the quadratic equation.

Practice Exercise

For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant K_p is 50.4 at 500 K. A gas cylinder at 500 K is charged with $PCl_5(g)$ at an initial pressure of 168.2 kPa. What are the equilibrium pressures of PCl_5, PCl_3, and Cl_2 at this temperature?

Self-Assessment Exercise

15.16 In an experiment, 0.200 mol of $PCl_3(g)$ and 0.100 mol of $Cl_2(g)$ were mixed in a 1.00 L container at 250 °C. When equilibrium was established, it was found that $[PCl_5] = 0.091$. Calculate the value of K_c at this temperature.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

(a) $K = 0.22$

(b) $K = 93$

Exercises

15.17 Methanol (CH_3OH) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen: $CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$. An equilibrium mixture in a 10.00 L vessel is found to contain 0.050 mol CH_3OH, 0.850 mol CO, and 0.750 mol H_2 at 500 K. Calculate K_c at this temperature.

15.18 A mixture of 0.140 mol of NO, 0.060 mol of H_2, and 0.260 mol of H_2O is placed in a 2.0 L vessel at 330 K. Assume that the following equilibrium is established:

$$2\,NO(g) + 2\,H_2(g) \rightleftharpoons N_2(g) + 2\,H_2O(g)$$

At equilibrium $[H_2] = 0.010\,M$. (**a**) Calculate the equilibrium concentrations of NO, N_2, and H_2O. (**b**) Calculate K_c.

15.19 A chemist at a pharmaceutical company is measuring equilibrium constants for reactions in which drug candidate molecules bind to a protein involved in cancer. The drug molecules bind the protein in a 1:1 ratio to form a drug–protein complex. The protein concentration in aqueous solution at 25 °C is $1.50 \times 10^{-6}\,M$. Drug A is introduced into the protein solution at an initial concentration of $2.00 \times 10^{-6}\,M$. Drug B is introduced into a separate, identical protein solution at an initial concentration of $2.00 \times 10^{-6}\,M$. At equilibrium, the drug A–protein solution has an A–protein complex concentration of $1.00 \times 10^{-6}\,M$, and the drug B solution has a B–protein complex concentration of $1.40 \times 10^{-6}\,M$. Calculate the K_c value for the A–protein binding reaction and for the B–protein binding reaction. Assuming that the drug that binds more strongly will be more effective, which drug is the better choice for further research?

15.20 (**a**) If $Q_c > K_c$, how must the reaction proceed to reach equilibrium? (**b**) At the start of a certain reaction, only reactants are present; no products have been formed. What is the value of Q_c at this point in the reaction?

15.21 As shown in Table 15.2, K_p for the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

is 4.39×10^{-9} at 450 °C. For each of the mixtures listed here, indicate whether the mixture is at equilibrium at 450 °C. If it is not at equilibrium, indicate the direction (toward product or toward reactants) in which the mixture must shift to achieve equilibrium.

(**a**) 9.93 MPa NH_3, 4.56 MPa N_2, 5.57 MPa H_2

(**b**) 5.78 MPa NH_3, 14.49 MPa N_2, no H_2

(**c**) 1.32 MPa NH_3, 2.74 MPa N_2, 8.31 Mpa H_2

15.22 For $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, $K_p = 3.0 \times 10^2$ at 700 K. In a 2.00 L vessel, the equilibrium mixture contains 1.17 g of SO_3 and 0.105 g of O_2. How many grams of SO_2 are in the vessel?

15.23 For the equilibrium

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g)$$

at 400 K, $K_c = 7.0$. If 0.25 mol of Br_2 and 0.55 mol of Cl_2 are introduced into a 3.0 L container at 400 K, what will be the equilibrium concentrations of Br_2, Cl_2, and BrCl?

15.24 At 80 °C, $K_c = 1.87 \times 10^{-3}$ for the reaction

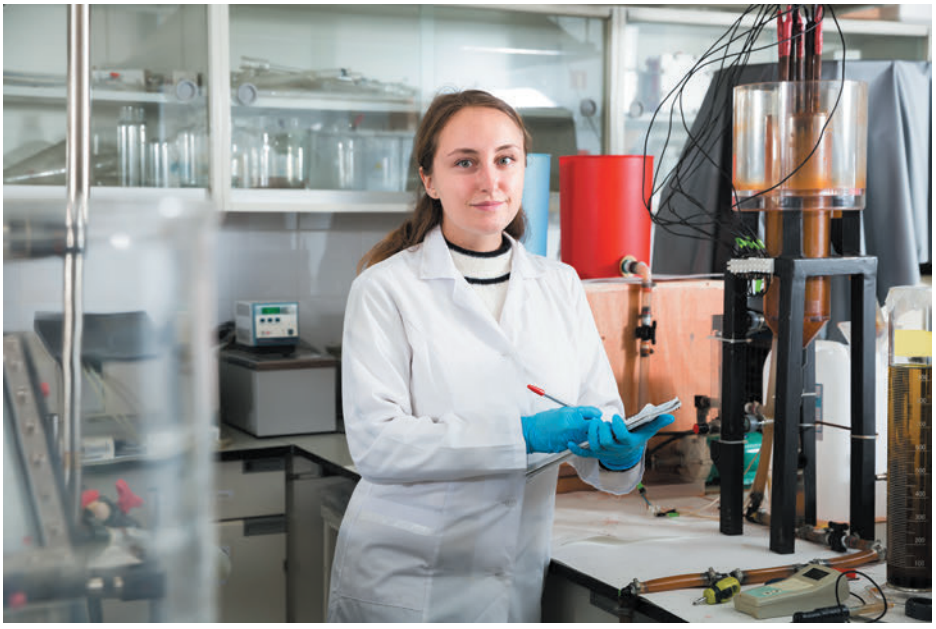
$$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g)$$

(**a**) Calculate the equilibrium concentrations of PH_3 and BCl_3 if a solid sample of PH_3BCl_3 is placed in a closed vessel at 80 °C and decomposes until equilibrium is reached. (**b**) If the flask has a volume of 0.250 L, what is the minimum mass of $PH_3BCl_3(s)$ that must be added to the flask to achieve equilibrium?

Answers to Self-Assessment Exercise

15.16 (b)

15.5 | Le Châtelier's Principle



Many of the products we use in everyday life are obtained from the chemical industry. Chemists and chemical engineers in industry spend a great deal of time and effort to maximize the yield of valuable products and minimize waste. For example, when Haber developed his process for making ammonia from N_2 and H_2, he examined how reaction conditions might be varied to increase yield. Using the values of the equilibrium constant at various temperatures, he calculated the equilibrium amounts of NH_3 formed under a variety of conditions. By the end of this section, you should be able to

- Use Le Châtelier's principle to predict how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

Some of Haber's results are shown in **Figure 15.9**. Notice that the percent of NH_3 present at equilibrium decreases with increasing temperature and increases with increasing pressure.

We can understand these effects in terms of a principle first put forward by Henri-Louis Le Châtelier* (1850–1936), a French industrial chemist:

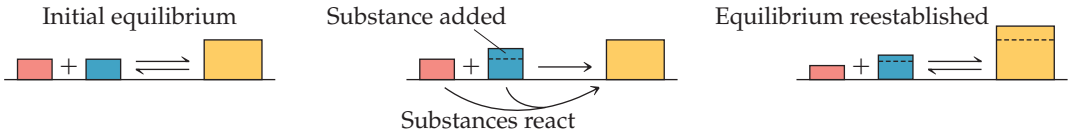
> *If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.*

Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in **concentration**, **pressure**, or **temperature**, the system will shift its equilibrium position so as to counter the effect of the disturbance.

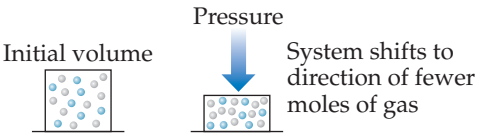
Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.



Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.



Temperature:

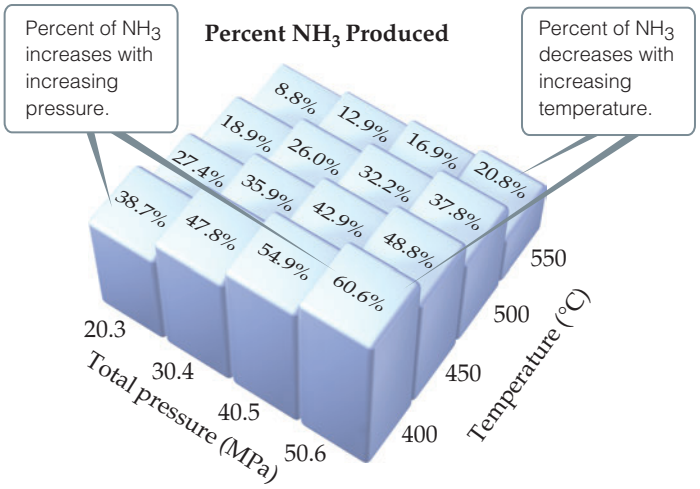
If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reagent," namely, heat.

Endothermic		Exothermic	
Increasing T	Reaction shifts right	Increasing T	Reaction shifts left
Decreasing T	Reaction shifts left	Decreasing T	Reaction shifts right

In this section, we use Le Châtelier's principle to make qualitative predictions about how a system at equilibrium responds to various changes in external conditions. We consider three ways in which a chemical equilibrium can be disturbed: (1) adding or removing a reactant or product, (2) changing the pressure by changing the volume, and (3) changing the temperature.

* Pronounced "le-SHOT-lee-ay."

Go Figure At what combination of pressure and temperature should you run the reaction to maximize NH_3 yield?



▲ **Figure 15.9 Effect of temperature and pressure on NH_3 yield in the Haber process.** Each mixture was produced by starting with a 3 : 1 molar mixture of H_2 and N_2.

Change in Reactant or Product Concentration

A system at dynamic equilibrium is in a state of balance. When the concentrations of species in the reaction are altered, the equilibrium shifts until a new state of balance is attained. What does *shift* mean? It means that reactant and product concentrations change over time to accommodate the new situation. *Shift* does *not* mean that the equilibrium constant itself is altered; the equilibrium constant remains the same. Le Châtelier's principle states that the shift is in the direction that minimizes or reduces the effect of the change.

> *If a chemical system is already at equilibrium and the concentration of any substance in the mixture is increased (either reactant or product), the system reacts to consume some of that substance. Conversely, if the concentration of a substance is decreased, the system reacts to produce some of that substance.*

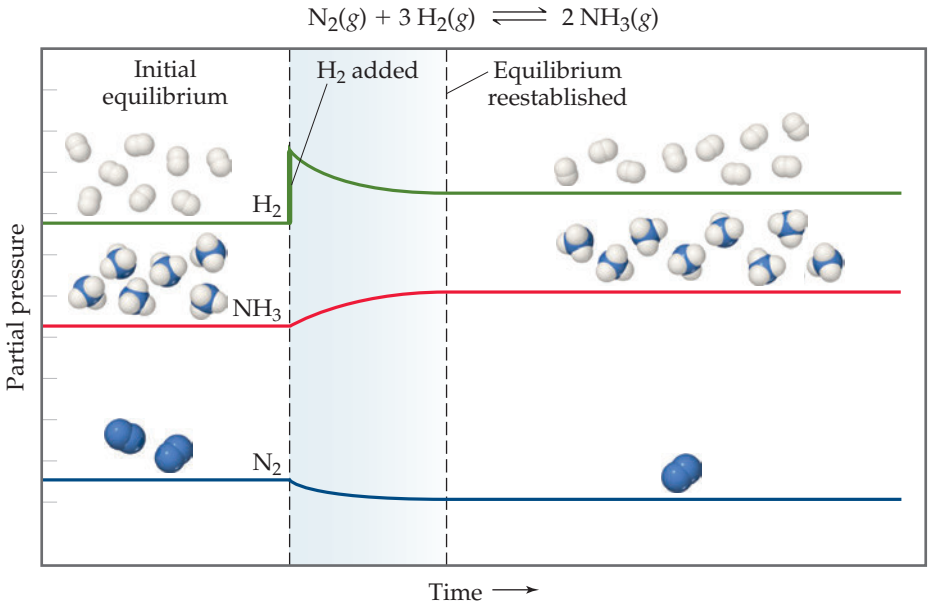
There is no change in the equilibrium constant when we change the concentrations of reactants or products. As an example, consider our familiar equilibrium mixture of N_2, H_2, and NH_3:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

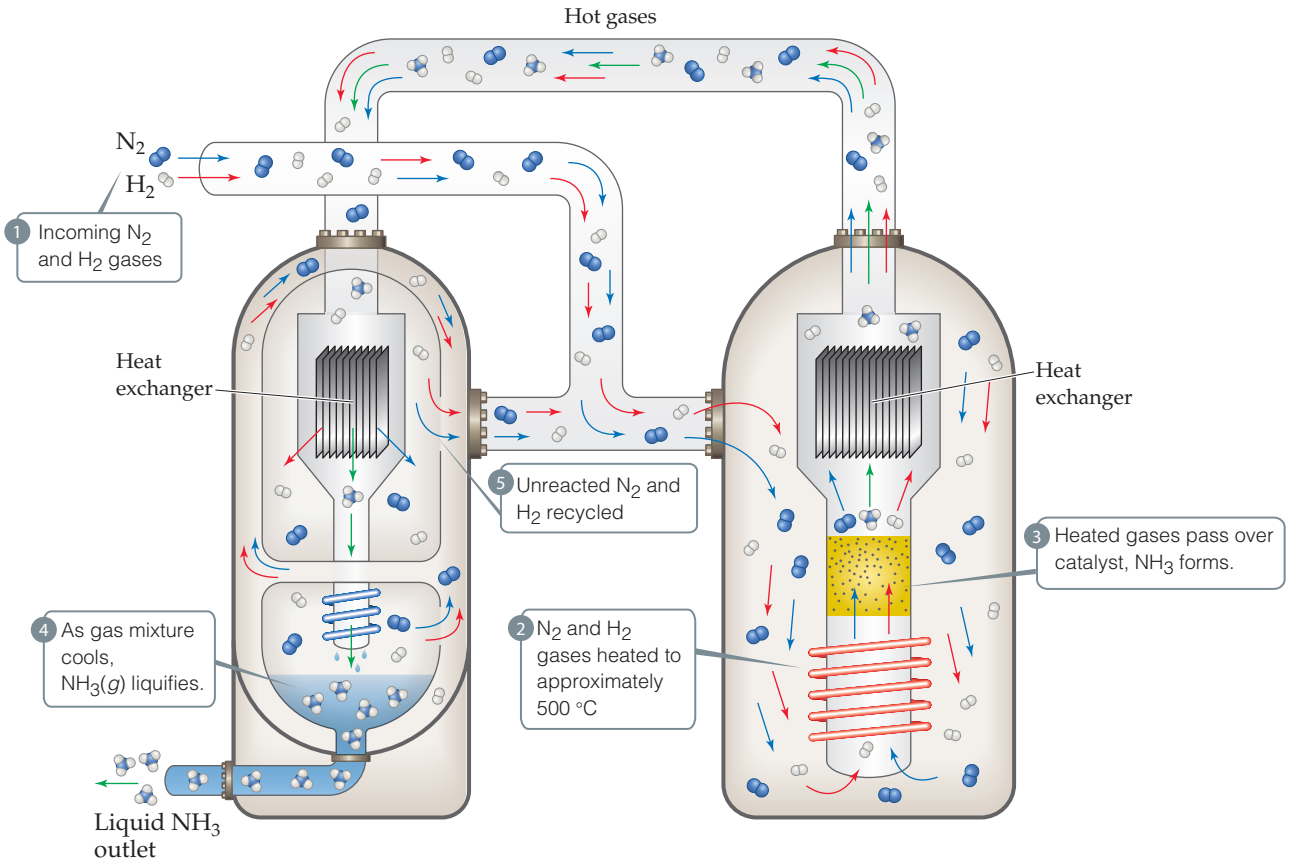
Adding H_2 causes the system to shift so as to reduce the increased concentration of H_2 (**Figure 15.10**). This change can occur only if the reaction consumes H_2 and simultaneously consumes N_2 to form more NH_3. Adding N_2 to the equilibrium mixture likewise causes the reaction to shift toward forming more NH_3. Removing NH_3 also causes a shift toward producing more NH_3, whereas *adding* NH_3 to the system at equilibrium causes the reaction to shift in the direction that reduces the increased NH_3 concentration: Some of the added ammonia decomposes to form N_2 and H_2. All of these "shifts" are entirely consistent with predictions that we would make by comparing the reaction quotient Q with the equilibrium constant K.

In the Haber reaction, therefore, removing NH_3 from an equilibrium mixture of N_2, H_2, and NH_3 causes the reaction to shift right to form more NH_3. If the NH_3 can be removed continuously as it is produced, the yield can be increased dramatically. In the industrial production of ammonia, the NH_3 is continuously removed by selectively liquefying it (**Figure 15.11**). (The boiling point of NH_3, −33 °C, is much higher than those of N_2, −196 °C, and H_2, −253 °C.) The liquid NH_3 is removed, and the N_2 and H_2 are recycled to form more NH_3. As a result of the product being continuously removed, the reaction is driven essentially to completion.

Go Figure Why does the nitrogen concentration decrease after hydrogen is added?



▲ **Figure 15.10 Effect of adding H_2 to an equilibrium mixture of N_2, H_2, and NH_3.** Adding H_2 causes the reaction as written to shift to the right, consuming some N_2 to produce more NH_3.



▲ **Figure 15.11 Diagram of the industrial production of ammonia.** Incoming $N_2(g)$ and $H_2(g)$ are heated to approximately 500 °C and passed over a catalyst. When the resultant N_2, H_2, and NH_3 mixture is cooled, the NH_3 liquefies and is removed from the mixture, shifting the reaction to produce more NH_3.

Effects of Volume and Pressure Changes

If a system containing one or more gases is at equilibrium and its volume is decreased, thereby increasing its total pressure, Le Châtelier's principle indicates that the system responds by shifting its equilibrium position to reduce the pressure. A system can reduce its pressure by reducing the total number of gas molecules (fewer molecules of gas exert a lower pressure). Thus, at constant temperature, *reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas*. Increasing the volume causes a shift in the direction that produces more gas molecules (**Figure 15.12**).

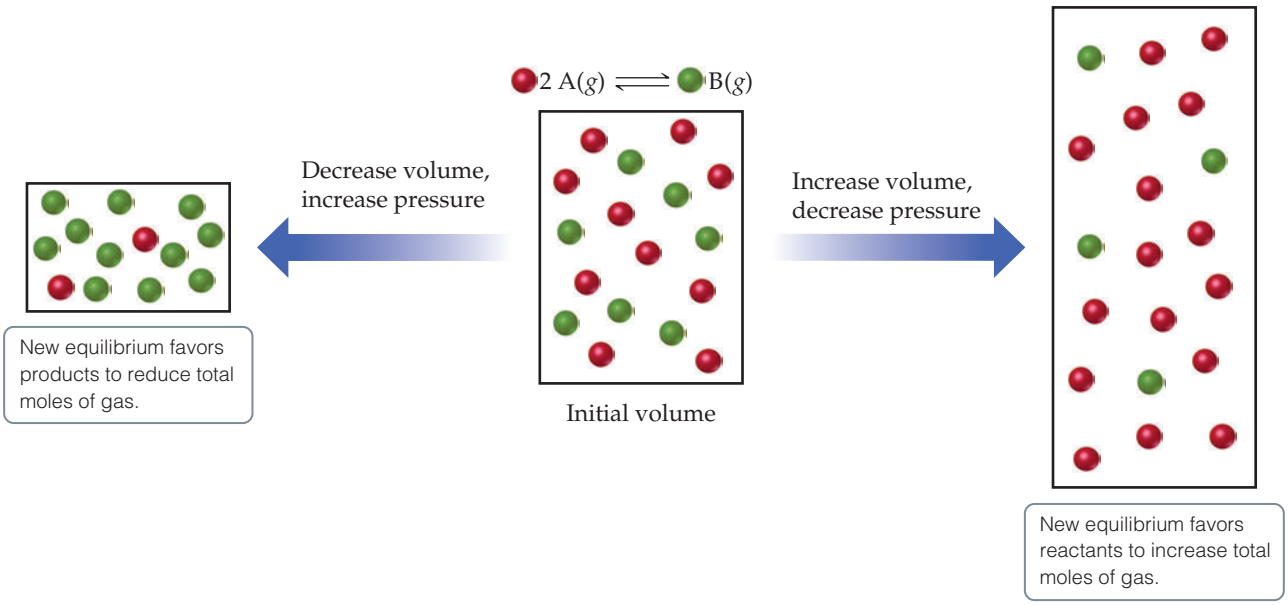
In the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (caused by a decrease in volume) shifts the reaction in the direction that produces fewer gas molecules, which leads to the formation of more NH_3, as indicated in Figure 15.9. In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure does not influence the position of equilibrium.

Keep in mind that, as long as temperature remains constant, pressure–volume changes do *not* change the value of K. Rather, these changes alter the partial pressures of the gaseous substances. In Sample Exercise 15.7, we calculated $K_p = 2.71 \times 10^{-9}$ for the Haber reaction, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, in an equilibrium mixture at 472 °C containing 249.3 kPa H_2, 747.8 kPa N_2, and 16.82 kPa NH_3. Consider what happens when we suddenly reduce the volume of the system by one-half. If there were no shift in equilibrium, this volume change would cause the partial pressures of all substances to double, giving $P_{H_2} = 1495.6$ kPa, $P_{N_2} = 498.6$ kPa, and $P_{NH_3} = 33.64$ kPa. The reaction quotient would then no longer equal the equilibrium constant:

$$Q_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(33.6\text{ kPa})^2}{(498.6\text{ kPa})(1495.6\text{ kPa})^3} = 6.79 \times 10^{-10} \neq K_p$$

Because $Q_p < K_p$, the system would no longer be at equilibrium. Equilibrium would be reestablished by increasing P_{NH_3} and decreasing both P_{N_2} and P_{H_2} until $Q_p = K_p = 2.71 \times 10^{-9}$. Therefore, the equilibrium shifts to the right in the reaction as written, as Le Châtelier's principle predicts.

It is possible to change the pressure of a system in which a chemical reaction is running without changing its volume. For example, pressure increases if additional amounts of any reacting components are added to the system. We have already seen how to deal



▲ **Figure 15.12** **Pressure and Le Châtelier's principle.**

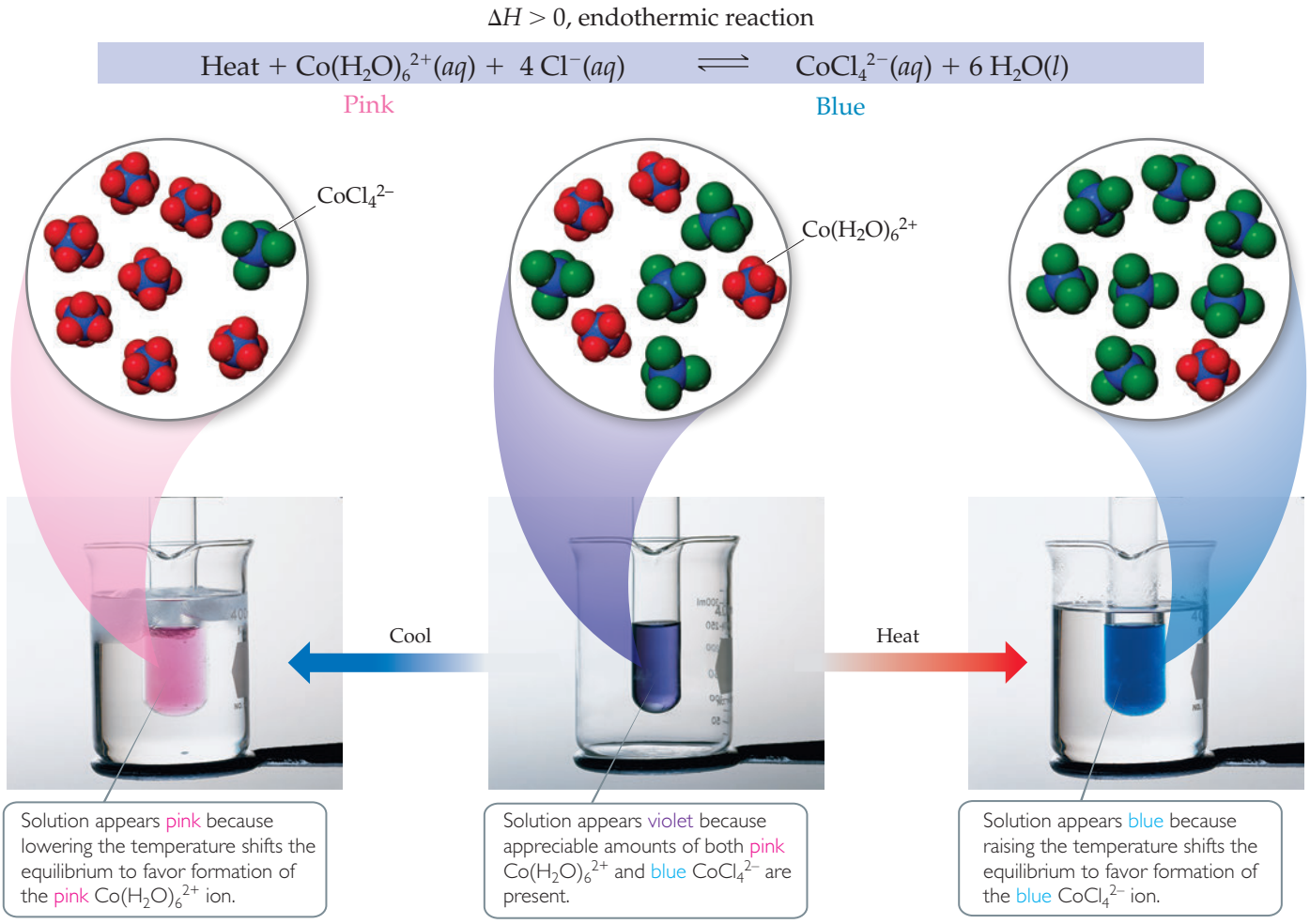
with a change in concentration of a reactant or product. However, the *total* pressure in the reaction vessel might also be increased by adding a gas that is not involved in the equilibrium. For example, argon might be added to the ammonia equilibrium system. The argon would not alter the *partial* pressures of any of the reacting components and therefore would not cause a shift in equilibrium.

Effect of Temperature Changes

Changes in concentrations or partial pressures shift equilibria without changing the value of the equilibrium constant. In contrast, almost every equilibrium constant changes as the temperature changes. For example, consider the equilibrium established when cobalt(II) chloride ($CoCl_2$) is dissolved in hydrochloric acid, HCl(*aq*), in the endothermic reaction

$$\underset{\text{Pale pink}}{Co(H_2O)_6^{2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{Deep blue}}{CoCl_4^{2-}(aq)} + 6\,H_2O(l) \qquad \Delta H > 0 \qquad [15.25]$$

Because $Co(H_2O)_6^{2+}$ is pink and $CoCl_4^{2-}$ is blue, the position of this equilibrium is readily apparent from the color of the solution (**Figure 15.13**). When the solution is heated it turns blue, indicating that the equilibrium has shifted to form more $CoCl_4^{2-}$. Cooling the solution leads to a pink solution, indicating that the equilibrium has shifted to produce more $Co(H_2O)_6^{2+}$. We can monitor this reaction by spectroscopic methods, measuring the concentration of all species at the different temperatures. We can then calculate the equilibrium constant at each temperature. How do we explain why the equilibrium constants and therefore the position of equilibrium both depend on temperature?



▲ **Figure 15.13 Temperature and Le Châtelier's principle.** In the molecular level views, only the $CoCl_4^{2-}$ and $Co(H_2O)_6^{2+}$ ions are shown for clarity.

We can deduce the rules for the relationship between K and temperature from Le Châtelier's principle. We do this by treating heat as a chemical reagent. In an *endothermic* (heat-absorbing) reaction, we consider heat a *reactant*, and in an *exothermic* (heat-releasing) reaction, we consider heat a *product*:

Endothermic: Reactants + *heat* $\rightleftharpoons$ products

Exothermic: Reactants $\rightleftharpoons$ products + *heat*

When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the excess reactant (or product), namely heat.

In an endothermic reaction, such as Equation 15.25, heat is absorbed as reactants are converted to products. Thus, increasing the temperature causes the equilibrium to shift to the right, in the direction of making more products, and K increases. In an exothermic reaction, the opposite occurs: Heat is produced as reactants are converted to products. Thus, increasing the temperature in this case causes the equilibrium to shift to the left, in the direction of making more reactants, and K decreases.

Endothermic: Increasing T results in higher K value

Exothermic: Increasing T results in lower K value

Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts in the direction that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing K, as shown in Figure 15.13, and cooling an exothermic reaction shifts the equilibrium to the right, increasing K.

Sample Exercise 15.12

Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 58.0\ \text{kJ}$$

In which direction will the equilibrium shift when (**a**) N_2O_4 is added, (**b**) NO_2 is removed, (**c**) the pressure is increased by addition of $N_2(g)$, (**d**) the volume is increased, (**e**) the temperature is decreased?

SOLUTION

Analyze We are given a series of changes to be made to a system at equilibrium and are asked to predict what effect each change will have on the position of the equilibrium.

Plan Le Châtelier's principle can be used to determine the effects of each of these changes.

Solve

(**a**) The system will adjust to decrease the concentration of the added N_2O_4, so the equilibrium shifts to the right, in the direction of the product.

(**b**) The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2; thus, the equilibrium shifts to the right.

(**c**) Adding N_2 will increase the total pressure of the system, but N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged, and there is no shift in the position of the equilibrium.

(**d**) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.

(**e**) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more N_2O_4. Note that only this last change also affects the value of the equilibrium constant, K.

Practice Exercise

For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H^\circ = 87.9\ \text{kJ}$$

in which direction will the equilibrium shift when (**a**) $Cl_2(g)$ is removed, (**b**) the temperature is decreased, (**c**) the volume of the reaction system is increased, (**d**) $PCl_3(g)$ is added?

A CLOSER LOOK Temperature Changes and Le Châtelier's Principle

By thinking of heat as a chemical reagent, we can use Le Châtelier's principle to predict how an equilibrium mixture of reactants and products will respond to a change in temperature. For an endothermic reaction, the equilibrium constant K increases as the temperature rises and decreases as the temperature is lowered, while exothermic reactions respond in the opposite manner. The underlying reason for this behavior can be understood by taking a closer look at the relationships among the equilibrium constant, the forward and reverse reaction rates, and their activation energies.

To illustrate the underlying relationships consider an elementary reaction A $\rightleftharpoons$ B. At equilibrium, the rates of the forward and reverse reactions are equal:

$$k_f[\mathrm{A}] = k_r[\mathrm{B}] \qquad [15.26]$$

The equilibrium constant, $K = [\mathrm{B}]/[\mathrm{A}]$ can be expressed in terms of reaction rates by rearranging Equation 15.26

$$K = \frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_f}{k_r} \qquad [15.27]$$

It's instructive to consider shifts in equilibrium through the lens of Equation 15.27. If the reaction in question is an endothermic reaction, a decrease in temperature will lead to a decrease in K, thereby shifting the equilibrium to the left. Equation 15.27 tells us that in order for K to decrease, the rate constant of the forward reaction k_f must decrease by a larger amount than the rate constant of the reverse reaction k_r.

To understand why k_f decreases faster than k_r consider the relationship between reaction rate and activation energy, E_a. For the sake of illustration, consider the effect of decreasing the temperature from $T_1 = 400$ K to $T_2 = 300$ K. We can calculate the change in the forward rate constant using Equation 14.23:

$$\ln\frac{k_{f1}}{k_{f2}} = \frac{E_a(\text{forward})}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad [15.28]$$

$$\ln\frac{k_{f1}}{k_{f2}} = \frac{E_a(\text{forward})}{R}\left(\frac{1}{300\ \mathrm{K}} - \frac{1}{400\ \mathrm{K}}\right) = 1200\,\frac{E_a(\text{forward})}{R} \qquad [15.29]$$

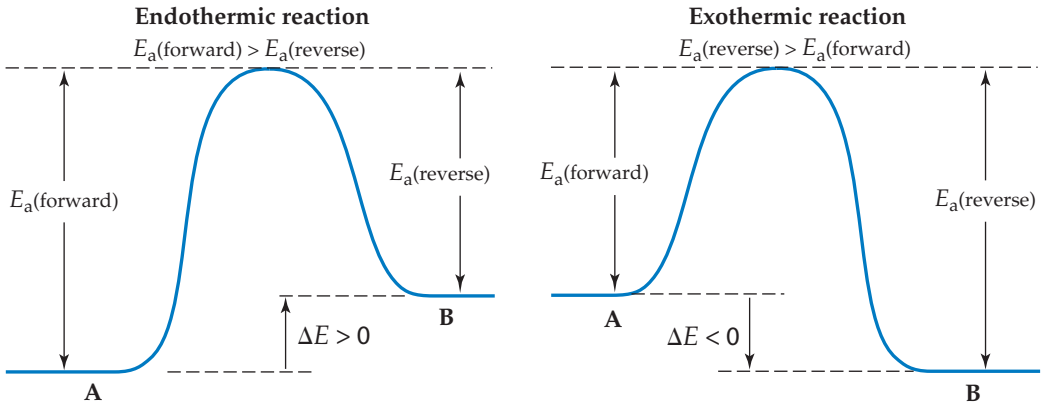
Using the same approach, we can write an equation that gives the change in the reverse rate constant:

$$\ln\frac{k_{r1}}{k_{r2}} = \frac{E_a(\text{reverse})}{R}\left(\frac{1}{300\ \mathrm{K}} - \frac{1}{400\ \mathrm{K}}\right) = 1200\,\frac{E_a(\text{reverse})}{R} \qquad [15.30]$$

These equations are identical with one exception: the activation energies for the forward and reverse reactions are not the same, as shown on the left-hand side of **Figure 15.14**. For an endothermic reaction, the activation energy in the forward direction is always larger than that of the reverse reaction, $E_a(\text{forward}) > E_a(\text{reverse})$. Consequently, the decrease in the forward rate constant (Equation 15.29) will be larger than the decrease in the reverse rate constant (Equation 15.30), and the overall value of the equilibrium constant K must decrease.

For an exothermic reaction, $E_a(\text{reverse}) > E_a(\text{forward})$ and the opposite relationships apply as shown on the right-hand side of Figure 15.14. As temperature is lowered, the reverse rate constant will decrease more rapidly than the forward rate constant and the equilibrium constant K will increase; that is, the equilibrium will shift to the right.

Related Exercises: 15.32, 15.80, 15.99, 15.104

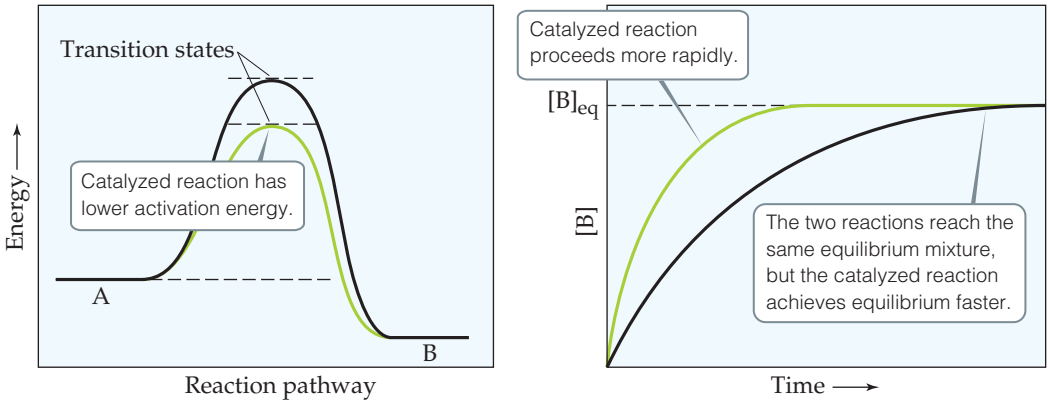


▲ **Figure 15.14** **The energy profile for an endothermic reaction (left) and an exothermic reaction (right).**

The Effect of Catalysts

What happens if we add a catalyst to a chemical system that is at equilibrium? As shown in **Figure 15.15**, a catalyst lowers the activation barrier between reactants and products. The activation energies for both the forward and reverse reactions are lowered. The catalyst thereby increases the rates of both forward and reverse reactions. Since K is the ratio of the forward and reverse rate constants for a reaction, you can predict, correctly, that the presence of a catalyst, even though it changes the reaction *rate,* does not affect the numeric value of K (Figure 15.15). As a result, *a catalyst increases the rate at which equilibrium is achieved but does not change the composition of the equilibrium mixture.*

Go Figure What quantity dictates the speed of a reaction: (**a**) the energy difference between the initial state and the transition state or (**b**) the energy difference between the initial state and the final state?



▲ **Figure 15.15 An energy profile for the reaction A ⇌ B (left), and the change in concentration of B as a function of time (right), with and without a catalyst.** Green curves show the reaction with a catalyst; black curves show the reaction without a catalyst.

TABLE 15.2 Variation in K_p with Temperature for $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

Temperature (°C)	K_p
300	4.23×10^{-7}
400	1.60×10^{-8}
450	4.39×10^{-9}
500	1.41×10^{-9}
550	5.24×10^{-10}
600	2.19×10^{-10}

The rate at which a reaction approaches equilibrium is an important practical consideration. As an example, let's again consider the synthesis of ammonia from N_2 and H_2. In designing his process, Haber had to deal with a rapid decrease in the equilibrium constant with increasing temperature, as you can see from Table 15.2. At temperatures sufficiently high to give a satisfactory reaction rate, the amount of ammonia formed was too small. The solution to this dilemma was to develop a catalyst that would produce a reasonably rapid approach to equilibrium at a sufficiently low temperature, so that the equilibrium constant remained reasonably large. The development of a suitable catalyst thus became the focus of Haber's research efforts.

After trying different substances to see which would be most effective, Carl Bosch settled on iron mixed with metal oxides, and variants of this catalyst formulation are still used today. These catalysts make it possible to obtain a reasonably rapid approach to equilibrium at around 400 to 500 °C and 20 to 60 MPa. The high pressures are needed to obtain a satisfactory equilibrium amount of NH_3. If a catalyst could be found that leads to sufficiently rapid reaction at temperatures lower than 400 °C, it would be possible to obtain the same extent of equilibrium conversion at pressures much lower than 20 to 60 MPa. This would result in great savings in both the cost of the high-pressure equipment and the energy consumed in the production of ammonia. It is estimated that the Haber process consumes approximately 1% of the energy generated in the world each year. Not surprisingly, chemists and chemical engineers are actively searching for improved catalysts for the Haber process. A breakthrough in this field would not only increase the supply of ammonia for fertilizers, it would also reduce the global consumption of fossil fuels in a significant way.

Self-Assessment Exercises

15.25 What happens to the equilibrium $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, if the volume of the system is increased?

(a) Shift to the left

(b) Shift to the left

(b) No change

15.26 Based on Le Châtelier's principle, would you predict the vapor pressure of a gas will increase or decrease as the temperature increases?

(a) Increase

(b) Decrease

15.27 If a reaction is carried out in the presence of a catalyst, will the amount of product present at equilibrium increase, decrease, or stay the same?

(a) Increase

(b) Decrease

(c) No change

Exercises

15.28 Consider the reaction

$$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g),\ \Delta H = -904.4\ kJ$$

Does each of the following increase, decrease, or leave unchanged the yield of NO at equilibrium? (**a**) increase $[NH_3]$; (**b**) increase $[H_2O]$; (**c**) decrease $[O_2]$; (**d**) decrease the volume of the container in which the reaction occurs; (**e**) add a catalyst; (**f**) increase temperature.

15.29 For a certain gas-phase reaction, the fraction of products in an equilibrium mixture is increased by either increasing the temperature or by increasing the volume of the reaction vessel. (**a**) Is the reaction exothermic or endothermic? (**b**) Does the balanced chemical equation have more molecules on the reactant side or product side?

15.30 Methanol (CH_3OH) can be made by the reaction of CO with H_2:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

(**a**) Use thermochemical data in Appendix C to calculate $\Delta H°$ for this reaction. (**b**) To maximize the equilibrium yield of methanol, would you use a high or low temperature? (**c**) To maximize the equilibrium yield of methanol, would you use a high or low pressure?

15.31 Bromine and hydrogen react in the gas phase to form hydrogen bromide: $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$. The reaction enthalpy is $\Delta H° = -6$ kJ. (**a**) To increase the equilibrium yield of hydrogen bromide would you use high or low temperature? (**b**) Could you increase the equilibrium yield of hydrogen bromide by controlling the pressure of this reaction? If so, would high or low pressure favor formation of $HBr(g)$?

15.32 (**a**) Is the dissociation of fluorine molecules into atomic fluorine, $F_2(g) \rightleftharpoons 2\,F(g)$ an exothermic or endothermic process? (**b**) If the temperature is raised by 100 K, does the equilibrium constant for this reaction increase or decrease? (**c**) If the temperature is raised by 100 K, does the forward rate constant k_f increase by a larger or smaller amount than the reverse rate constant k_r?

Answers to Self-Assessment Exercises

15.25 (a) **15.26** (a) **15.27** (c)

Sample Integrative Exercise

Putting Concepts Together

At temperatures near 800 °C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called *water gas*. (**a**) At 800 °C the equilibrium constant for this reaction is $K_p = 14.3$ What are the equilibrium partial pressures of H_2O, CO, and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00 L vessel? (**b**) What is the minimum amount of carbon required to achieve equilibrium under these conditions? (**c**) What is the total pressure in the vessel at equilibrium? (**d**) At 25 °C the value of K_p for this reaction is 1.7×10^{-23}. Is the reaction exothermic or endothermic? (**e**) To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?

SOLUTION

(**a**) To determine the equilibrium partial pressures, we use the ideal gas equation, first determining the starting partial pressure of water.

$$P_{H_2O} = \frac{n_{H_2O}RT}{V} = \frac{(0.100\ \text{mol})(8.314\ \text{L kPa/mol K})(1073\ \text{K})}{1.00\ \text{L}} = 8.92\ \text{bar}$$

We then construct a table of initial partial pressures and their changes as equilibrium is achieved:

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

Initial partial pressure (bar)		8.92	0	0
Change in partial pressure (bar)		$-x$	$+x$	$+x$
Equilibrium partial pressure (bar)		$8.92 - x$	x	x

There are no entries in the table under C(*s*) because the reactant, being a solid, does not appear in the equilibrium expression. Substituting the equilibrium partial pressures of the other species into the equilibrium expression for the reaction gives:

$$K_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \frac{(x)(x)}{(8.92 - x)} = 14.3$$

Multiplying through by the denominator gives a quadratic equation in x:

$$x^2 = (14.3)(892 - x)$$

Solving this equation for x using the quadratic formula yields $x = 6.22$ bar. Hence, the equilibrium partial pressures are $P_{CO} = x = 6.22$ bar, $P_{H_2} = x = 6.22$ bar, and $P_{H_2O} = (892 - x) = 2.70$ bar.

$$x^2 + 14.3\,x - 127.55 = 0$$

Continued

(b) Part (a) shows that $x = 6.22$ bar of H_2O must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

Thus, 0.0697 mol of H_2O and the same amount of C must react to achieve equilibrium. As a result, there must be at least 0.0697 mol of C (0.836 g C) present among the reactants at the start of the reaction.

$$n = \frac{PV}{RT} = \frac{(6.22\ \text{bar})(1.00\ \text{L})}{(0.08314\ \text{L bar/mol K})(1073\ \text{K})} = 0.0697\ \text{mol}$$

(c) The total pressure in the vessel at equilibrium is simply the sum of the equilibrium partial pressures:

$$P_{\text{total}} = P_{H_2O} + P_{CO} + P_{H_2} = 2.70\ \text{bar} + 6.22\ \text{bar} + 6.22\ \text{bar} = 15.14\ \text{bar}$$

(d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in K_p with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction:

$$\Delta H^\circ = \Delta H_f^\circ(CO(g)) + \Delta H_f^\circ(H_2(g)) - \Delta H_f^\circ(C(s, \text{graphite})) - \Delta H_f^\circ(H_2O(g)) = +131.3\ \text{kJ}$$

The positive sign for ΔH° indicates that the reaction is endothermic.

(e) According to Le Châtelier's principle, a decrease in the pressure causes a gaseous equilibrium to shift toward the side of the equation with the greater number of moles of gas. In this case, there are 2 mol of gas on the product side and only one on the reactant side. Therefore, the pressure should be decreased to maximize the yield of the CO and H_2.

CHEMISTRY PUT TO WORK Controlling Nitric Oxide Emissions

The formation of NO from N_2 and O_2,

$$\tfrac{1}{2}\,N_2(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons NO(g) \qquad \Delta H^\circ = 90.4\ \text{kJ} \qquad [15.31]$$

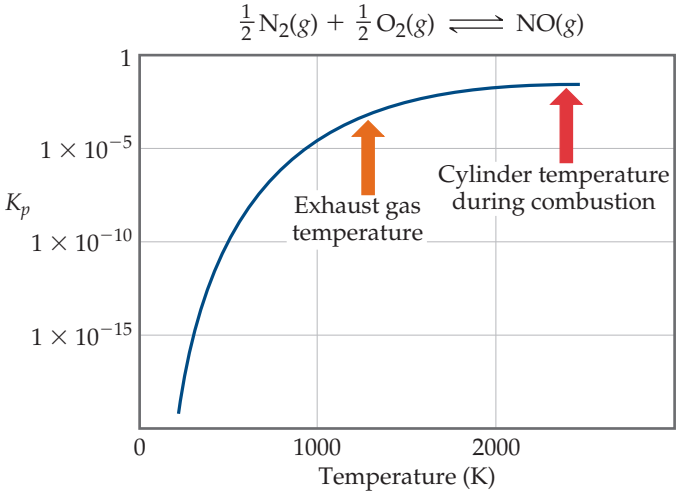
provides an interesting example of the practical importance of the fact that equilibrium constants and reaction rates change with temperature. By applying Le Châtelier's principle to this endothermic reaction and treating heat as a reactant, we deduce that an increase in temperature shifts the equilibrium in the direction of more NO. The equilibrium constant K_p for formation of 1 mol of NO from its elements at 300 K is only about 1×10^{-15} (**Figure 15.16**). At 2400 K, however, the equilibrium constant is about 0.05, which is 10^{13} times larger than the 300 K value.

Figure 15.16 helps explain why NO is a pollution problem. In the cylinder of a modern high-compression automobile engine, the temperature during the fuel-burning part of the cycle is approximately 2400 K. Also, there is a fairly large excess of air in the cylinder. These conditions favor the formation of NO. After combustion, however, the gases cool quickly. As the temperature drops, the equilibrium in Equation 15.26 shifts to the left (because the reactant heat is being removed). However, the lower temperature also means that the reaction rate decreases, so the NO formed at 2400 K is essentially "trapped" in that form as the gas cools.

The gases exhausting from the cylinder are still quite hot, perhaps 1200 K. At this temperature, as shown in Figure 15.16, the equilibrium constant for formation of NO is about 5×10^{-4}, much smaller than the value at 2400 K. However, the rate of conversion of NO to N_2 and O_2 is too slow to permit much loss of NO before the gases are cooled further.

As discussed in the "Chemistry Put to Work" box in Section 14.7, one of the goals of automotive catalytic converters is to achieve rapid conversion of NO to N_2 and O_2 at the temperature of the exhaust gas. Some catalysts developed for this reaction are reasonably effective under the grueling conditions in automotive exhaust systems. Nevertheless, scientists and engineers are continuously searching for new materials that provide even more effective catalysis of the decomposition of nitrogen oxides.

Go Figure Estimate the value of K_p at 1200 K, the exhaust gas temperature.



▲ **Figure 15.16 Equilibrium and temperature.** The equilibrium constant increases with increasing temperature because the reaction is endothermic. It is necessary to use a log scale for K_p because the values vary over such a large range.

Chapter Summary and Key Terms

THE CONCEPT OF EQUILIBRIUM (SECTION 15.1) A chemical reaction can achieve a state in which the forward and reverse processes are occurring at the same rate. This condition is called **chemical equilibrium**, and it results in the formation of an equilibrium mixture of reactants and products. The composition of an equilibrium mixture does not change with time if temperature is held constant.

THE EQUILIBRIUM CONSTANT (SECTION 15.2) An equilibrium that is used throughout this chapter is the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. This reaction is the basis of the **Haber process** for the production of ammonia. The relationship between the concentrations of the reactants and products of a system at equilibrium is given by the **law of mass action**. For an equilibrium equation of the form $a\,A + b\,B \rightleftharpoons d\,D + e\,E$, the **equilibrium expression** is written as

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

where K_c is a dimensionless constant called the **equilibrium constant**. When the equilibrium system of interest consists of gases, it is often convenient to express the concentrations of reactants and products in terms of gas pressures:

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

K_c and K_p are related by the expression $K_p = K_c(RT)^{\Delta n}$.

UNDERSTANDING AND WORKING WITH EQUILIBRIUM CONSTANTS (SECTION 15.3) The value of the equilibrium constant changes with temperature. A large value of K_c indicates that the equilibrium mixture contains more products than reactants and therefore lies toward the product side of the equation. A small value for the equilibrium constant means that the equilibrium mixture contains less products than reactants and therefore lies toward the reactant side. The equilibrium expression and the equilibrium constant of the reverse of a reaction are the reciprocals of those of the forward reaction. If a reaction is the sum of two or more reactions, its equilibrium constant will be the product of the equilibrium constants for the individual reactions.

Equilibria can be divided into two types: **homogeneous equilibria** where all of the reactants and products are in the same phase, and **heterogeneous equilibria** where more than one phase is present. Because their activities are exactly 1, the concentrations of pure solids and liquids are left out of the equilibrium expression for a heterogeneous equilibrium.

CALCULATING EQUILIBRIUM CONSTANTS (SECTION 15.4) If the concentrations of all species in an equilibrium are known, the equilibrium expression can be used to calculate the equilibrium constant. The changes in the concentrations of reactants and products on the way to achieving equilibrium are governed by the stoichiometry of the reaction.

The **reaction quotient**, Q, is found by substituting reactant and product concentrations or partial pressures at any point during a reaction into the equilibrium expression. If the system is at equilibrium, $Q = K$. If $Q \neq K$, however, the system is not at equilibrium. When $Q < K$, the reaction will move toward equilibrium by forming more products (the reaction proceeds from left to right); when $Q > K$, the reaction will move toward equilibrium by forming more reactants (the reaction proceeds from right to left). Knowing the value of K makes it possible to calculate the equilibrium amounts of reactants and products, often by the solution of an equation in which the unknown is the change in a partial pressure or concentration.

LE CHÂTELIER'S PRINCIPLE (SECTION 15.5) Le Châtelier's principle states that if a system at equilibrium is disturbed, the equilibrium will shift to minimize the disturbing influence. Therefore, if a reactant or product is added to a system at equilibrium, the equilibrium will shift to consume the added substance. The effects of removing reactants or products and of changing the pressure or volume of a reaction can be similarly deduced. For example, if the volume of the system is reduced, the equilibrium will shift in the direction that decreases the number of gas molecules. While changes in concentration or pressure lead to shifts in the equilibrium concentrations, they do not change the value of the equilibrium constant, K.

Changes in temperature affect both the equilibrium concentrations and the equilibrium constant. We can use the enthalpy change for a reaction to determine how an increase in temperature affects the equilibrium: For an endothermic reaction, an increase in temperature shifts the equilibrium to the right; for an exothermic reaction, a temperature increase shifts the equilibrium to the left. Catalysts affect the speed at which equilibrium is reached but do not affect the magnitude of K.

Learning Outcomes

After studying this chapter, you should be able to:

- Explain what is meant by chemical equilibrium and how it relates to reaction rates. (Section 15.1)
  Related Exercises: 15.2, 15.33, 15.45
- Write the equilibrium expression for any reaction. (Section 15.2) *Related Exercises: 15.5, 15.46*
- Convert K_c to K_p and vice versa. (Section 15.2)
  Related Exercises: 15.8, 15.49
- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture. (Section 15.3) *Related Exercises: 15.6, 15.47, 15.48*
- Manipulate the equilibrium constant to reflect changes in the chemical equation. (Section 15.3)
  Related Exercises: 15.14, 15.50–15.52
- Write the equilibrium expression for a heterogeneous reaction. (Section 15.4) *Related Exercises: 15.15, 15.39, 15.53*
- Calculate an equilibrium constant from concentration measurements. (Section 15.5)
  Related Exercises: 15.17, 15.54–15.56
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products. (Section 15.6)
  Related Exercises: 15.20, 15.21, 15.61, 15.62
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration. (Section 15.6)
  Related Exercises: 15.22, 15.65–15.67
- Calculate equilibrium concentrations, given the equilibrium constant and the starting concentrations. (Section 15.6)
  Related Exercises: 15.23, 15.68, 15.72, 15.74
- Use Le Châtelier's principle to predict how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position. (Section 15.7)
  Related Exercises: 15.28, 15.31, 15.76, 15.78

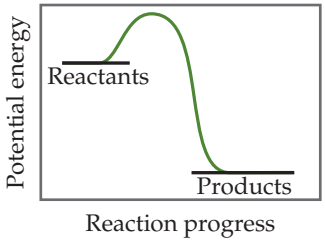
Key Equations

- $K_c = \dfrac{[D]^d[E]^e}{[A]^a[B]^b}$ [15.8] The equilibrium expression for a general reaction of the type $a\,A + b\,B \rightleftharpoons d\,D + e\,E$, the concentrations are equilibrium concentrations only
- $K_p = \dfrac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$ [15.11] The equilibrium expression in terms of equilibrium partial pressures
- $K_p = K_c(RT)^{\Delta n}$ [15.15] Relating the equilibrium constant based on pressures to the equilibrium constant based on concentrations
- $Q_c = \dfrac{[D]^d[E]^e}{[A]^a[B]^b}$ [15.24] The reaction quotient. The concentrations are for any time during a reaction. If the concentrations are equilibrium concentrations, then $Q_c = K_c$.

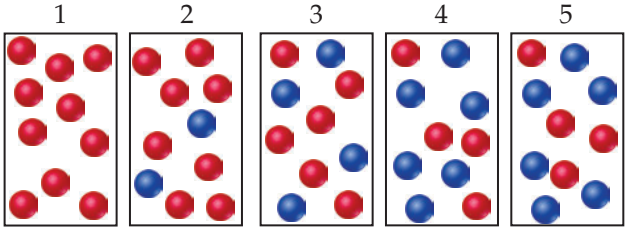
Exercises

Visualizing Concepts

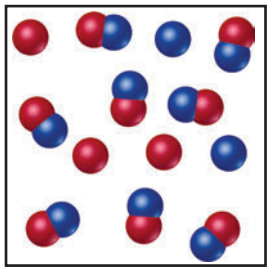
15.33 (**a**) Based on the following energy profile, predict whether $k_f > k_r$ or $k_f < k_r$. (**b**) Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



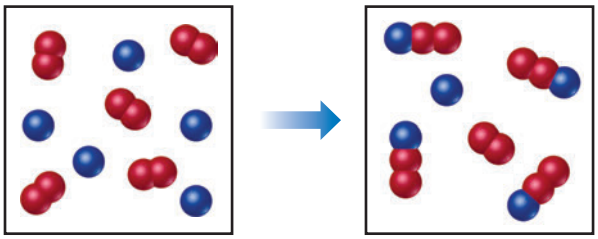
15.34 The following diagrams represent a hypothetical reaction A ⟶ B, with A represented by red spheres and B represented by blue spheres. The sequence from left to right represents the system as time passes. Does the system reach equilibrium? If so, in which diagram(s) is the system in equilibrium? [Sections 15.1 and 15.2]



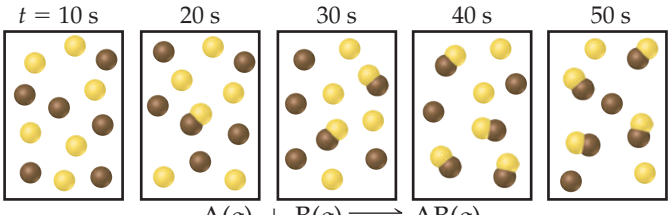
15.35 The following diagram represents an equilibrium mixture produced for a reaction of the type A + X ⇌ AX. Is K greater or smaller than 1 if the volume is 1 L and each atom/molecule in the diagram represents 1 mol? [Section 15.2]



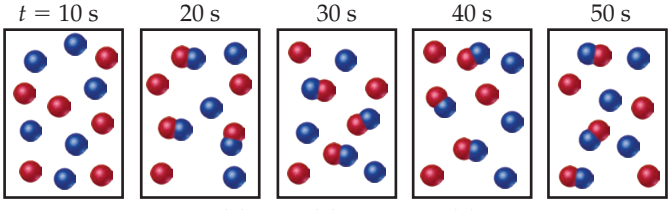
15.36 The following diagram represents a reaction shown going to completion. Each molecule in the diagram represents 0.1 mol, and the volume of the box is 1.0 L. (**a**) Letting A = red spheres and B = blue spheres, write a balanced equation for the reaction. (**b**) Write the equilibrium-constant expression for the reaction. (**c**) Calculate the value of K_c. (**d**) Assuming that all of the molecules are in the gas phase, calculate Δn, the change in the number of gas molecules that accompanies the reaction. (**e**) Calculate the value of K_p. [Section 15.2]



15.37 Snapshots of two hypothetical reactions, A(*g*)+ B(*g*) ⇌ AB(*g*) and X(*g*) + Y(*g*) ⇌ XY(*g*) at five different times are shown here. Which reaction has a larger equilibrium constant? [Sections 15.1 and 15.2]



A(*g*) + B(*g*) ⇌ AB(*g*)

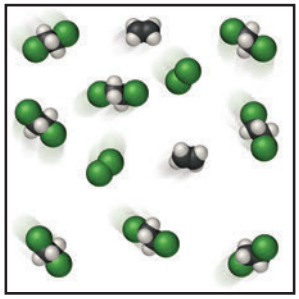


X(*g*) + Y(*g*) ⇌ XY(*g*)

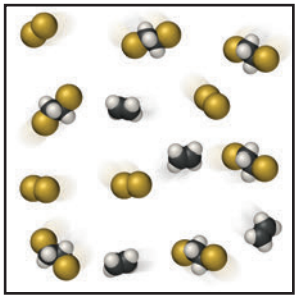
15.38 Ethene (C_2H_4) reacts with halogens (X_2) by the following reaction:

$$C_2H_4(g) + X_2(g) \rightleftharpoons C_2H_4X_2(g)$$

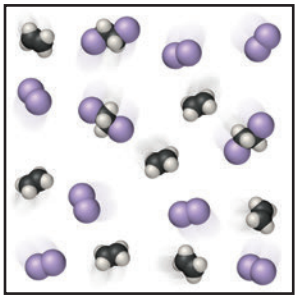
The following figures represent the concentrations at equilibrium at the same temperature when X_2 is Cl_2 (green), Br_2 (brown), and I_2 (purple). List the equilibria from smallest to largest equilibrium constant. [Section 15.3]



(a)

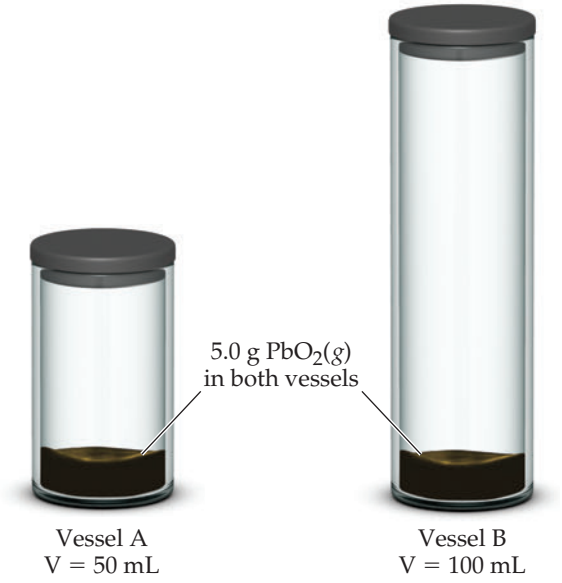


(b)

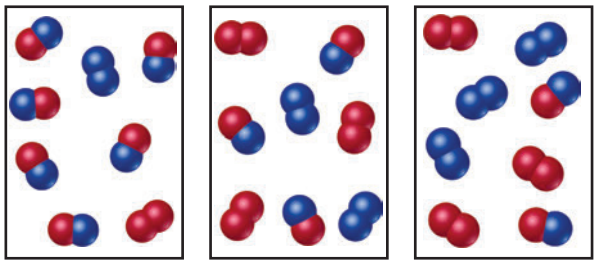


(c)

15.39 When lead(IV) oxide is heated above 300 °C, it decomposes according to the following reaction $PbO_2(s) \rightleftharpoons PbO(s) + O_2(g)$. Consider the two sealed vessels of PbO_2 shown here. If both vessels are heated to 400 °C and allowed to come to equilibrium, which of the following statements is true? (**a**) There will be less PbO_2 remaining in vessel A, (**b**) There will be less PbO_2 remaining in vessel B, (**c**) The amount of PbO_2 remaining in each vessel will be the same. [Section 15.3]

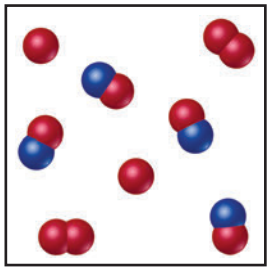


15.40 The reaction $A_2 + B_2 \rightleftharpoons 2\,AB$ has an equilibrium constant $K_c = 1.5$. The following diagrams represent reaction mixtures containing A_2 molecules (red), B_2 molecules (blue), and AB molecules. (**a**) Which reaction mixture is at equilibrium? (**b**) For those mixtures that are not at equilibrium, how will the reaction proceed to reach equilibrium? [Sections 15.4]

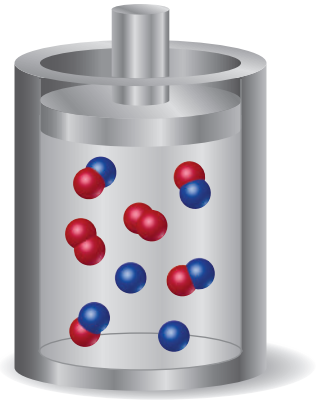


(i) (ii) (iii)

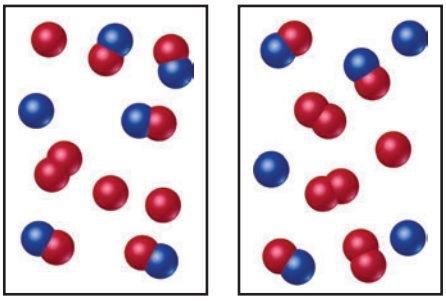
15.41 The reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$ has an equilibrium constant of $K_p = 2$. The accompanying diagram shows a mixture containing A atoms (red), A_2 molecules, and AB molecules (red and blue). How many B atoms should be added to the diagram to illustrate an equilibrium mixture? [Section 15.4]



15.42 The diagram shown here represents the equilibrium state for the reaction $A_2(g) + 2\,B(g) \rightleftharpoons 2\,AB(g)$. (**a**) Assuming the volume is 2 L, calculate the equilibrium constant K_c for the reaction. (**b**) If the volume of the equilibrium mixture is decreased, will the number of AB molecules increase or decrease? [Sections 15.4 and 15.5]

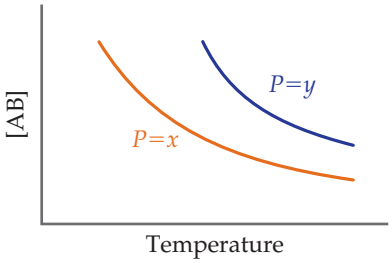


15.43 The following diagrams represent equilibrium mixtures for the reaction $A_2 + B \rightleftharpoons A + AB$ at 300 K and 500 K. The A atoms are red, and the B atoms are blue. Is the reaction exothermic or endothermic? [Section 15.5]



300 K 500 K

15.44 The following graph represents the yield of the compound AB at equilibrium in the reaction $A(g) + B(g) \longrightarrow AB(g)$ at two different pressures, *x* and *y*, as a function of temperature.



(**a**) Is this reaction exothermic or endothermic? (**b**) Is $P = x$ greater or smaller than $P = y$? [Section 15.5]

Equilibrium; The Equilibrium Constant (Sections 15.1–15.3)

15.45 Assume that the equilibrium constant for the dissociation of molecular bromine, $Br_2(g) \rightleftharpoons 2\,Br(g)$, at 800 K is $K_c = 5.4 \times 10^{-3}$.(**a**) Which species predominates at equilibrium, Br_2 or Br, assuming that the concentration of Br_2 is larger than 5.4×10^{-3} mol/L? (**b**)Assuming both forward and reverse reactions are elementary processes, which reaction has the larger numeric value of the rate constant, the forward or the reverse reaction?

15.46 Write the expression for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

(**a**) $I_2(g) \rightleftharpoons 2I(g)$

(**b**) $2SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$

(**c**) $CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$

(**d**) $H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$

(**e**) $CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$

(**f**) $Fe^{2+}(aq) + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Fe(s)$

(**g**) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

15.47 When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

(**a**) $H_2O(g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 900 K $K_c = 2.24$

(**b**) $2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$ at 1300 K $K_p = 5.27 \times 10^{-5}$

15.48 Which of the following statements are true and which are false? (**a**) The equilibrium constant can never be a negative number. (**b**) In reactions that we draw with a single-headed arrow, the equilibrium constant has a value that is very close to zero. (**c**) As the value of the equilibrium constant increases, the speed at which a reaction reaches equilibrium increases.

15.49 If $K_c = 0.013$ L/mol for $2\,NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$ at 1000 K, what is the value of K_p for this reaction at this temperature?

15.50 The equilibrium constant for the reaction

$$2\,NO(g) + Br_2(g) \rightleftharpoons 2\,NOBr(g)$$

is $K_c = 1.3 \times 10^{-2}$ at 1000 K. (**a**) At this temperature does the equilibrium favor NO and Br_2, or does it favor NOBr? (**b**) Calculate K_c for $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$. (**c**) Calculate K_c for $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2}\,Br_2(g)$.

15.51 At 1000 K, $K_p = 0.184$ for the reaction

$$SO_2(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons SO_3(g)$$

(**a**) What is the value of K_p for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}\,O_2(g)$? (**b**) What is the value of K_p for the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$? (**c**) What is the value of K_c for the reaction in part (b)?

15.52 The following equilibria were attained at 298 K:

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s) \quad K_c = 5.6 \times 10^9$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

$$K_c = 1.6 \times 10^7$$

Based on these equilibria, calculate the equilibrium constant for $AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2(aq) + Cl^-(aq)$ at 298 K.

15.53 Mercury(I) oxide decomposes into elemental mercury and elemental oxygen: $2\,Hg_2O(s) \rightleftharpoons 4\,Hg(l) + O_2(g)$. (**a**) Write the equilibrium expression for this reaction in terms of partial pressures. (**b**) Suppose you run this reaction in a solvent that dissolves elemental mercury and elemental oxygen. Rewrite the equilibrium-constant expression in terms of molarities for the reaction, using (solv) to indicate solvation.

Calculating Equilibrium Constants (Section 15.4)

15.54 Gaseous hydrogen iodide is placed in a closed container at 450 °C, where it partially decomposes to hydrogen and iodine: $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$. At equilibrium it is found that $[HI] = 4.50 \times 10^{-3}\,M$, $[H_2] = 5.75 \times 10^{-4}\,M$, and $[I_2] = 5.75 \times 10^{-4}\,M$. What is the value of K_c at this temperature?

15.55 The equilibrium $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$ is established at 550 K. An equilibrium mixture of the three gases has partial pressures of 10.13 kPa, 20.27 kPa, and 35.46 kPa for NO, Cl_2, and NOCl, respectively.(**a**) Calculate K_p for this reaction at 500.0 K. (**b**) If the vessel has a volume of 5.00 L, calculate K_c at this temperature.

15.56 Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$. A 7.5 L gas vessel is charged with a mixture of $PCl_3(g)$ and $Cl_2(g)$, which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are $P_{PCl_3} = 12.56$ kPa, $P_{Cl_2} = 15.91$ kPa, and $P_{PCl_5} = 131.7$ kPa. (**a**) What is the value of K_p at this temperature? (**b**) Does the equilibrium favor reactants or products? (**c**) Calculate K_c for this reaction at 450 K.

15.57 A mixture of 1.374 g of H_2 and 70.31 g of Br_2 is heated in a 2.00 L vessel at 700 K. These substances react according to

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$

At equilibrium, the vessel is found to contain 0.566 g of H_2. (**a**) Calculate the equilibrium concentrations of H_2, Br_2, and HBr. (**b**) Calculate K_c.

15.58 A mixture of 0.886 mol of CO_2, 0.443 mol of H_2, and 0.713 mol of H_2O is placed in a 10.00 L vessel. The following equilibrium is established at 550 K:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

(**a**) Calculate the initial partial pressures of CO_2, H_2, and H_2O. (**b**) At equilibrium $P_{H_2} = 182$ kPa, calculate the equilibrium partial pressures of CO_2, CO, and H_2O. (**c**) Calculate K_p for the reaction. (**d**) Calculate K_c for the reaction.

15.59 A flask is charged with 152.0 kPa of $N_2O_4(g)$ and 101.3 kPa $NO_2(g)$ at 25 °C, and the following equilibrium is achieved:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

After equilibrium is reached, the partial pressure of NO_2 is 51.9 kPa. (**a**) What is the equilibrium partial pressure of N_2O_4? (**b**) Calculate the value of K_p for the reaction. (**c**) Calculate K_c for the reaction.

15.60 Two different proteins X and Y are dissolved in aqueous solution at 37 °C. The proteins bind in a 1:1 ratio to form XY. A solution that is initially 1.00 m*M* in each protein is allowed to reach equilibrium. At equilibrium, 0.20 m*M* of free X and 0.20 m*M* of free Y remain. What is K_c for the reaction?

15.61 (**a**) What is the value of Q_c at the end of a certain reaction, when only products are present? (**b**) How will the value of Q_c change as a forward reaction proceeds? (**b**) What condition must be satisfied so that $Q_c = K_c$?

15.62 At 100 °C, the equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures of $COCl_2$, CO, and Cl_2 at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

(**a**) $[COCl_2] = [CO] = 1.00 \times 10^{-4}\,M$, $[Cl_2] = 7.2 \times 10^{-6}\,M$

(**b**) $[COCl_2] = 2.20 \times 10^{-2}\,M$, $[CO] = 2.2 \times 10^{-7}\,M$, $[Cl_2] = 3.0 \times 10^{-6}\,M$

(**c**) $[COCl_2] = 0.0100\,M$, $[CO] = [Cl_2] = 7.2 \times 10^{-6}\,M$

15.63 At 120 °C, $K_c = 0.090$ for the reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

In an equilibrium mixture of the three gases, the concentrations of SO_2, Cl_2, and SO_2 are 0.100 *M* and 0.075 *M*, respectively. What is the partial pressure of Cl_2 in the equilibrium mixture?

15.64 At 850 K, the following reaction has $K_p = 0.0035$:

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

In an equilibrium mixture the partial pressures of SO_2 and O_2 are 18.24 kPa and 50.66 kPa, respectively. What is the equilibrium partial pressure of SO_3 in the mixture?

15.65 At 1285 °C, the equilibrium constant for the reaction $Br_2(g) \rightleftharpoons 2\,Br(g)$ is $K_c = 1.04 \times 10^{-3}$. A 1.00 L vessel containing an equilibrium mixture of the gases has 1.50 g $Br_2(g)$ in it. What is the mass of $Br(g)$ in the vessel?

15.66 For the reaction, at $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$ at 700 K. In a 10.0 L flask containing an equilibrium mixture of the three gases, there are 1.30 g H_2 and 21.0 g I_2. What is the mass of HI in the flask?

15.67 At 800 K, the equilibrium constant for $I_2(g) \rightleftharpoons 2\,I(g)$ is $K_c = 3.1 \times 10^{-5}$. If an equilibrium mixture in a 5.00 L vessel contains 30.5 mg of $I(g)$, how many grams of I_2 are in the mixture?

15.68 At 2000 °C, the equilibrium constant for the reaction $2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$ is $K_c = 2.4 \times 10^3$. If the initial concentration of NO is 0.250 *M*, what are the equilibrium concentrations of NO, N_2, and O_2?

15.69 At 900 °C, $K_p = 51.2$ for the equilibrium

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

If the pressure of $NO(g)$ is half the pressure of $NOBr(g)$, what is the equilibrium pressure of $Br_2(g)$?

15.70 At 218 °C, $K_c = 1.2 \times 10^{-4}$ for the equilibrium

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Calculate the equilibrium concentrations of NH_3 and H_2S if a sample of solid NH_4SH is placed in a closed vessel at 218 °C and decomposes until equilibrium is reached.

15.71 Consider the reaction

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

At 25 °C, the equilibrium constant is $K_c = 2.4 \times 10^{-5}$ for this reaction. (**a**) If excess $CaSO_4(s)$ is mixed with water at 25 °C to produce a saturated solution of $CaSO_4$, what are the equilibrium concentrations of Ca^{2+} and SO_4^{2-}? (**b**) If the resulting solution has a volume of 1.4 L, what is the minimum mass of $CaSO_4(s)$ needed to achieve equilibrium?

15.72 For the reaction $I_2(g) + Br_2(g) \rightleftharpoons 2\,IBr(g)$, $K_c = 310$ at 140 °C. Suppose that 1.00 mol IBr in a 5.00 L flask is allowed to reach equilibrium at 140 °C. What are the equilibrium concentrations of IBr, I_2, and Br_2?

15.73 At 25 °C, the reaction

$$CaCrO_4(s) \rightleftharpoons Ca^{2+}(aq) + CrO_4^{2-}(aq)$$

has an equilibrium constant $K_c = 7.1 \times 10^{-4}$. What are the equilibrium concentrations of Ca^{2+} and CrO_4^{2-} in a saturated solution of $CaCrO_4$?

15.74 Methane, CH_4, reacts with I_2 according to the reaction $CH_4(g) + I_2(g) \rightleftharpoons CH_3I(g) + HI(g)$. At 600 K, K_p for this reaction is 1.95×10^{-4}. A reaction was set up at 600 K with initial partial pressures of methane of 13.3 kPa and of 6.67 kPa for I_2. Calculate the pressures, in kPa, of all reactants and products at equilibrium.

15.75 The reaction of an organic acid with an alcohol, in organic solvent, to produce an ester and water is commonly done in the pharmaceutical industry. This reaction is catalyzed by strong acid (usually H_2SO_4). A simple example is the reaction of acetic acid with ethyl alcohol to produce ethyl acetate and water:

$$CH_3COOH(solv) + CH_3CH_2OH(solv) \rightleftharpoons CH_3COOCH_2CH_3(solv) + H_2O(solv)$$

where "(*solv*)" indicates that all reactants and products are in solution but not an aqueous solution. The equilibrium constant for this reaction at 55 °C is 6.68. A pharmaceutical chemist makes up 15.0 L of a solution that is initially 0.275 *M* in acetic acid and 3.85 *M* in ethanol. At equilibrium, how many grams of ethyl acetate are formed?

Le Châtelier's Principle (Section 15.5)

15.76 Consider the following exothermic equilibrium (Boudouard reaction)

$$2\,CO(g) \rightleftharpoons C(s) + CO_2(g)$$

How will each of the following changes affect an equilibrium mixture of the three gases: (**a**) a catalyst is added to the mixture; (**b**) $CO_2(g)$ is added to the system; (**c**) $CO(g)$is added from the system; (**d**) the reaction mixture is heated; (**e**) the volume of the reaction vessel is doubled; (**f**) the total pressure of the system is increased by adding a noble gas?

15.77 How do the following changes affect the value of the K_P for a gas-phase endothermic reaction: (**a**) increase in the total pressure by adding a noble gas, (**b**) addition of a reactant, (**c**) increase in the temperature (**d**) increase in the volume, (**e**) decrease in the temperature?

15.78 Consider the following equilibrium between oxides of nitrogen

$$3\,NO(g) \rightleftharpoons NO_2(g) + N_2O(g)$$

(**a**) Use data in Appendix C to calculate $\Delta H°$ for this reaction. (**b**) Will the equilibrium constant for the reaction increase or decrease with increasing temperature? (**c**) At constant temperature, would a change in the volume of the container affect the fraction of products in the equilibrium mixture?

15.79 Ozone, O_3, decomposes to molecular oxygen in the stratosphere according to the reaction $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Would an increase in pressure favor the formation of ozone or of oxygen?

15.80 True or false: When the temperature of an exothermic reaction increases, the rate constant of the forward reaction decreases, which leads to a decrease in the equilibrium constant, K_c.

Additional Exercises

15.81 Both the forward reaction and the reverse reaction in the following equilibrium are believed to be elementary steps:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl(g) + Cl(g)$$

At 25 °C, the rate constants for the forward and reverse reactions are $1.4 \times 10^{-28}\,M^{-1}\,s^{-1}$ and $9.3 \times 10^{10}\,M^{-1}\,s^{-1}$, respectively. (**a**) What is the value for the equilibrium constant at 25 °C? (**b**) Are reactants or products more plentiful at equilibrium?

15.82 If $K_c = 1$ for the equilibrium $3A(g) \rightleftharpoons 2B(g)$, what is the relationship between [A] and [B] at equilibrium?

15.83 A mixture of CH_4 and H_2O is passed over a nickel catalyst at 1000 K. The emerging gas is collected in a 5.00 L flask and is found to contain 8.62 g of CO, 2.60 g of H_2, 43.0 g of CH_4, and 48.4 g of H_2O. Assuming that equilibrium has been reached, calculate K_c and K_p for the reaction $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$.

15.84 When 2.00 mol of SO_2Cl_2 is placed in a 5.00 L flask at 310 K, 40% of the SO_2Cl_2 decomposes to SO_2 and Cl_2:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

(**a**) Calculate K_c for this reaction at this temperature. (**b**) Calculate K_P for this reaction at 310 K. (**c**) According to Le Châtelier's principle, would the percent of SO_2Cl_2 that decomposes increase, decrease or stay the same if the mixture was transferred to a 1.00 L vessel? (**d**) Use the equilibrium constant you calculated to determine the percentage of SO_2Cl_2 that decomposes when 2.00 mol of SO_2Cl_2 is placed in a 1.00 L vessel at 310 K.

15.85 The value of the equilibrium constant K_c for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ changes in the following manner as a function of temperature

Temperature (°C)	K_c
300	9.6
400	0.50
500	0.058

(**a**) Based on the changes in K_c is this reaction exothermic or endothermic? (**b**) Use the standard enthalpies of formation given in Appendix C to determine the ΔH for this reaction at standard conditions. Does this value agree with your prediction from part (a)? (**c**) If 0.025 mole of gaseous NH_3 is added to a 1.00 L container and heated to 500 °C, what is the concentration of NH_3 once the sample reaches equilibrium?

15.86 A sample of nitrosyl bromide (NOBr) decomposes according to the equation

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

An equilibrium mixture in a 5.00 L vessel at 100 °C contains 3.22 g of NOBr, 3.08 g of NO, and 4.19 g of Br_2. (**a**) Calculate K_c. (**b**) What is the total pressure exerted by the mixture of gases? (**c**) What was the mass of the original sample of NOBr?

15.87 Consider the hypothetical reaction

$$A(g) \rightleftharpoons B(g) + 2\,C(g)$$

A flask is charged with 100 kPa of pure A, after which it is allowed to reach equilibrium at 25 °C. At equilibrium, the partial pressure of B is 25 kPa. (**a**) What is the total pressure in the flask at equilibrium? (**b**) What is the value of K_p? (**c**) What could we do to maximize the yield of B?

15.88 Solid NH_4SH is introduced into an evacuated flask at 24 °C. The following reaction takes place:

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

At equilibrium, the total pressure (for NH_3 and H_2S taken together) is 0.62 bar. What is K_p for this equilibrium at 24 °C?

15.89 At 900 °C, $K_c = 0.0108$ for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

A mixture of $CaCO_3$, CaO, and CO_2 is placed in a 10.0 L vessel at 900 °C. For the following mixtures, will the amount of $CaCO_3$ increase, decrease, or remain the same as the system approaches equilibrium?

(**a**) 15.0 g $CaCO_3$, 15.0 g CaO, and 4.25 g CO_2

(**b**) 2.50 g $CaCO_3$, 25.0 g CaO, and 5.66 g CO_2

(**a**) 30.5 g $CaCO_3$, 25.5 g CaO, and 6.48 g CO_2

15.90 When 1.50 mol CO_2 and 1.50 mol H_2 are placed in a 3.00 L container at 395 °C, the following reaction occurs: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. If $K_c = 0.802$, what are the concentrations of each substance in the equilibrium mixture?

15.91 The equilibrium constant K_c for $C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K. (**a**) If excess C is allowed to react with 25.0 g of CO_2 in a 3.00 L vessel at 1000 K, how many grams of CO are produced? (**b**) How many grams of C are consumed? (**c**) If a smaller vessel is used for the reaction, will the yield of CO be greater or smaller? (**d**) Is the reaction endothermic or exothermic?

15.92 NiO is to be reduced to nickel metal in an industrial process by use of the reaction

$$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$$

At 1600 K, the equilibrium constant for the reaction is $K_p = 6.0 \times 10^2$. If a CO pressure of 0.20 bar is to be employed in the furnace and total pressure never exceeds 1.0 bar, will reduction occur?

15.93 Le Châtelier noted that many industrial processes of his time could be improved by an understanding of chemical equilibria. For example, the reaction of iron oxide with carbon monoxide was used to produce elemental iron and CO_2 according to the reaction

$$Fe_2O_3(s) + 3\,CO(g) \rightleftharpoons 2\,Fe(s) + 3\,CO_2(g)$$

Even in Le Châtelier's time, it was noted that a great deal of CO was wasted, expelled through the chimneys over the furnaces. Le Châtelier wrote, "Because this incomplete reaction was thought to be due to an insufficiently prolonged contact between carbon monoxide and the iron ore [oxide], the dimensions of the furnaces have been increased. In England, they have been made as high as 30 m. But the proportion of carbon monoxide escaping has not diminished, thus demonstrating, by an experiment costing several hundred thousand francs, that the reduction of iron oxide by carbon monoxide is a limited reaction. Acquaintance with the laws of chemical equilibrium would have permitted the same conclusion to be reached more rapidly and far more economically." What does this anecdote tell us about the equilibrium constant for this reaction?

15.94 At 700 K, the equilibrium constant for the reaction

$$CCl_4(g) \rightleftharpoons C(s) + 2\,Cl_2(g)$$

is $K_p = 77$. A flask is charged with 202.7 kPa of CCl_4, which then reaches equilibrium at 700 K. (**a**) What fraction of the CCl_4 is converted into C and Cl_2? (**b**) What are the partial pressures of CCl_4 and Cl_2 at equilibrium?

15.95 The reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ has $K_p = 8.59 \times 10^{-4}$ at 300 °C. A flask is charged with 50.7 kPa PCl_3, 50.7 kPa Cl_2, and 20.3 kPa PCl_5 at this temperature. (**a**) Use the reaction quotient to determine the direction the reaction must proceed to reach equilibrium. (**b**) Calculate the equilibrium partial pressures of the gases. (**c**) What effect will increasing the volume of the system have on the mole fraction of Cl_2 in the equilibrium mixture? (**d**) The reaction is exothermic. What effect will increasing the temperature of the system have on the mole fraction of Cl_2 in the equilibrium mixture?

15.96 An equilibrium mixture of H_2, I_2 at HI at 500 °C contains 0.150 mol H_2, 0.150 mol I_2 and 1.000 mol HI in a 10.00 L vessel. What are the equilibrium partial pressures when equilibrium is reestablished following the addition of 0.100 mol of HI?

15.97 Consider the hypothetical reaction $A(g) + 2\,B(g) \rightleftharpoons 2\,C(g)$, for which $K_c = 0.25$ at a certain temperature. A 1.00 L reaction vessel is loaded with 1.00 mol of compound C, which is allowed to reach equilibrium. Let the variable x represent the number of mol/L of compound A present at equilibrium. (**a**) In terms of x, what are the equilibrium concentrations of compounds B and C? (**b**) What limits must be placed on the value of x so that all concentrations are positive? (**c**) By putting the equilibrium concentrations (in terms of x) into the equilibrium-constant expression, derive an equation that can be solved for x. (**d**) The equation from part (c) is a cubic equation (one that has the form $ax^3 + bx^2 + cx + d = 0$). In general, cubic equations cannot be solved in closed form. However, you can estimate the solution by plotting the cubic equation in the allowed range of x that you specified in part (b). The point at which the cubic equation crosses the x-axis is the solution. (**e**) From the plot in part (d), estimate the equilibrium concentrations of A, B, and C. (*Hint:* You can check the accuracy of your answer by substituting these concentrations into the equilibrium expression.)

15.98 At 1200 K, the approximate temperature of automobile exhaust gases (Figure 15.14), K_p for the reaction

$$2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)$$

is about 1×10^{-11}. Assuming that the exhaust gas (total pressure 1 atm) contains 0.2% CO, 12% CO_2, and 3% O_2 by volume, is the system at equilibrium with respect to the CO_2 reaction? Based on your conclusion, would the CO concentration in the exhaust be decreased or increased by a catalyst that speeds up the CO_2 reaction? Recall that at a fixed pressure and temperature, volume% = mol%.

15.99 At a temperature of 700 K, the forward and reverse rate constants for the reaction $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$ are $k_f = 1.8 \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_r = 0.063\ M^{-1}\ s^{-1}$. (**a**) What is the value of the equilibrium constant K_c at 700 K? (**b**) Is the forward reaction endothermic or exothermic if the rate constants for the same reaction have values of $k_f = 0.097\ M^{-1}\ s^{-1}$ and $k_r = 2.6\ M^{-1}\ s^{-1}$ at 800 K?

Integrative Exercises

15.100 Consider the reaction $IO_4^-(aq) + 2\,H_2O(l) \rightleftharpoons H_4IO_6^-(aq)$; $K_c = 3.5 \times 10^{-2}$. If you start with 25.0 mL of a 0.905 M solution of $NaIO_4$, and then dilute it with water to 500.0 mL, what is the concentration of $H_4IO_6^-$ at equilibrium?

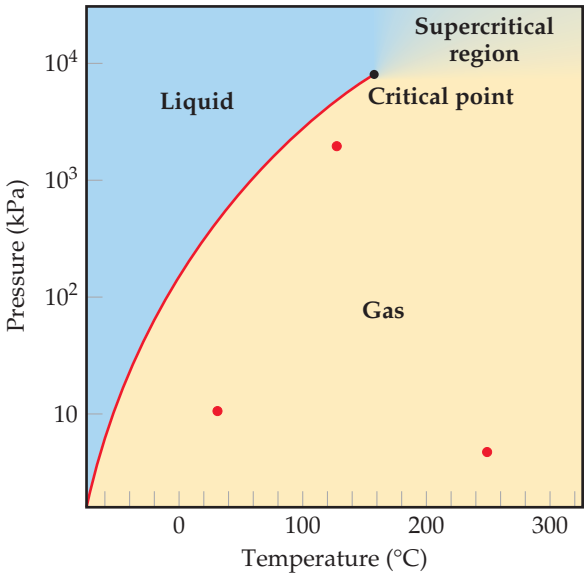
15.101 The following equilibria were measured at 823 K:

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g) \quad K_c = 67$$
$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad K_c = 0.14$$

(**a**) Use these equilibria to calculate the equilibrium constant, K_c, for the reaction $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$ at 823 K. (**b**) Based on your answer to part (a), would you say that carbon monoxide is a stronger or weaker reducing agent than H_2 at $T = 823$ K? (**c**) If you were to place 5.00 g of $CoO(s)$ in a sealed tube with a volume of 250 mL that contains $CO(g)$ at a pressure of 1 atm and a temperature of 298 K, what is the concentration of the CO gas? Assume there is no reaction at this temperature and that the CO behaves as an ideal gas (you can neglect the volume of the solid). (**d**) If the reaction vessel from part (c) is heated to 823 K and allowed to come to equilibrium, how much $CoO(s)$ remains?

15.102 Consider the equilibrium $A \rightleftharpoons B$ in which both the forward and reverse reactions are elementary (single-step) reactions. Assume that the only effect of a catalyst on the reaction is to lower the activation energies of the forward and reverse reactions, as shown in Figure 15.14. Using the Arrhenius equation (Section 14.5), prove that the equilibrium constant is the same for the catalyzed reaction as for the uncatalyzed one.

15.103 The phase diagram for SO_2 is shown here. (**a**) What does this diagram tell you about the enthalpy change in the reaction $SO_2(l) \longrightarrow SO_2(g)$? (**b**) Calculate the equilibrium constant for this reaction at 100 °C and at 0 °C. (**c**) Why is it not possible to calculate an equilibrium constant between the gas and liquid phases in the supercritical region? (**d**) At which of the three points marked in red does $SO_2(g)$ most closely approach ideal gas behavior? (**e**) At which of the three red points does $SO_2(g)$ behave least ideally?



15.104 At 800 K, the equilibrium constant for the reaction $A_2(g) \rightleftharpoons 2\,A(g)$ is $K_c = 3.1 \times 10^{-4}$. (**a**) Assuming both forward and reverse reactions are elementary reactions, which rate constant do you expect to be larger, k_f or k_r? (**b**) If the value of $k_f = 0.27\ s^{-1}$, what is the value of k_r at 800 K? (**c**) Based on the nature of the reaction, do you expect the forward reaction to be endothermic or exothermic? (**d**) If the temperature is raised to 1000 K, will the reverse rate constant k_r increase or decrease? Will the change in k_r be larger or smaller than the change in k_f?

15.105 In Section 11.5, we defined the vapor pressure of a liquid in terms of an equilibrium. (**a**) Write the equation representing the equilibrium between liquid water and water vapor and the corresponding expression for K_p. (**b**) By using data in Appendix B, give the value of K_p for this reaction at 30 °C. (**c**) What is the value of K_p for any liquid in equilibrium with its vapor at the normal boiling point of the liquid?

15.106 Water molecules in the atmosphere can form hydrogen-bonded dimers, $(H_2O)_2$. The presence of these dimers is thought to be important in the nucleation of ice crystals in the atmosphere and in the formation of acid rain. (**a**) Using VSEPR theory, draw the structure of a water dimer, using dashed lines to indicate intermolecular interactions. (**b**) What kind of intermolecular forces are involved in water dimer formation? (**c**) The K_p for water dimer formation in the gas phase is 0.050 at 300 K and 0.020 at 350 K. Is water dimer formation endothermic or exothermic?

15.107 The protein hemoglobin (Hb) transports O_2 in mammalian blood. Each Hb can bind 4 O_2 molecules. The equilibrium constant for the O_2 binding reaction is higher in fetal hemoglobin than in adult hemoglobin. In discussing protein oxygen-binding capacity, biochemists use a measure called the *P50 value*, defined as the partial pressure of oxygen at which 50% of the protein is saturated. Fetal hemoglobin has a P50 value of 2.53 kPa, and adult hemoglobin has a P50 value of 3.57 kPa. Use these data to estimate how much larger K_c is for the aqueous reaction $4\,O_2(g) + Hb(aq) \rightleftharpoons [Hb(O_2)_4(aq)]$ in a fetus, compared to K_c for the same reaction in an adult.

Design an Experiment

The reaction between hydrogen and iodine to form hydrogen iodide was used to illustrate Beer's law in Chapter 14 (Figure 14.5). The reaction can be monitored using visible-light spectroscopy because I_2 has a violet color while H_2 and HI are colorless. At 300 K, the equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ is $K_c = 794$. To answer the following questions assume you have access to hydrogen, iodine, hydrogen iodide, a transparent reaction vessel, a visible-light spectrometer, and a means for changing the temperature. (**a**) Which gas or gases concentration could you readily monitor with the spectrometer? (**b**) To use Beer's law (Equation 14.5), you need to determine the extinction coefficient, ε, for the substance in question. How would you determine ε? (**c**) Describe an experiment for determining the equilibrium constant at 600 K. (**d**) Use the bond enthalpies in Table 8.3 to estimate the enthalpy of this reaction. (**e**) Based on your answer to part (d), would you expect K_c at 600 K to be larger or smaller than at 300 K?

16

ACID–BASE EQUILIBRIA

WHAT'S AHEAD

16.1 ▶ Acid–Base Equilibria

16.2 ▶ The Autoionization of Water

16.3 ▶ The pH Scale

16.4 ▶ Strong Acids and Bases

16.5 ▶ Weak Acids

16.6 ▶ Weak Bases

16.7 ▶ Acid–Base Properties of Salt Solutions

16.8 ▶ Acid–Base Behavior and Chemical Structure

16.1 | Acid–Base Equilibria



Acids and bases are common both in nature and in the laboratory. From the earliest days of experimental chemistry, scientists have recognized acids and bases by their characteristic properties. Acids have a sour taste and cause certain dyes to change color, whereas bases have a bitter taste and feel slippery (soap is a good example). Use of the term *base* comes from the old English meaning of the word, "to bring low." (We still use the word *debase* in this sense, meaning to lower the value of something.) When a base is added to an acid, the base "lowers" the amount of acid. Indeed, when acids and bases are mixed in the right proportions, their characteristic properties seem to disappear altogether.

We first encountered acids and bases in Sections 2.8 and 4.3, in which we discussed the naming of acids and some simple acid–base reactions, respectively. In the sections ahead, we take a closer look at how acids and bases are identified and characterized. In doing so, we consider their behavior both in terms of their structure and bonding and in terms of the chemical equilibria in which they participate.

By the end of this section, you should be able to

- Identify an Arrhenius acid and base and a Brønsted-Lowry acid and base
- Recognize a conjugate acid-base pair and correlate the strength of an acid to the strength of its conjugate base.

Arrhenius Acids and Bases

By 1830 it was evident that all acids contain hydrogen but not all hydrogen-containing substances are acids. During the 1880s, the Swedish chemist Svante Arrhenius (1859–1927) defined acids as substances that produce H^+ ions in water and bases as substances that produce OH^- ions in water. Over time the Arrhenius concept of acids and bases came to be stated in the following way:

- An *acid* is a substance that, when dissolved in water, increases the concentration of H^+ ions.
- A *base* is a substance that, when dissolved in water, increases the concentration of OH^- ions.

Hydrogen chloride gas, which is highly soluble in water, is an example of an Arrhenius acid. When it dissolves in water, $HCl(g)$ produces hydrated H^+ and Cl^- ions:

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq) \qquad [16.1]$$

The aqueous solution of HCl is known as *hydrochloric acid*. Concentrated hydrochloric acid is about 37% HCl by mass and is 12 *M* in HCl.

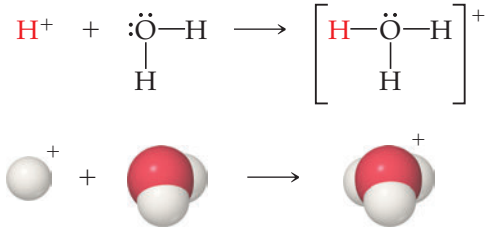
Sodium hydroxide is an Arrhenius base. Because NaOH is an ionic compound, it dissociates into Na^+ and OH^- ions when it dissolves in water, thereby increasing the concentration of OH^- ions in the solution.

Brønsted–Lowry Acids and Bases

The Arrhenius concept of acids and bases, while useful, is rather limited. For one thing, it is restricted to aqueous solutions. In 1923 the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936) independently proposed a more general definition of acids and bases. Their concept is based on the fact that *acid–base reactions involve the transfer of H^+ ions from one substance to another*. To understand this definition better, we need to examine the behavior of the H^+ ion in water more closely.

The H^+ Ion in Water

We might at first imagine that ionization of HCl in water produces just H^+ and Cl^-. A hydrogen ion is no more than a bare proton—a very small particle with a positive charge. As such, an H^+ ion interacts strongly with any source of electron density, such as the nonbonding electron pairs on the oxygen atoms of water molecules. For example, the interaction of a proton with water forms the **hydronium ion**, $H_3O^+(aq)$:

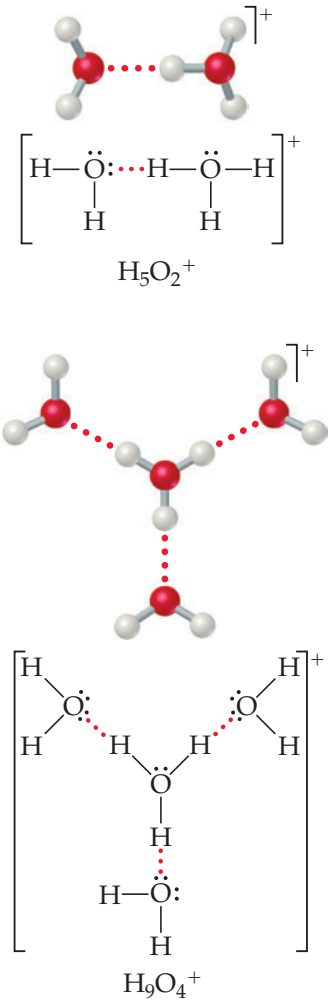


[16.2]

The behavior of H^+ ions in liquid water is complex because hydronium ions interact with additional water molecules via the formation of hydrogen bonds. For example, the H_3O^+ ion bonds to additional H_2O molecules to generate such ions as $H_5O_2^+$ and $H_9O_4^+$ (Figure 16.1).

Go Figure

Which type of intermolecular force do the dotted lines in this figure represent?



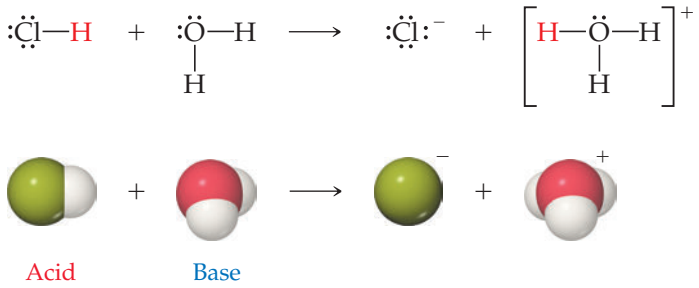
▲ **Figure 16.1** **Ball-and-stick models and Lewis structures for two hydrated hydronium ions.**

Chemists use the notations $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton responsible for the characteristic properties of aqueous solutions of acids. We often use the notation $H^+(aq)$ for simplicity and convenience, as we did in Chapter 4 and Equation 16.1. The notation $H_3O^+(aq)$, however, more closely represents reality.

Proton-Transfer Reactions

In the reaction that occurs when HCl dissolves in water, the HCl molecule transfers an H^+ ion (a proton) to a water molecule. Thus, we can represent the reaction as occurring between an HCl molecule and a water molecule to form hydronium and chloride ions:

$$HCl(g) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq) \qquad [16.3]$$

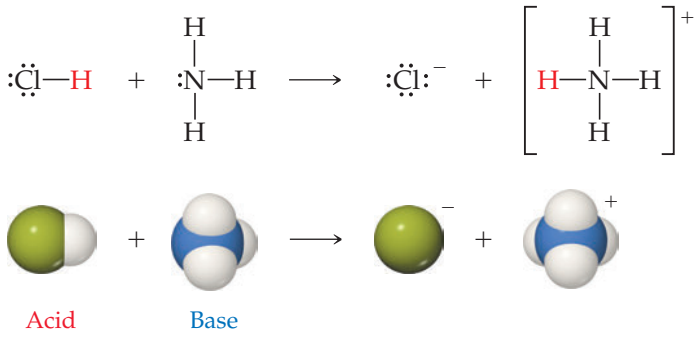


Notice that the reaction in Equation 16.3 involves a *proton donor* (HCl) and a *proton acceptor* (H_2O). The notion of transfer from a proton donor to a proton acceptor is the key idea in the Brønsted–Lowry definition of acids and bases:

- **Brønsted–Lowry acid** An *acid* is a substance (molecule or ion) that *donates* a proton to another substance.
- **Brønsted–Lowry base** A *base* is a substance that *accepts* a proton.

Thus, when HCl dissolves in water (Equation 16.3), HCl acts as a Brønsted–Lowry acid (it donates a proton to H_2O), and H_2O acts as a Brønsted–Lowry base (it accepts a proton from HCl). We see that the H_2O molecule serves as a proton acceptor by using one of the nonbonding pairs of electrons on the O atom to "attach" the proton.

Because the emphasis in the Brønsted–Lowry concept is on proton transfer, the concept also applies to reactions that do not occur in aqueous solution. In the reaction between gas phase HCl and NH_3, for example, a proton is transferred from the acid HCl to the base NH_3:



[16.4]

The hazy film that forms on the windows of general chemistry laboratories and on glassware in the laboratory (**Figure 16.2**) is largely solid NH_4Cl formed by the gas-phase reaction between HCl and NH_3.

Let's consider another example that compares the relationship between the Arrhenius and Brønsted–Lowry definitions of acids and bases—an aqueous solution of ammonia, in which we have the equilibrium:

$$\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [16.5]$$



▲ **Figure 16.2** **Fog of $NH_4Cl(s)$ caused by the reaction of $HCl(g)$ and $NH_3(g)$.**

Ammonia is a Brønsted–Lowry base because it accepts a proton from H_2O. Ammonia is also an Arrhenius base because adding it to water leads to an increase in the concentration of $OH^-(aq)$.

The transfer of a proton always involves both an acid (donor) and a base (acceptor).

In other words, a substance can function as an acid only if another substance simultaneously behaves as a base. To be a Brønsted–Lowry acid, a molecule or ion must have a hydrogen atom it can lose as an H^+ ion. To be a Brønsted–Lowry base, a molecule or ion must have a nonbonding pair of electrons it can use to bind the H^+ ion.

Some substances can act as an acid in one reaction and as a base in another. For example, H_2O is a Brønsted–Lowry base in Equation 16.3 and a Brønsted–Lowry acid in Equation 16.5. A substance capable of acting as either an acid or a base is called **amphiprotic**. An amphiprotic substance acts as a base when combined with something more strongly acidic than itself and as an acid when combined with something more strongly basic than itself.

Conjugate Acid–Base Pairs

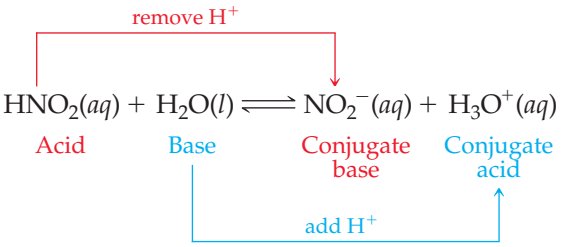
In any acid–base equilibrium, both the forward reaction (to the right) and the reverse reaction (to the left) involve proton transfer. For example, consider the reaction of an acid HA with water:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq) \qquad [16.6]$$

In the forward reaction, HA donates a proton to H_2O. Therefore, HA is the Brønsted–Lowry acid and H_2O is the Brønsted–Lowry base. In the reverse reaction, the H_3O^+ ion donates a proton to the A^- ion, so H_3O^+ is the acid and A^- is the base. When the acid HA donates a proton, it leaves behind a substance, A^-, that can act as a base. Likewise, when H_2O acts as a base, it generates H_3O^+, which can act as an acid.

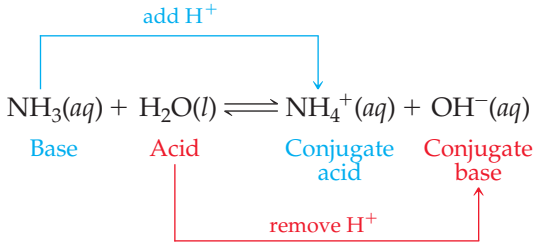
An acid and a base such as HA and A^- that differ only in the presence or absence of a proton are called a **conjugate acid–base pair**. Every acid has a **conjugate base**, formed by removing a proton from the acid. For example, OH^- is the conjugate base of H_2O, and A^- is the conjugate base of HA. Every base has a **conjugate acid**, formed by adding a proton to the base. Thus, H_3O^+ is the conjugate acid of H_2O, and HA is the conjugate acid of A^-.

In any acid–base (proton-transfer) reaction, we can identify two sets of conjugate acid–base pairs. For example, consider the reaction between nitrous acid and water:



[16.7]

Likewise, for the reaction between NH_3 and H_2O (Equation 16.5), we have



[16.8]

Sample Exercise 16.1

Identifying Conjugate Acids and Bases

(**a**) What is the conjugate base of $HClO_4$, H_2S, PH_4^+, HCO_3^-?

(**b**) What is the conjugate acid of CN^-, SO_4^{2-}, H_2O, HCO_3^-?

SOLUTION

Analyze We are asked to give the conjugate base for several acids and the conjugate acid for several bases.

Plan The conjugate base of a substance is simply the parent substance minus one proton, and the conjugate acid of a substance is the parent substance plus one proton.

Solve

(**a**) If we remove a proton from $HClO_4$, we obtain ClO_4^-, which is its conjugate base. The other conjugate bases are HS^-, PH_3, and CO_3^{2-}.

(**b**) If we add a proton to CN^-, we get HCN, its conjugate acid. The other conjugate acids are HSO_4^-, H_3O^+, and H_2CO_3.

Notice that the hydrogen carbonate ion (HCO_3^-) is amphiprotic. It can act as either an acid or a base.

Practice Exercise

Consider the following equilibrium reaction:

$$HSO_4^-(aq) + OH^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2O(l)$$

Which substances are acting as acids in the reaction?
(**a**) HSO_4^- and OH^-
(**b**) HSO_4^- and H_2O
(**c**) OH^- and SO_4^{2-}
(**d**) SO_4^{2-} and H_2O
(**e**) None of the substances are acting as acids in this reaction.

Sample Exercise 16.2

Writing Equations for Proton-Transfer Reactions

The hydrogen sulfite ion (HSO_3^-) is amphiprotic. Write an equation for the reaction of HSO_3^- with water **(a)** in which the ion acts as an acid and **(b)** in which the ion acts as a base. In both cases identify the conjugate acid–base pairs.

SOLUTION

Analyze and Plan We are asked to write two equations representing reactions between HSO_3^- and water, one in which HSO_3^- should donate a proton to water, thereby acting as a Brønsted–Lowry acid, and one in which HSO_3^- should accept a proton from water, thereby acting as a base. We are also asked to identify the conjugate pairs in each equation.

Solve

(**a**) $$HSO_3^-(aq) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq) + H_3O^+(aq)$$

The conjugate pairs in this equation are HSO_3^- (acid) and SO_3^{2-} (conjugate base), and H_2O (base) and H_3O^+ (conjugate acid).

(**b**) $$HSO_3^-(aq) + H_2O(l) \rightleftharpoons H_2SO_3(aq) + OH^-(aq)$$

The conjugate pairs in this equation are H_2O (acid) and OH^- (conjugate base), and HSO_3^- (base) and H_2SO_3 (conjugate acid).

Practice Exercise

The dihydrogen phosphate ion, $H_2PO_4^-$, is amphiprotic. In which of the following reactions is this ion serving as a base?

(i) $H_3O^+(aq) + H_2PO_4^-(aq) \rightleftharpoons H_3PO_4(aq) + H_2O(l)$
(ii) $H_3O^+(aq) + HPO_4^{2-}(aq) \rightleftharpoons H_2PO_4^-(aq) + H_2O(l)$
(iii) $H_3PO_4(aq) + HPO_4^{2-}(aq) \rightleftharpoons 2\,H_2PO_4^-(aq)$

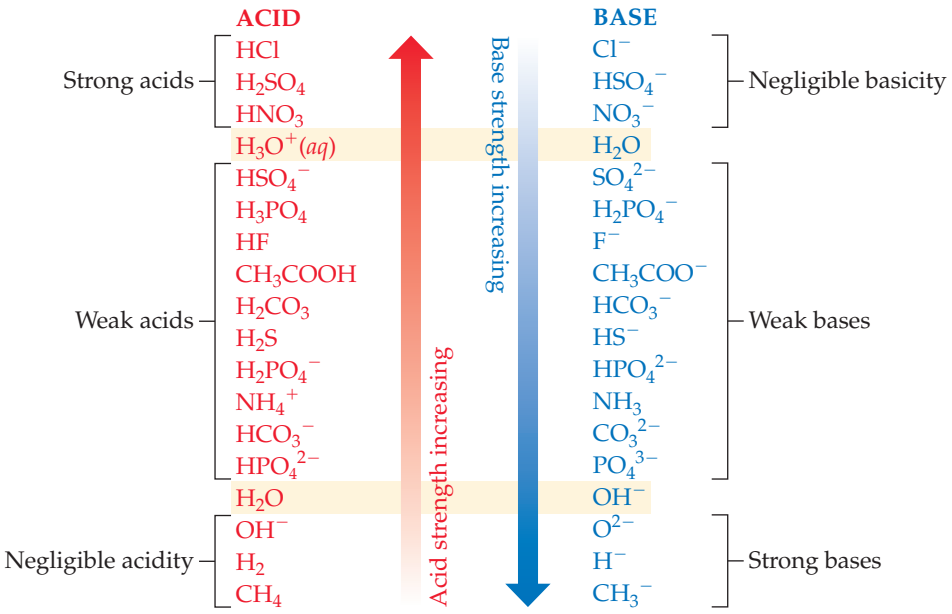
(**a**) i only (**b**) i and ii (**c**) i and iii (**d**) ii and iii
(**e**) i, ii, and iii

Once you become proficient at identifying conjugate acid–base pairs it is not difficult to write equations for reactions involving Brønsted–Lowry acids and bases (proton-transfer reactions).

Relative Strengths of Acids and Bases

Some acids are better proton donors than others, and some bases are better proton acceptors than others. If we arrange acids in order of their ability to donate a proton, we find that the more easily a substance gives up a proton, the less easily its conjugate base accepts a proton. Similarly, the more easily a base accepts a proton, the less easily its conjugate acid gives up a proton. In other words, *the stronger an acid, the weaker its conjugate base*, and *the stronger a base, the weaker its conjugate acid*. Thus, if we know how readily an acid donates protons, we also know something about how readily its conjugate base accepts protons.

Go Figure If O^{2-} ions are added to water, what reaction, if any, occurs?



▲ **Figure 16.3 Relative strengths of select conjugate acid–base pairs.** The two members of each pair are listed opposite each other in the two columns.

The inverse relationship between the strengths of acids and their conjugate bases is illustrated in **Figure 16.3**. Here we have grouped acids and bases into three broad categories based on their behavior in water:

1. A *strong acid* completely transfers its protons to water, leaving essentially no undissociated molecules in solution. Its conjugate base has a negligible tendency to accept protons in aqueous solution. (*The conjugate base of a strong acid shows negligible basicity.*)
2. A *weak acid* only partially dissociates in aqueous solution and therefore exists in the solution as a mixture of the undissociated acid and its conjugate base. The conjugate base of a weak acid shows a slight ability to remove protons from water. (*The conjugate base of a weak acid is a weak base.*)
3. A substance with *negligible acidity* contains hydrogen but does not demonstrate any acidic behavior in water. Its conjugate base is a strong base, reacting completely with water, to form OH^- ions. (*The conjugate base of a substance with negligible acidity is a strong base.*)

The ions $H_3O^+(aq)$ and $OH^-(aq)$ are, respectively, the strongest possible acid and strongest possible base that can exist at equilibrium in aqueous solution. Stronger acids react with water to produce $H_3O^+(aq)$ ions, and stronger bases react with water to produce $OH^-(aq)$ ions, a phenomenon known as the *leveling effect*.

We can think of proton-transfer reactions as being governed by the relative abilities of two bases to abstract protons. For example, consider the proton transfer that occurs when an acid HA dissolves in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad [16.9]$$

If H_2O (the base in the forward reaction) is a stronger base than A^- (the conjugate base of HA), it is favorable to transfer the proton from HA to H_2O, producing H_3O^+ and A^-. As a result, the equilibrium lies to the right. This describes the behavior of a strong acid in

water. For example, when HCl dissolves in water, the solution consists almost entirely of H_3O^+ and Cl^- ions with a negligible concentration of HCl molecules:

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq) \qquad [16.10]$$

H_2O is a stronger base than Cl^- (Figure 16.3), so H_2O acquires the proton to become the hydronium ion. Because the reaction lies completely to the right, we write Equation 16.10 with only an arrow to the right rather than using the double arrows for an equilibrium.

When A^- is a stronger base than H_2O, the equilibrium lies to the left. This situation occurs when HA is a weak acid. For example, an aqueous solution of acetic acid consists mainly of CH_3COOH molecules with relatively few H_3O^+ and CH_3COO^- ions:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \qquad [16.11]$$

The CH_3COO^- ion is a stronger base than H_2O (Figure 16.3) and therefore the reverse reaction is favored more than the forward reaction.

From these examples, we conclude that *in every acid–base reaction, equilibrium favors transfer of the proton from the stronger acid to the stronger base to form the weaker acid and the weaker base.*

Sample Exercise 16.3

Predicting the Position of a Proton-Transfer Equilibrium

For the following proton-transfer reaction, use Figure 16.3 to predict whether the equilibrium lies to the left ($K_c < 1$) or to the right ($K_c > 1$):

$$HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$$

SOLUTION

Analyze We are asked to predict whether an equilibrium lies to the right, favoring products, or to the left, favoring reactants.

Plan This is a proton-transfer reaction, and the position of the equilibrium will favor the proton going to the stronger of two bases. The two bases in the equation are CO_3^{2-}, the base in the forward reaction, and SO_4^{2-}, the conjugate base of HSO_4^-. We can find the relative positions of these two bases in Figure 16.3 to determine which is the stronger base.

Solve The CO_3^{2-} ion appears lower in the right-hand column in Figure 16.3 and is therefore a stronger base than SO_4^{2-}. Therefore, CO_3^{2-} will get the proton preferentially to become HCO_3^-, while SO_4^{2-} will remain mostly unprotonated. The resulting equilibrium lies to the right, favoring products (that is, $K_c > 1$):

$$\underset{\text{Acid}}{HSO_4^-(aq)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons \underset{\text{Conjugate base}}{SO_4^{2-}(aq)} + \underset{\text{Conjugate acid}}{HCO_3^-(aq)} \quad K_c > 1$$

Comment Of the two acids HSO_4^- and HCO_3^-, the stronger one (HSO_4^-) gives up a proton more readily, and the weaker one (HCO_3^-) tends to retain its proton. Thus, the equilibrium favors the direction in which the proton moves from the stronger acid and becomes bonded to the stronger base.

Practice Exercise

Based on information in Figure 16.3, place the following equilibria in order from smallest to largest value of K_c:

(i) $CH_3COOH(aq) + HS^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2S(aq)$

(ii) $F^-(aq) + NH_4^+(aq) \rightleftharpoons HF(aq) + NH_3(aq)$

(iii) $H_2CO_3(aq) + Cl^-(aq) \rightleftharpoons HCO_3^-(aq) + HCl(aq)$

(a) i < ii < iii **(b)** ii < i < iii **(c)** iii < i < ii
(d) ii < iii < i **(e)** iii < ii < i

Self-Assessment Exercises

16.1 The following substances dissolve in water. Which one is a Brønsted-Lowry acid or base?

(a) NaCl

(b) $CaBr_2$

(c) H_3PO_4

(d) $C_6H_{12}O_6$

16.2 The hydrogen phosphate ion, HPO_4^{2-}, is amphoteric. What is the conjugate acid of the hydrogen phosphate ion?

(a) H_3PO_4

(b) $H_2PO_4^-$

(c) HPO_4^{2-}

(d) PO_4^{3-}

Exercises

16.3 Which of the following statements is false?

(**a**) An Arrhenius base increases the concentration of OH^- in water.

(**b**) A Brønsted-Lowry base is a proton acceptor.

(**c**) Water can act as a Brønsted–Lowry acid.

(**d**) Water can act as a Brønsted–Lowry base.

(**e**) Any compound that contains an –OH group acts as a Brønsted-Lowry base.

16.4 (**a**) Give the conjugate base of the following Brønsted—Lowry acids: (**i**) H_2SO_3, (**ii**) HSO_3^- (**b**) Give the conjugate acid of the following Brønsted—Lowry bases: (**i**) CH_3NH_2, (**ii**) CH_3COO^-.

16.5 Identify the Brønsted–Lowry acid and the Brønsted–Lowry base on the left side of each equation, and also identify the conjugate acid and conjugate base of each on the right side.

(**a**) $HBrO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO^-(aq)$

(**b**) $HSO_4^-(aq) + HCO_3^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H_2CO_3(aq)$

(**c**) $HSO_3^-(aq) + H_3O^+(aq) \rightleftharpoons H_2SO_3(aq) + H_2O(l)$

16.6 (**a**) Write an equation for the react ion in which $HSO_4^-(aq)$ acts as a base in $H_2O(l)$. (**b**) Write an equation for the reaction in which $HSO_4^-(aq)$ acts as an acid in $H_2O(l)$. (**c**) What is the conjugate acid of $HSO_4^-(aq)$? What is its conjugate base?

16.7 Label each of the following as being a strong acid, a weak acid, or a species with negligible acidity. In each case write the formula of its conjugate base, and indicate whether the conjugate base is a strong base, a weak base, or a species with negligible basicity: (**a**) HCOOH, (**b**) H_2, (**c**) CH_4, (**d**) HF, (**e**) NH_4^+.

16.8 (**a**) Which of the following is the stronger Brønsted–Lowry acid, $HClO_3$ or $HClO_2$? (**b**) Which is the stronger Brønsted–Lowry base, HS^- or HSO_4^-?

16.9 Predict the products of the following acid–base reactions, and predict whether the equilibrium lies to the left or to the right of the reaction arrow:

(**a**) $NH_4^+(aq) + OH^-(aq) \rightleftharpoons$

(**b**) $CH_3COO^-(aq) + H_3O^+(aq) \rightleftharpoons$

(**c**) $HCO_3^-(aq) + F^-(aq) \rightleftharpoons$

Answers to Self-Assessment Exercises

16.1 (c) **16.2** (b)

16.2 The Autoionization of Water



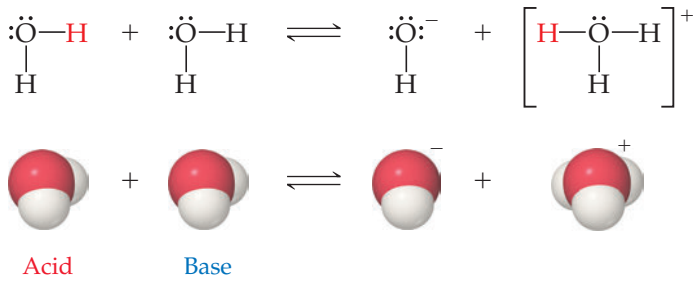
Water is unusual in so many ways. Uniquely, its solid phase is less dense than its liquid phase at 0 °C. It has a boiling point that is unusually high for a small molecule, and it can dissolve a very wide range of substances. It is essential for life. It is not a surprise that considerable effort is directed towards its analysis to ensure a supply of clean drinking water, to monitor pollution and to better understand the hydrology of rain, rivers and our oceans.

In this section, we come across yet another unusual property—that of autoionization. By the end of this section, you should be able to

- Relate the concentrations of H^+ and OH^- to one another using K_w.

One of the most important chemical properties of water is its ability to act as either a Brønsted–Lowry acid or a Brønsted–Lowry base. In the presence of an acid, it acts as a proton acceptor; in the presence of a base, it acts as a proton donor. In fact, one water molecule can donate a proton to another water molecule:

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq) \qquad [16.12]$$



Acid Base

We call this process the **autoionization** of water.

Because the forward and reverse reactions in Equation 16.12 are extremely rapid, no water molecule remains ionized for long. At room temperature only about two out of every 10^9 water molecules are ionized at any given instant. Thus, pure water consists almost entirely of H_2O molecules and is an extremely poor conductor of electricity. Nevertheless, the autoionization of water is very important, as we will soon learn.

The Ion Product of Water

The equilibrium expression for the autoionization of water is

$$K_c = [H_3O^+][OH^-] \qquad [16.13]$$

The term $[H_2O]$ is excluded from the equilibrium expression because we exclude the concentrations of pure solids and liquids. Because this expression refers specifically to the autoionization of water, we use the symbol K_w to denote the equilibrium constant, which we call the **ion-product constant** for water. At 25 °C, K_w equals 1.0×10^{-14}. Thus, we have

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad (\text{at } 25\,^\circ\text{C}) \qquad [16.14]$$

Because we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to represent the hydrated proton, the autoionization reaction for water can also be written as

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad [16.15]$$

Likewise, the expression for K_w can be written in terms of either H_3O^+ or H^+, and K_w has the same value in either case:

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14} \quad (\text{at } 25\,^\circ\text{C}) \qquad [16.16]$$

This equilibrium expression and the value of K_w at 25 °C are extremely important, and you should commit them to memory.

A solution in which $[H^+] = [OH^-]$ is said to be *neutral*. In most solutions, however, the H^+ and OH^- concentrations are not equal. As the concentration of one of these ions increases, the concentration of the other must decrease, so that the product of their concentrations always equals 1.0×10^{-14} (**Figure 16.4**). Aqueous solutions in which $[H^+] > [OH^-]$ are called *acidic*, and aqueous solutions in which $[OH^-] > [H^+]$ are called *basic*.

What makes Equation 16.16 particularly useful is that it is applicable both to pure water and to any aqueous solution. Although the equilibrium between $H^+(aq)$ and $OH^-(aq)$ as well as other ionic equilibria are affected somewhat by the presence of additional ions in solution, it is customary to ignore these ionic effects except in work requiring exceptional accuracy. Thus, Equation 16.16 is taken to be valid for any dilute aqueous solution and can be used to calculate either $[H^+]$ (if $[OH^-]$ is known) or $[OH^-]$ (if $[H^+]$ is known).

Go Figure Suppose that equal volumes of the middle and right samples in the figure were mixed. Would the resulting solution be acidic, neutral, or basic?



Acidic solution	Neutral solution	Basic solution
$[H^+] > [OH^-]$	$[H^+] = [OH^-]$	$[H^+] < [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$	$[H^+][OH^-] = 1.0 \times 10^{-14}$	$[H^+][OH^-] = 1.0 \times 10^{-14}$

▲ **Figure 16.4** **Relative concentrations of H^+ and OH^- in aqueous solutions at 25 °C.**

Sample Exercise 16.4

Calculating $[H^+]$ for Pure Water

Calculate the values of $[H^+]$ and $[OH^-]$ in a neutral aqueous solution at 25 °C.

SOLUTION

Analyze We are asked to determine the concentrations of H^+ and OH^- ions in a neutral solution at 25 °C.

Plan We will use Equation 16.16 and the fact that, by definition, $[H^+] = [OH^-]$ in a neutral solution.

Solve We will represent the concentration of H^+ and OH^- in neutral solution with x. This gives

$$[H^+][OH^-] = (x)(x) = 1.0 \times 10^{-14}$$
$$x^2 = 1.0 \times 10^{-14}$$
$$x = 1.0 \times 10^{-7} M = [H^+] = [OH^-]$$

In an acid solution $[H^+]$ is greater than $1.0 \times 10^{-7}\,M$; in a basic solution $[H^+]$ is less than $1.0 \times 10^{-7}\,M$.

Practice Exercise

In a certain acidic solution at 25 °C, $[H^+]$ is 100 times greater than $[OH^-]$. What is the value for $[OH^-]$ for the solution?
(**a**) $1.0 \times 10^{-8}\,M$ (**b**) $1.0 \times 10^{-7}\,M$ (**c**) $1.0 \times 10^{-6}\,M$
(**d**) $1.0 \times 10^{-2}\,M$ (**e**) $1.0 \times 10^{-9}\,M$

Sample Exercise 16.5

Calculating $[H^+]$ from $[OH^-]$

Calculate the concentration of $H^+(aq)$ in (**a**) a solution in which $[OH^-]$ is 0.010 *M*, (**b**) a solution in which $[OH^-]$ is $1.8 \times 10^{-9}\,M$. *Note:* In this problem and all that follow, we assume, unless stated otherwise, that the temperature is 25 °C.

SOLUTION

Analyze We are asked to calculate the $[H^+]$ concentration in an aqueous solution where the hydroxide concentration is known.

Plan We can use the equilibrium expression for the autoionization of water and the value of K_w to solve for each unknown concentration.

Solve

(**a**) Using Equation 16.16, we have

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$
$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\,M$$

This solution is basic because $[OH^-] > [H^+]$

(**b**) In this instance

$$[H^+] = \frac{(1.0 \times 10^{-14})}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-9}} = 5.6 \times 10^{-6}\,M$$

This solution is acidic because $[H^+] > [OH^-]$

Practice Exercise
A solution has $[OH^-] = 4.0 \times 10^{-8}$. What is the value of $[H^+]$ for the solution?

(a) $2.5 \times 10^{-8}\,M$ **(b)** $4.0 \times 10^{-8}\,M$ **(c)** $2.5 \times 10^{-7}\,M$
(d) $2.5 \times 10^{-6}\,M$ **(e)** $4.0 \times 10^{-6}\,M$

Self-Assessment Exercise

16.10 At our body temperature of 37 °C, $K_w = 2.1 \times 10^{-14}$. What is $[H^+]$ and $[OH^-]$?

(a) $[H^+] = 1.0 \times 10^{-7}$ and $[OH^-] = 1.0 \times 10^{-7}$
(b) $[H^+] = 1.4 \times 10^{-7}$ and $[OH^-] = 1.4 \times 10^{-7}$
(c) $[H^+] = 1.0 \times 10^{-7}$ and $[OH^-] = 2.1 \times 10^{-7}$
(c) $[H^+] = 2.1 \times 10^{-7}$ and $[OH^-] = 1.0 \times 10^{-7}$

Exercises

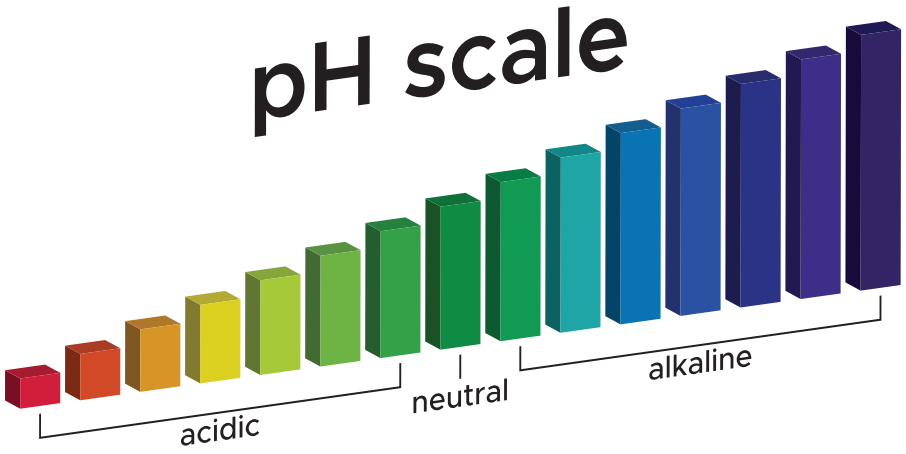
16.11 (**a**) Write a chemical equation that illustrates the autoionization of water. (**b**) Write the expression for the ion-product constant for water, K_w. (**c**) If a solution is described as basic, which of the following is true: (i) $[H^+] > [OH^-]$, (ii) $[H^+] = [OH^-]$, or (iii) $[H^+] < [OH^-]$?

16.12 Calculate $[OH^-]$ for each of the following solutions, and indicate whether the solution is acidic, basic, or neutral: (**a**) $[H^+] = 0.00010\,M$; (**b**) $[H^+] = 7.3 \times 10^{-14}\,M$; (**c**) a solution in which $[OH^-]$ is 100 times greater than $[H^+]$.

16.13 Deuterium oxide (D_2O, where D is deuterium, the hydrogen-2 isotope) has an ion-product constant, K_w, of 8.9×10^{-16} at 20 °C. Calculate $[D^+]$ and $[OD^-]$ for pure (neutral) D_2O at this temperature.

Answers to Self-Assessment Exercises
16.10 (b)

16.3 The pH Scale



In the days before computers, a method to store large amounts of data, as you might find in a scientific journal, was on microfilm. Now, with almost limitless storage potential, computers have taken over that role. In mathematics, a log function is one way that you can take a very wide range of values and compress them onto a more manageable scale. When

dealing with acids and bases, the $[H^+]$ can vary over many orders of magnitude. This is an ideal situation in which to apply a log scale and bring the numbers under control!

By the end of this section, you should be able to

- Calculate the pH of a solution given $[H_3O^+]$ or $[OH^-]$

The molar concentration of $H^+(aq)$ in an aqueous solution is usually very small. For convenience, we therefore express $[H^+]$ in terms of **pH**, which is the negative logarithm in base 10 of $[H^+]$:*

$$pH = -\log[H^+] \qquad [16.17]$$

If you need to review the use of logarithms, see Appendix A.

In Sample Exercise 16.4, we saw that $[H^+] = 1.0 \times 10^{-7}\,M$ for a neutral aqueous solution at 25 °C. We can now use Equation 16.17 to calculate the pH of a neutral solution at 25 °C:

$$pH = -\log(1.0 \times 10^{-7}) = -(-7.00) = 7.00$$

Notice that the pH is reported with two decimal places. We do so because *only the numbers to the right of the decimal point are the significant figures in a logarithm*. Because our original value for the concentration ($1.0 \times 10^{-7}\,M$) has two significant figures, the corresponding pH has two decimal places (7.00).

What happens to the pH of a solution as we make the solution more acidic, so that $[H^+]$ increases? Because of the negative sign in the logarithm term of Equation 16.17, *the pH decreases as* $[H^+]$ *increases*. For example, when we add sufficient acid to make $[H^+] = 1.0 \times 10^{-3}\,M$, the pH is

$$pH = -\log(1.0 \times 10^{-3}) = -(-3.00) = 3.00$$

At 25 °C the pH of an acidic solution is less than 7.00.

We can also calculate the pH of a basic solution, one in which $[OH^-] > 1.0 \times 10^{-7}\,M$. Suppose $[OH^-] = 2.0 \times 10^{-3}\,M$. We can use Equation 16.16 to calculate $[H^+]$ for this solution and Equation 16.17 to calculate the pH:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\,M$$

$$pH = -\log(5.0 \times 10^{-12}) = 11.30$$

At 25 °C the pH of a basic solution is greater than 7.00. The relationships among $[H^+]$, $[OH^-]$, and pH are summarized in Table 16.1.

One might think that when $[H^+]$ is very small, as is often the case, it would be unimportant. That reasoning is quite incorrect! Remember that many chemical processes depend on the ratio of changes in concentration. For example, if a kinetic rate law is first order in $[H^+]$, doubling the H^+ concentration doubles the rate even if the change is merely from $1 \times 10^{-7}\,M$ to $2 \times 10^{-7}\,M$. In biological systems, many reactions involve proton transfers and have rates that depend on $[H^+]$. Because the speeds of these reactions are crucial, the pH of biological fluids must be maintained within narrow limits. For example, human blood has a normal pH range of 7.35 to 7.45. Illness and even death can result if the pH varies much from this narrow range.

TABLE 16.1 Relationships between $[H^+]$, $[OH^-]$, and pH at 25 °C for Acidic, Neutral, and Basic Aqueous Solutions

	Acidic	Neutral	Basic
pH	<7.00	7.00	>7.00
$[H^+](M)$	$>1.0 \times 10^{-7}$	1.0×10^{-7}	$<1.0 \times 10^{-7}$
$[OH^-](M)$	$<1.0 \times 10^{-7}$	1.0×10^{-7}	$>1.0 \times 10^{-7}$

*Because $[H^+]$ and $[H_3O^+]$ are used interchangeably, you might see pH defined as $-\log[H_3O^+]$.

Sample Exercise 16.6

Calculating pH from $[H^+]$

Calculate the pH values for the two solutions of Sample Exercise 16.5.

SOLUTION

Analyze We are asked to determine the pH of aqueous solutions for which we have already calculated $[H^+]$.

Plan We can calculate pH using its defining equation, Equation 16.17.

Solve

(**a**) In the first instance we found $[H^+]$ to be $1.0 \times 10^{-12}\,M$, so that

$$\text{pH} = -\log(1.0 \times 10^{-12}) = -(-12.00) = 12.00$$

Because 1.0×10^{-12} has two significant figures, the pH has two decimal places, 12.00.

(**b**) For the second solution, $[H^+] = 5.6 \times 10^{-6}\,M$. Before performing the calculation, it is helpful to estimate the pH. To do so, we note that $[H^+]$ lies between 1×10^{-6} and 1×10^{-5}. Thus, we expect the pH to lie between 6.0 and 5.0. We use Equation 16.17 to calculate the pH:

$$\text{pH} = -\log(5.6 \times 10^{-6}) = 5.25$$

Check After calculating a pH, it is useful to compare it to your estimate. In this case the pH, as we predicted, falls between 6 and 5. Had the calculated pH and the estimate not agreed, we should have reconsidered our calculation or estimate or both.

Practice Exercise

A solution at 25 °C has $[OH^-] = 6.7 \times 10^{-3}$. What is the pH of the solution?

(**a**) 0.83 (**b**) 2.2 (**c**) 2.17 (**d**) 11.83 (**e**) 12

pOH and Other "p" Scales

The negative logarithm is a convenient way of expressing the magnitudes of other small quantities. We use the convention that the negative logarithm of a quantity is labeled "p" (quantity). Thus, we can express the concentration of OH^- as pOH:

$$\text{pOH} = -\log[OH^-] \qquad [16.18]$$

Likewise, pK_w equals $-\log K_w$.

By taking the negative logarithm of both sides of the equilibrium-constant expression for water, $K_w = [H^+][OH^-]$, we obtain

$$-\log[H^+] + (-\log[OH^-]) = -\log K_w \qquad [16.19]$$

from which we obtain the useful expression

$$\text{pH} + \text{pOH} = 14.00 \quad (\text{at } 25\,^\circ\text{C}) \qquad [16.20]$$

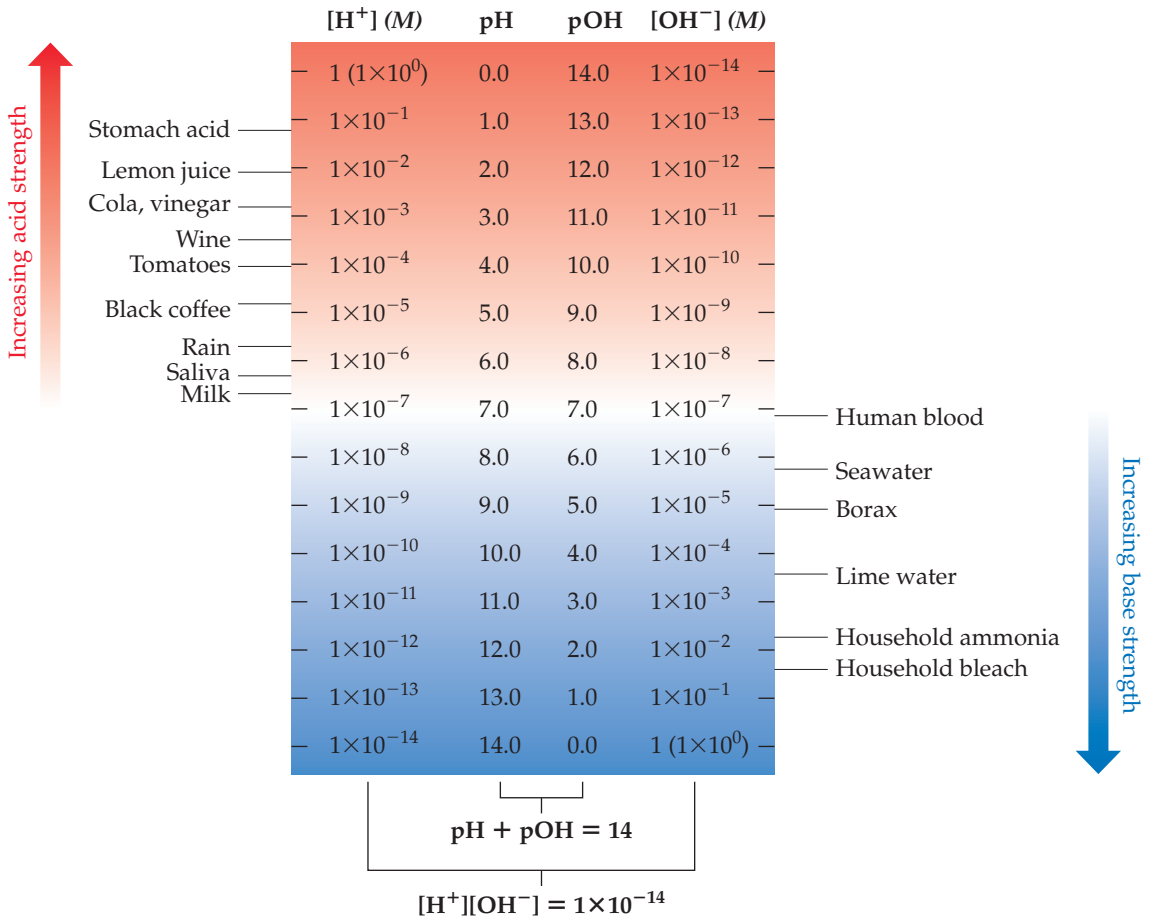
The pH and pOH values characteristic of a number of familiar solutions are shown in **Figure 16.5**. Notice that a change in $[H^+]$ by a factor of 10 causes the pH to change by 1. Thus, the concentration of $H^+(aq)$ in a solution of pH 5 is 10 times the $H^+(aq)$ concentration in a solution of pH 6.

Measuring pH

The pH of a solution can be measured with a *pH meter* (**Figure 16.6**). A complete understanding of how this important device works requires knowledge of electrochemistry, a subject we take up in Chapter 20. In brief, a pH meter consists of a pair of electrodes connected to a meter capable of measuring small voltages, on the order of millivolts. A voltage, which varies with pH, is generated when the electrodes are placed in a solution. This voltage is read by the meter, which is calibrated to give pH.

Although less precise, acid–base indicators can be used to measure pH. An acid–base indicator is a colored substance that can exist in either an acid or a base form. The two forms have different colors. Thus, the indicator has one color at lower pH and another at higher pH. If you know the pH at which the indicator turns from one form to the other, you can determine whether a solution has a higher or lower pH than this value. Litmus, for example, changes color in the vicinity of pH 7. The color change, however, is not very sharp. Red litmus indicates a pH of about 5 or lower, and blue litmus indicates a pH of about 8 or higher.

Go Figure Which is more acidic, black coffee or lemon juice?



▲ **Figure 16.5** Concentrations of H^+ and OH^-, and pH and pOH values of some common substances at 25 °C.

Sample Exercise 16.7

Calculating $[H^+]$ from pOH

A sample of freshly pressed apple juice has a pOH of 10.24. Calculate $[H^+]$.

SOLUTION

Analyze We need to calculate $[H^+]$ from pOH.

Plan We will first use Equation 16.20, pH + pOH = 14.00, to calculate pH from pOH. Then we will use Equation 16.17 to determine the concentration of H^+.

Solve From Equation 16.20, we have

$$pH = 14.00 - pOH$$
$$pH = 14.00 - 10.24 = 3.76$$

Next we use Equation 16.17:

$$pH = -\log[H^+] = 3.76$$

Thus,

$$\log[H^+] = -3.76$$

To find $[H^+]$, we need to determine the *antilogarithm* of −3.76. Your calculator will show this command as 10^x or INV log (these functions are usually above the log key). We use this function to perform the calculation:

$$[H^+] = \text{antilog}(-3.76) = 10^{-3.76} = 1.7 \times 10^{-4}\,M$$

Comment The number of significant figures in $[H^+]$ is two because the number of decimal places in the pH is two.

Check Because the pH is between 3.0 and 4.0, we know that $[H^+]$ will be between $1.0 \times 10^{-3}\,M$ and $1.0 \times 10^{-4}\,M$. Our calculated $[H^+]$ falls within this estimated range.

Practice Exercise

A solution at 25 °C has pOH = 10.53. Which of the following statements is or are true?
(i) The solution is acidic.
(ii) The pH of the solution is 14.00 − 10.53.
(iii) For this solution, $[OH^-] = 10^{-10.53}M$.

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

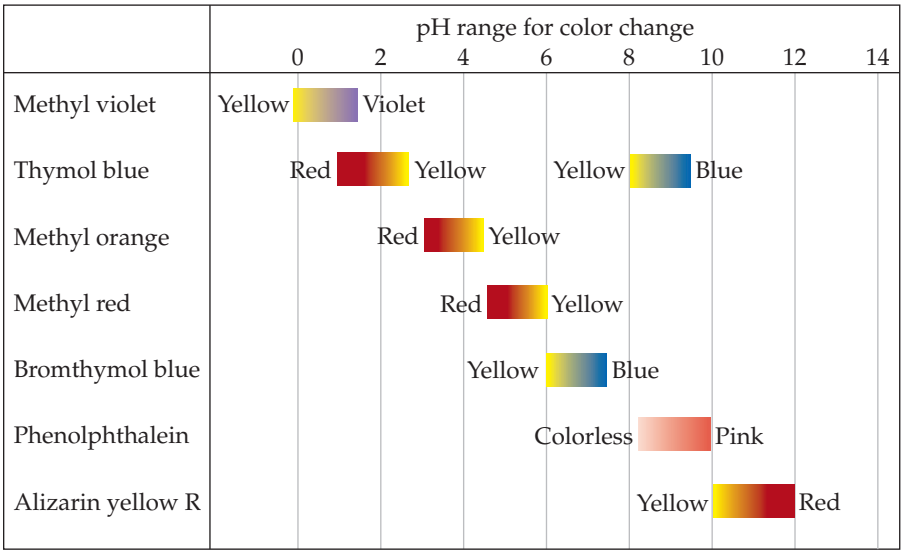
Some common indicators are listed in Figure 16.7. The chart tells us, for instance, that methyl red changes color over the pH interval from about 4.5 to 6.0. Below pH 4.5 it is in the acid form, which is red. In the interval between 4.5 and 6.0, it is gradually converted to its basic form, which is yellow. Once the pH rises above 6 the conversion is complete, and the solution is yellow. This color change, along with that of the indicators bromthymol blue and phenolphthalein, is shown in Figure 16.8. Paper tape impregnated with several indicators is widely used for determining approximate pH values.



▲ **Figure 16.6 A digital pH meter.** The electrodes immersed in a solution produce a voltage that depends on the pH of the solution.

Go Figure

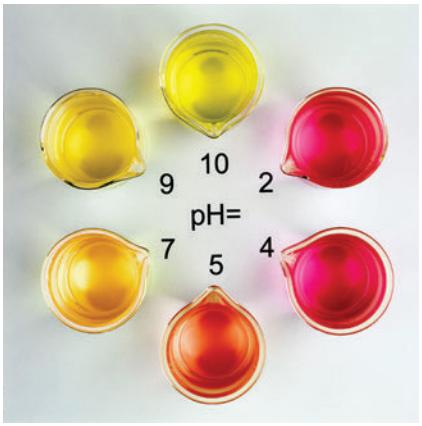
If a colorless solution turns pink when we add phenolphthalein, what can we conclude about the pH of the solution?



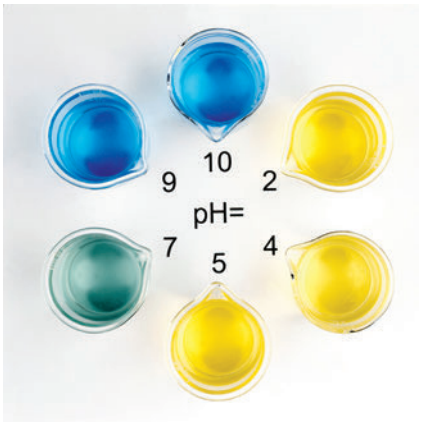
▲ **Figure 16.7 pH ranges for common acid–base indicators.** Most indicators have a useful range of about 2 pH units.

Go Figure

Which of these indicators is best suited to distinguish between a solution that is slightly acidic and one that is slightly basic?



Methyl red



Bromthymol blue



Phenolphthalein

▲ **Figure 16.8 Solutions containing three common acid–base indicators at various pH values.**

Self-Assessment Exercise

16.14 A sample of seawater at 25 °C has a measured pH = 8.40. What is $[OH^-]$ in this seawater?

(a) $2.5 \times 10^{-6}\,M$
(b) $4.0 \times 10^{-9}\,M$
(c) $8.4 \times 10^{-7}\,M$

Exercises

16.15 Consider two solutions, solution A and solution B. $[H^+]$ in solution A is 25 times greater than that in solution B. What is the difference in the pH values of the two solutions?

16.16 Complete the following table by calculating the missing entries. In each case, indicate whether the solution is acidic or basic.

pH	pOH	$[H^+]$	$[OH^-]$	Acidic or Basic?
9.25				
	12.45			
		$3.4 \times 10^{-14} M$		
			$8.5 \times 10^{-13} M$	

16.17 Carbon dioxide in the atmosphere dissolves in raindrops to produce carbonic acid (H_2CO_3), causing the pH of clean, unpolluted rain to range from about 5.2 to 5.6. What are the ranges of $[H^+]$ and $[OH^-]$ in the raindrops?

16.18 Addition of phenolphthalein to an unknown colorless solution does not cause a color change. The addition of bromthymol blue to the same solution leads to a yellow color. (**a**) Is the solution acidic, neutral, or basic? (**b**) Which of the following can you establish about the solution: (i) A minimum pH, (ii) A maximum pH, or (iii) A specific range of pH values? (**c**) What other indicator or indicators would you want to use to determine the pH of the solution more precisely?

Answers to Self-Assessment Exercises

16.14 (a)

16.4 Strong Acids and Bases



Sulfur is the starting point in the manufacture of sulfuric acid, the most commonly produced chemical in the world. Sulfuric acid is used in the manufacture of fertilizers, synthetic fibers, extraction of some minerals, in batteries, for cleaning, in detergents, for paper making and in the production of paints and dyes to name just a few applications. It is classed as a strong acid, which has a very specific meaning as we shall see in this section.

By the end of this section, you should be able to

- Calculate the pH of a strong acid or strong base given its concentration.

The chemistry of an aqueous solution often depends critically on pH. It is therefore important to examine how pH relates to acid and base concentrations. The simplest cases are those involving strong acids and strong bases. Strong acids and bases are *strong electrolytes*, existing in aqueous solution entirely as ions. There are relatively few common strong acids and bases (see Table 4.2).

Strong Acids

The seven most common strong acids include six monoprotic acids (HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$), and one diprotic acid (H_2SO_4). Nitric acid (HNO_3) exemplifies the behavior of the monoprotic strong acids. For all practical purposes, an aqueous solution of HNO_3 consists entirely of H_3O^+ and NO_3^- ions:

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(complete ionization)} \qquad [16.21]$$

We have not used equilibrium arrows for this equation because the reaction lies entirely to the right. As noted in Section 16.2, we use $H_3O^+(aq)$ and $H^+(aq)$ interchangeably to represent the hydrated proton in water. Thus, we can simplify this acid ionization equation to

$$HNO_3(aq) \longrightarrow H^+(aq) + NO_3^-(aq)$$

In an aqueous solution of a strong acid, the acid is normally the only significant source of H^+ ions.* As a result, calculating the pH of a solution of a strong monoprotic acid is straightforward because $[H^+]$ equals the original concentration of acid. In a 0.20 *M* solution of $HNO_3(aq)$, for example, $[H^+] = [NO_3^-] = 0.20\ M$. The situation with the diprotic acid H_2SO_4 is somewhat more complex, as we will see in Section 16.5.

Sample Exercise 16.8

Calculating the pH of a Strong Acid Solution

What is the pH of a 0.040 *M* solution of $HClO_4$?

SOLUTION

Analyze and Plan Because $HClO_4$ is a strong acid, it is completely ionized, giving $[H^+] = [ClO_4^-] = 0.040\ M$.

Solve

$$pH = -\log(0.040) = 1.40$$

Check Because $[H^+]$ lies between 1×10^{-2} and 1×10^{-1}, the pH will be between 2.0 and 1.0. Our calculated pH falls within the estimated range. Furthermore, because the concentration has two significant figures, the pH has two decimal places.

Practice Exercise

Order the following three solutions from smallest to largest pH:
(i) 0.20 *M* $HClO_3$ (ii) 0.0030 *M* HNO_3 (iii) 1.50 *M* HCl

(**a**) i < ii < iii (**b**) ii < i < iii (**c**) iii < i < ii
(**d**) ii < iii < i (**e**) iii < ii < i

Strong Bases

The most common soluble strong bases are the ionic hydroxides of the alkali metals, such as NaOH, KOH, and the ionic hydroxides of heavier alkaline earth metals, such as $Sr(OH)_2$. These compounds completely dissociate into ions in aqueous solution. Thus, a solution labeled 0.30 *M* NaOH consists of 0.30 *M* $Na^+(aq)$ and 0.30 *M* $OH^-(aq)$; there is essentially no undissociated NaOH.

Although all of the alkali metal hydroxides are strong electrolytes, LiOH, RbOH, and CsOH are not commonly encountered in the laboratory. The hydroxides of the heavier alkaline earth metals—$Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$—are also strong electrolytes. They have limited solubility, however, so they are used only when high solubility is not critical.

Strongly basic solutions are also created by certain substances that react with water to form $OH^-(aq)$. The most common of these contain the oxide ion. Ionic metal oxides, especially Na_2O and CaO, are often used in industry when a strong base is needed. The O^{2-} reacts very exothermically with water to form OH^-, leaving virtually no O^{2-} in the solution:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\ OH^-(aq) \qquad [16.22]$$

*If the concentration of the acid is $10^{-6}\ M$ or less, we also need to consider H^+ ions that result from H_2O autoionization. Normally, the concentration of H^+ from H_2O is so small that it can be neglected.

Sample Exercise 16.9

Calculating the pH of a Strong Base

What is the pH of **(a)** a 0.028 *M* solution of NaOH, **(b)** a 0.0011 *M* solution of $Ca(OH)_2$?

SOLUTION

Analyze We are asked to calculate the pH of two solutions of strong bases.

Plan We can calculate each pH by either of two equivalent methods. First, we could use Equation 16.16 to calculate $[H^+]$ and then use Equation 16.17 to calculate the pH. Alternatively, we could use $[OH^-]$ to calculate pOH and then use Equation 16.20 to calculate the pH.

Solve

(**a**) NaOH dissociates in water to give one OH^- ion per formula unit. Therefore, the OH^- concentration for the solution in (a) equals the stated concentration of NaOH, namely 0.028 *M*.

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.028} = 3.57 \times 10^{-13}\,M$$

$$pH = -\log(3.57 \times 10^{-13}) = 12.45$$

Method 2:

$$pOH = -\log(0.028) = 1.55$$

$$pH = 14.00 - pOH = 12.45$$

(**b**) $Ca(OH)_2$ is a strong base that dissociates in water to give *two* OH^- ions per formula unit. Thus, the concentration of $OH^-(aq)$ for the solution in part (b) is $2 \times (0.0011\,M) = 0.0022\,M$.

Method 1:

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.0022} = 4.55 \times 10^{-12}\,M$$

$$pH = -\log(4.55 \times 10^{-12}) = 11.34$$

Method 2:

$$pOH = -\log(0.0022) = 2.66$$

$$pH = 14.00 - pOH = 11.34$$

Practice Exercise

Order the following three solutions from smallest to largest pH: (i) 0.030 *M* $Ba(OH)_2$ (ii) 0.040 *M* KOH (iii) pure water.

(**a**) i < ii < iii (**b**) ii < i < iii (**c**) iii < i < ii
(**d**) ii < iii < i (**e**) iii < ii < i

Thus, a solution formed by dissolving 0.010 mol of $Na_2O(s)$ in enough water to form 1.0 L of solution has $[OH^-] = 0.020\,M$ and a pH of 12.30.

Self-Assessment Exercise

16.19 Which solution has the higher pH, a 0.001 *M* solution of CsOH or a 0.001 *M* solution of $Sr(OH)_2$?

(a) 0.001 *M* CsOH
(b) 0.001 *M* $Sr(OH)_2$

Exercises

16.20 Determine whether each of the following is true or false: (**a**) All strong bases are salts of the hydroxide ion. (**b**) The addition of a strong base to water produces a solution of pH > 7.0. (**c**) Because $Mg(OH)_2$ is not very soluble, it cannot be a strong base.

16.21 Calculate the pH of each of the following strong acid solutions: (**a**) 0.0178 *M* HNO_3, (**b**) 0.500 g of $HClO_3$ in 5.00 L of solution, (**c**) 5.00 mL of 2.00 *M* HCl diluted to 0.500 L, (**d**) a mixture formed by adding 75.0 mL of 0.010 *M* HCl to 125 mL of 0.020 *M* HBr.

16.22 Calculate $[OH^-]$ and pH for each of the following strong base solutions: (**a**) 0.182 *M* KOH, (**b**) 3.165 g of KOH in 500.0 mL of solution, (**c**) 10.0 mL of 0.0105 *M* $Ca(OH)_2$ diluted to 500.0 mL, (**d**) a solution formed by mixing 20.0 mL of 0.015 *M* $Ba(OH)_2$ with 40.0 mL of 8.2×10^{-3} *M* NaOH.

16.23 Calculate the concentration of an aqueous solution of $Ca(OH)_2$ that has a pH of 10.05.

Answers to Self-Assessment Exercises

16.19 (b)

16.5 | Weak Acids

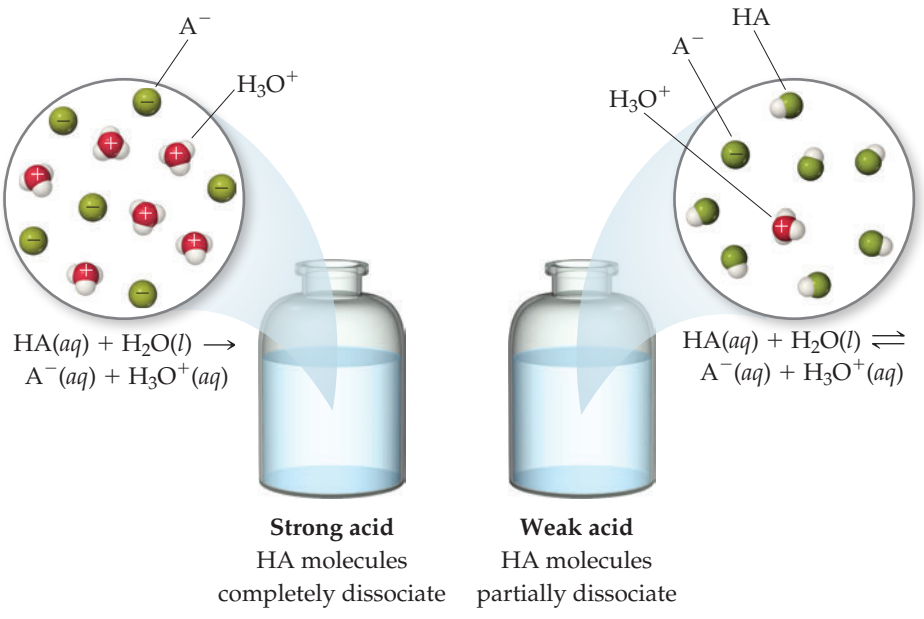


Acids and bases are common both in nature and in the laboratory and the overwhelming number are classed as 'weak'. They affect our daily lives in innumerable ways. Not only are they present in our foods, but acids and bases are also crucial components of living systems, such as the amino acids that are used to synthesize proteins and the nucleic acids that code genetic information. For example, citric acid and ascorbic acid (also known as Vitamin C) are what gives citrus fruits their characteristic tangy, sour tastes (Figure 16.9). Citric and malic acids are among several acids involved in the Krebs cycle (also called the citric acid cycle) that is used to generate energy in aerobic organisms. The application of acid–base chemistry has also had critical roles in shaping modern society, including such human-driven activities as industrial manufacturing, the creation of advanced pharmaceuticals, and many aspects of the environment.

By the end of this section, you shold be able to

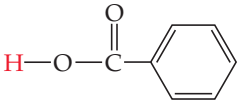
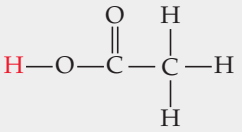
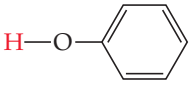
- Use pH and concentration to calculate *K* for a weak acid or weak base and vice versa.

Most acidic substances are weak acids and therefore only partially ionized in aqueous solution (**Figure 16.10**). We can use the equilibrium constant for the ionization



◀ **Figure 16.10** Species present in solutions of a strong acid and a weak acid.

TABLE 16.2 Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	H—O—Cl—O	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F^-	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

*The proton that ionizes is shown in red.

reaction to express the extent to which a weak acid ionizes. If we represent a general weak acid as HA, we can write the equation for its ionization in either of the following ways, depending on whether the hydrated proton is represented as $H_3O^+(aq)$ or $H^+(aq)$:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad [16.23]$$

or

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad [16.24]$$

These equilibria are in aqueous solution, so we will use equilibrium expressions based on concentrations. Because H_2O is the solvent, it is omitted from the equilibrium expression. Further, we add a subscript *a* on the equilibrium constant to indicate that it is an equilibrium constant for the ionization of an *acid*. Thus, we can write the equilibrium expression as either:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]} \qquad [16.25]$$

K_a is called the **acid-dissociation constant** for acid HA.

Table 16.2 shows the structural formulas, conjugate bases, and K_a values for a number of weak acids. Appendix D provides a more complete list. Many weak acids are organic compounds composed entirely of carbon, hydrogen, and oxygen. These compounds usually contain some hydrogen atoms bonded to carbon atoms and some bonded to oxygen atoms. In almost all cases, the hydrogen atoms bonded to carbon do not ionize in water; instead, the acidic behavior of these compounds is due to the hydrogen atoms attached to oxygen atoms.

The magnitude of K_a indicates the tendency of the acid to ionize in water: *The larger the value of K_a, the stronger the acid.* Chlorous acid ($HClO_2$), for example, is the strongest acid in Table 16.2, and phenol (HOC_6H_5) is the weakest. For most weak acids K_a values range from 10^{-2} to 10^{-10}.

Calculating K_a from pH

In order to calculate either the K_a value for a weak acid or the pH of its solutions, we will use many of the skills for solving equilibrium problems developed in Section 15.4. In many cases the small magnitude of K_a allows us to use approximations to simplify the problem. In doing these calculations, it is important to realize that proton-transfer

Sample Exercise 16.10

Calculating K_a from Measured pH

A student prepared a 0.10 *M* solution of formic acid (HCOOH) and found its pH at 25 °C to be 2.38. Calculate K_a for formic acid at this temperature.

SOLUTION

Analyze We are given the molar concentration of an aqueous solution of weak acid and the pH of the solution, and we are asked to determine the value of K_a for the acid.

Plan Although we are dealing specifically with the ionization of a weak acid, this problem is similar to the equilibrium problems in Chapter 15. We can solve this problem using the method outlined in Sample Exercise 15.8, starting with the chemical reaction and a tabulation of initial and equilibrium concentrations.

Solve

The first step in solving any equilibrium problem is to write the equation for the equilibrium reaction. The ionization of formic acid can be written as:

$$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

The equilibrium expression is:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

From the measured pH, we can calculate $[H^+]$:

$$pH = -\log[H^+] = 2.38$$

$$\log[H^+] = -2.38$$

$$[H^+] = 10^{-2.38} = 4.2 \times 10^{-3}\,M$$

To determine the concentrations of the species involved in the equilibrium, we consider that the solution is initially 0.10 *M* in HCOOH molecules. We then consider the ionization of the acid into H^+ and $HCOO^-$. For each HCOOH molecule that ionizes, one H^+ ion and one $HCOO^-$ ion are produced in solution. Because the pH measurement indicates that $[H^+] = 4.2 \times 10^{-3}\,M$ at equilibrium, we can construct the following table:

	$HCOOH(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $HCOO^-(aq)$
Initial concentration (*M*)	0.10	0	0
Change in concentration (*M*)	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equilibrium concentration (*M*)	$(0.10 - 4.2 \times 10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

Notice that we have neglected the very small concentration of $H^+(aq)$ due to H_2O autoionization. Notice also that the amount of HCOOH that ionizes is very small compared with the initial concentration of the acid. To the number of significant figures we are using, the subtraction yields 0.10 *M*:

$$(0.10 - 4.2 \times 10^{-3})\,M \simeq 0.10\,M$$

We can now insert the equilibrium concentrations into the expression for K_a:

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

Check The magnitude of our answer is reasonable because K_a for a weak acid is usually between 10^{-2} and 10^{-10}.

Practice Exercise

A 0.50 *M* solution of an acid HA has pH = 2.24. What is the value of K_a for the acid? (**a**) 1.7×10^{-12} (**b**) 3.3×10^{-5} (**c**) 6.6×10^{-5} (**d**) 5.8×10^{-3} (**e**) 1.2×10^{-2}

reactions are generally very rapid. As a result, the measured or calculated pH for a weak acid always represents an equilibrium condition.

Percent Ionization

We have seen that the magnitude of K_a indicates the strength of a weak acid. Another measure of acid strength is **percent ionization**, defined as

$$\text{Percent ionization} = \frac{\text{concentration of ionized HA}}{\text{original concentration of HA}} \times 100\% \qquad [16.26]$$

The stronger the acid, the greater the percent ionization.

If we assume that the autoionization of H_2O is negligible, the concentration of acid that ionizes equals the concentration of $H^+(aq)$ that forms. Thus, the percent ionization for an acid HA can be expressed as

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\% \qquad [16.27]$$

For example, a 0.035 *M* solution of HNO_2 contains $3.7 \times 10^{-3}\,M\,H^+(aq)$ and its percent ionization is

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HNO_2]_{\text{initial}}} \times 100\% = \frac{3.7 \times 10^{-3}\,M}{0.035\,M} \times 100\% = 11\%$$

Sample Exercise 16.11

Calculating Percent Ionization

As calculated in Sample Exercise 16.10, a 0.10 *M* solution of methanoic acid (HCOOH) contains $4.2 \times 10^{-3}\,M\,H^+(aq)$. Calculate the percentage of the acid that is ionized.

SOLUTION

Analyze We are given the molar concentration of an aqueous solution of weak acid and the equilibrium concentration of $H^+(aq)$ and asked to determine the percent ionization of the acid.

Plan The percent ionization is given by Equation 16.27.

Solve

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HCOOH]_{\text{initial}}} \times 100\%$$

$$= \frac{4.2 \times 10^{-3}\,M}{0.10\,M} \times 100\% = 4.2\%$$

Practice Exercise

A 0.077 *M* solution of an acid HA has pH = 2.16. What is the percentage of the acid that is ionized?

(**a**) 0.090% (**b**) 0.69% (**c**) 0.90% (**d**) 3.6% (**e**) 9.0%

Using K_a to Calculate pH

Knowing the value of K_a and the initial concentration of a weak acid, we can calculate the concentration of $H^+(aq)$ in a solution of the acid.

How to Calculate pH Using K_a

1. Write the ionization equilibrium.
2. Write the equilibrium expression and the value for the equilibrium constant.
3. Express the concentrations involved in the equilibrium reaction.
4. Substitute the equilibrium concentrations into the equilibrium-constant expression and solve for *x*.

Let's use this process to calculate the pH at 25 °C of a 0.30 *M* solution of acetic acid (CH_3COOH).

1. The ionization equilibrium is:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad [16.28]$$

Notice that the hydrogen that ionizes is the one attached to an oxygen atom.

2. Taking $K_a = 1.8 \times 10^{-5}$ from Table 16.2, we write the equilibrium expression and its value.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \qquad [16.29]$$

3. Next we express the concentrations involved in the equilibrium reaction. This can be done with a little accounting, as described in Sample Exercise 16.10. Because

we want to find the equilibrium value for $[H^+]$, let's call this quantity x. The concentration of acetic acid before any of it ionizes is 0.30 *M*. The chemical equation tells us that for each molecule of CH_3COOH that ionizes, one $H^+(aq)$ and one $CH_3COO^-(aq)$ are formed. Consequently, if x moles per liter of $H^+(aq)$ form at equilibrium, x moles per liter of $CH_3COO^-(aq)$ must also form and x moles per liter of CH_3COOH must be ionized:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Initial concentration (*M*)	0.30	0	0
Change in concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.30 - x)$	x	x

4. Finally, we substitute the equilibrium concentrations into the equilibrium expression and solve for x:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5} \qquad [16.30]$$

This expression leads to a quadratic equation in x, which we can solve by using either an equation-solving calculator or the quadratic formula. We can simplify the problem, however, by noting that the value of K_a is quite small. As a result, the equilibrium lies far to the left and x is much smaller than the initial concentration of acetic acid. Thus, we *assume* that x is negligible relative to 0.30, so that $0.30 - x$ is essentially equal to 0.30. We can (and should!) check the validity of this assumption when we finish the problem. By using this assumption, Equation 16.30 becomes

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

Solving for x, we have

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$
$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$
$$[H^+] = x = 2.3 \times 10^{-3}\,M$$
$$pH = -\log(2.3 \times 10^{-3}) = 2.64$$

Now we check the validity of our simplifying assumption that $0.30 - x \simeq 0.30$. The value of x we determined is so small that, for this number of significant figures, the assumption is entirely valid. We are thus satisfied that the assumption was a reasonable one to make. Because x represents the moles per liter of acetic acid that ionize, we see that, in this particular case, less than 1% of the acetic acid molecules ionize:

$$\text{Percent ionization of } CH_3COOH = \frac{0.0023\,M}{0.30\,M} \times 100\% = 0.77\%$$

As a general rule, if x *is more than about 5% of the initial concentration value, it is better to use the quadratic formula*. You should always check the validity of any simplifying assumptions after you have finished solving a problem.

We have also made one other assumption, namely, that all of the H^+ in the solution comes from ionization of CH_3COOH. Are we justified in neglecting the autoionization of H_2O? The answer is yes—the additional $[H^+]$ due to water, which would be on the order of $10^{-7}\,M$, is negligible compared to the $[H^+]$ from the acid (which in this case is on the order of $10^{-3}\,M$). In extremely precise work, or in cases involving very dilute solutions of acids, we would need to consider the autoionization of water more fully.

Finally, we can compare the pH value of this weak acid with the pH of a solution of a strong acid of the same concentration. The pH of the 0.30 *M* acetic acid is 2.64, but the pH of a 0.30 *M* solution of a strong acid such as HCl is $-\log(0.30) = 0.52$. As expected, the pH of a solution of a weak acid is higher than that of a solution of a strong acid of the same molarity. (Remember, the higher the pH value, the *less* acidic the solution.)

Sample Exercise 16.12

Using K_a to Calculate pH

Calculate the pH of a 0.20 *M* solution of HCN. (Refer to Table 16.2 or Appendix D for the value of K_a.)

SOLUTION

Analyze We are given the molarity of a weak acid and are asked for the pH. From Table 16.2, K_a for HCN is 4.9×10^{-10}.

Plan We proceed as in the example just worked in the text, writing the chemical equation and constructing a table of initial and equilibrium concentrations in which the equilibrium concentration of H^+ is our unknown.

Solve Writing both the chemical equation for the ionization reaction that forms $H^+(aq)$ and the equilibrium expression for the reaction:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 4.9 \times 10^{-10}$$

Next, we tabulate the concentrations of the species involved in the equilibrium reaction, letting $x = [H^+]$ at equilibrium:

	$HCN(aq)$	$\rightleftharpoons$ $H^+(aq)$	+ $CN^-(aq)$
Initial concentration (*M*)	0.20	0	0
Change in concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.20 - x)$	x	x

Substituting the equilibrium concentrations into the equilibrium expression yields:

$$K_a = \frac{(x)(x)}{0.20 - x} = 4.9 \times 10^{-10}$$

We next make the simplifying approximation that x, the amount of acid that dissociates, is small compared with the initial concentration of acid, $0.20 - x \simeq 0.20$. Thus,

$$\frac{x^2}{0.20} = 4.9 \times 10^{-10}$$

Solving for x, we have:

$$x^2 = (0.20)(4.9 \times 10^{-10}) = 0.98 \times 10^{-10}$$

$$x = \sqrt{0.98 \times 10^{-10}} = 9.9 \times 10^{-6}\,M = [H^+]$$

A concentration of $9.9 \times 10^{-6}\,M$ is much smaller than 5% of 0.20 *M*, the initial HCN concentration. Our simplifying approximation is therefore appropriate. We now calculate the pH of the solution:

$$pH = -\log[H^+] = -\log(9.9 \times 10^{-6}) = 5.00$$

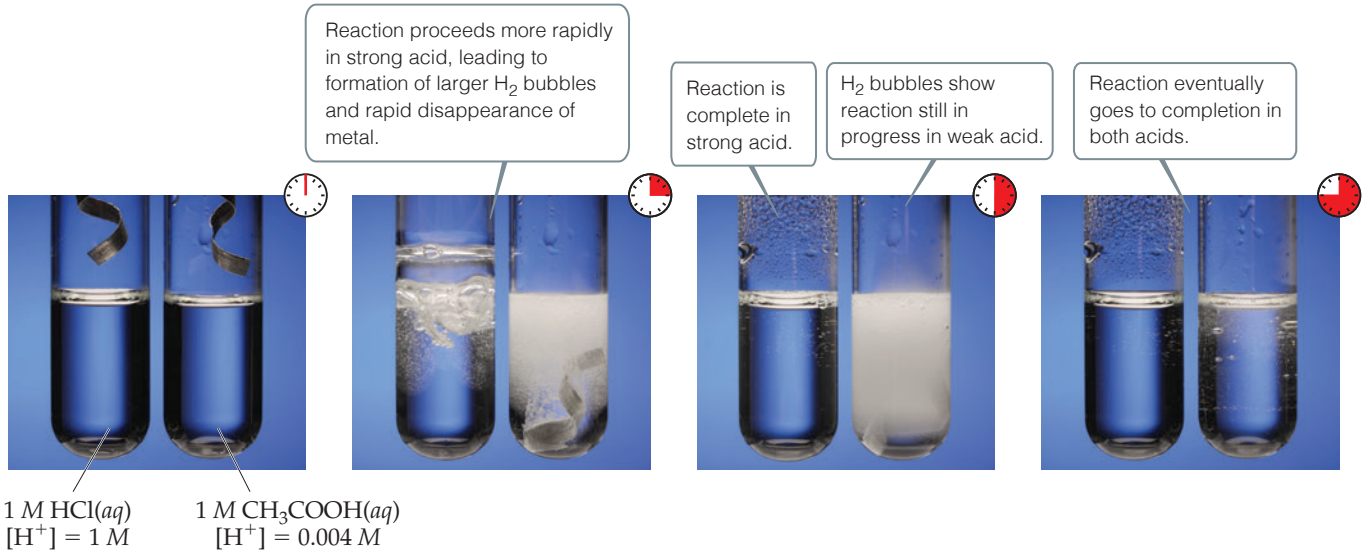
Practice Exercise

What is the pH of a 0.40 *M* solution of benzoic acid, C_6H_5COOH? (The K_a value for benzoic acid is given in Table 16.2.)

(a) 2.30 **(b)** 2.10 **(c)** 1.90 **(d)** 4.20 **(e)** 4.60

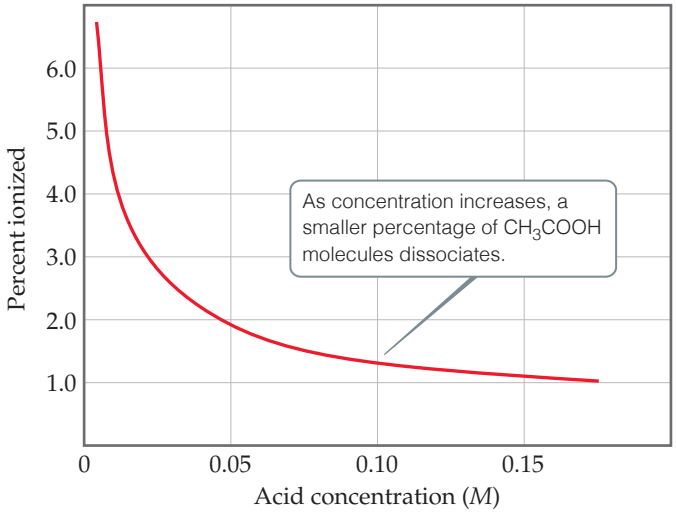
The properties of an acid solution that relate directly to the concentration of $H^+(aq)$, such as electrical conductivity and rate of reaction with an active metal, are less evident for a solution of a weak acid than for a solution of a strong acid of the same concentration. **Figure 16.11** presents an experiment that demonstrates this difference with 1 *M* CH_3COOH and 1 *M* HCl. The concentration of $H^+(aq)$ in 1 *M* CH_3COOH is only 0.004 *M*, whereas the 1 *M* HCl solution contains 1 *M* $H^+(aq)$. As a result, the reaction rate with the metal is much faster in the HCl solution.

As the concentration of a weak acid increases, the equilibrium concentration of $H^+(aq)$ increases, as expected. However, as shown in **Figure 16.12**, *the percent ionization decreases as the concentration increases*. Thus, the concentration of $H^+(aq)$ is not directly proportional to the concentration of the weak acid. For example, doubling the concentration of a weak acid does not double the concentration of $H^+(aq)$.



▲ **Figure 16.11** **The same reaction has different rates in a weak acid solution compared to a strong acid solution.** The bubbles are H_2 gas, which along with metal cations, is produced when a metal is oxidized by an acid.

Go Figure Is the trend observed in this graph consistent with Le Châtelier's principle? Explain.



▲ **Figure 16.12** **Effect of concentration on percent ionization in an acetic acid solution.**

Sample Exercise 16.13

Using the Quadratic Equation to Calculate pH and Percent Ionization

Calculate the pH and percentage of HF molecules ionized in a 0.10 M HF solution.

SOLUTION

Analyze We are asked to calculate the percent ionization of a solution of HF. From Appendix D, we find $K_a = 6.8 \times 10^{-4}$.

Plan We approach this problem as for previous equilibrium problems: We write the chemical equation for the equilibrium and tabulate the known and unknown concentrations of all species. We then substitute the equilibrium concentrations into the equilibrium expression and solve for the unknown concentration of H^+.

Solve

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

The equilibrium reaction and equilibrium concentrations are as follows:

Initial concentration (M)	0.10	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$(0.10 - x)$	x	x

The equilibrium expression is:

$$K_a = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{0.10 - x} = 6.8 \times 10^{-4}$$

When we try solving this equation using the approximation $0.10 - x \simeq 0.10$ (that is, by neglecting the concentration of acid that ionizes), we obtain:

$$x = 8.2 \times 10^{-3}\,M$$

Because this approximation is greater than 5% of 0.10 M, however, we should work the problem in standard quadratic form. Rearranging, we have:

$$x^2 = (0.10 - x)(6.8 \times 10^{-4})$$
$$= 6.8 \times 10^{-5} - (6.8 \times 10^{-4})x$$
$$x^2 + (6.8 \times 10^{-4})x - 6.8 \times 10^{-5} = 0$$

Substituting these values in the standard quadratic formula gives:

$$x = \frac{-6.8 \times 10^{-4} \pm \sqrt{(6.8 \times 10^{-4})^2 - 4(-6.8 \times 10^{-5})}}{2}$$
$$= \frac{-6.8 \times 10^{-4} \pm 1.6 \times 10^{-2}}{2}$$

Of the two solutions, only the positive value for x is chemically reasonable. From that value, we can determine $[H^+]$ and hence the pH:

$$x = [H^+] = [F^-] = 7.9 \times 10^{-3}\,M, \text{ so pH} = -\log[H^+] = 2.10$$

From our result, we can calculate the percent of molecules ionized:

$$\text{Percent ionization of HF} = \frac{\text{concentration ionized}}{\text{original concentration}} \times 100\%$$
$$= \frac{7.9 \times 10^{-3}\,M}{0.10\,M} \times 100\% = 7.9\%$$

Practice Exercise

What is the pH of a 0.010 M solution of HF?
(**a**) 1.58 (**b**) 2.10 (**c**) 2.30 (**d**) 2.58 (**e**) 2.64

Polyprotic Acids

Acids that have more than one ionizable H atom are known as **polyprotic acids**. Sulfurous acid (H_2SO_3), for example, can undergo two successive ionizations:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2} \qquad [16.31]$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8} \qquad [16.32]$$

Note that the acid-dissociation constants are labeled K_{a1} and K_{a2}. The numbers on the constants refer to the particular proton of the acid that is ionizing. Thus, K_{a2} always refers to the equilibrium involving removal of the second proton of a polyprotic acid.

We see that K_{a2} for sulfurous acid is much smaller than K_{a1}. Because of electrostatic attractions, we would expect a positively charged proton to be lost more readily from the neutral H_2SO_3 molecule than from the negatively charged HSO_3^- ion. This observation is general: *It is always easier to remove the first proton from a polyprotic acid than to remove the*

TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Carbonic	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Oxalic	HOOC—COOH	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Sulfuric	H_2SO_4	Large	1.2×10^{-2}	
Tartaric	$C_2H_2O_2(COOH)_2$	1.0×10^{-3}	4.6×10^{-5}	

second. Similarly, for an acid with three ionizable protons, it is easier to remove the second proton than the third. Thus, the K_a values become successively smaller as successive protons are removed.

The acid-dissociation constants for common polyprotic acids are listed in **Table 16.3**, and Appendix D provides a more complete list. The structure of citric acid illustrates the presence of multiple ionizable protons in **Figure 16.13**.

Notice in Table 16.3 that in most cases the K_a values for successive losses of protons differ by a factor of at least 10^3. Notice also that the value of K_{a1} for sulfuric acid is listed simply as "large." Sulfuric acid is a strong acid with respect to the removal of the first proton. Thus, the reaction for the first ionization step lies completely to the right:

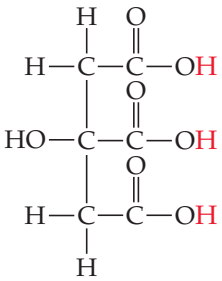
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad \text{(complete ionization)}$$

However, HSO_4^- is a weak acid for which $K_{a2} = 1.2 \times 10^{-2}$.

For many polyprotic acids K_{a1} is much larger than subsequent dissociation constants, in which case the $H^+(aq)$ in the solution comes almost entirely from the first ionization reaction. As long as successive K_a values differ by a factor of 10^3 or more, it is usually possible to obtain a satisfactory estimate of the pH of polyprotic acid solutions by treating the acids as if they were monoprotic, considering only K_{a1}.

Go Figure

How many protons per citric acid molecule are ionizable?



Citric acid

▲ **Figure 16.13 The structure of citric acid.**

Sample Exercise 16.14

Calculating the pH of a Solution of a Polyprotic Acid

The solubility of CO_2 in water at 25 °C and 10.13 kPa is 0.0037 *M*. The common practice is to assume that all the dissolved CO_2 is in the form of carbonic acid (H_2CO_3), which is produced in the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

What is the pH of a 0.0037 *M* solution of H_2CO_3?

SOLUTION

Analyze We are asked to determine the pH of a 0.0037 *M* solution of a polyprotic acid.

Plan H_2CO_3 is a diprotic acid; the two acid-dissociation constants, K_{a1} and K_{a2} (Table 16.3), differ by more than a factor of 10^3. Consequently, the pH can be determined by considering only K_{a1}, thereby treating the acid as if it were a monoprotic acid.

Solve

Proceeding as in Sample Exercises 16.12 and 16.13, we can write the equilibrium reaction and equilibrium concentrations as:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

	H_2CO_3	H^+	HCO_3^-
Initial concentration (*M*)	0.0037	0	0
Change in concentration (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.0037 - x)$	x	x

The equilibrium expression is:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.0037 - x} = 4.3 \times 10^{-7}$$

Solving this quadratic equation, we get:

$$x = 4.0 \times 10^{-5}\,M$$

Alternatively, because K_{a1} is small, we can make the simplifying approximation that x is small, so that:

$$0.0037 - x \simeq 0.0037$$

Thus,

$$\frac{(x)(x)}{0.0037} = 4.3 \times 10^{-7}$$

Solving for x, we have:

$$x^2 = (0.0037)(4.3 \times 10^{-7}) = 1.6 \times 10^{-9}$$

$$x = [H^+] = [HCO_3^-] = \sqrt{1.6 \times 10^{-9}} = 4.0 \times 10^{-5}\,M$$

Because we get the same value (to two significant figures) our simplifying assumption was justified. The pH is therefore:

$$pH = -\log[H^+] = -\log(4.0 \times 10^{-5}) = 4.40$$

Comment If we were asked for $[CO_3^{2-}]$ we would need to use K_{a2}. Let's illustrate that calculation. Using our calculated values of $[HCO_3^-]$ and $[H^+]$ and setting $[CO_3^{2-}] = y$, we have:

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

	HCO_3^-	H^+	CO_3^{2-}
Initial concentration (M)	4.0×10^{-5}	4.0×10^{-5}	0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$(4.0 \times 10^{-5} - y)$	$(4.0 \times 10^{-5} + y)$	y

Assuming that y is small relative to 4.0×10^{-5}, we have:

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(4.0 \times 10^{-5})(y)}{4.0 \times 10^{-5}} = 5.6 \times 10^{-11}$$

$$y = 5.6 \times 10^{-11}\,M = [CO_3^{2-}]$$

We see that the value for y is indeed very small compared with 4.0×10^{-5}, showing that our assumption was justified. It also shows that the ionization of HCO_3^- is negligible relative to that of H_2CO_3, as far as production of H^+ is concerned. However, it is the *only* source of CO_3^{2-}, which has a very low concentration in the solution. Our calculations thus tell us that in a solution of carbon dioxide in water, most of the CO_2 is in the form of CO_2 or H_2CO_3, only a small fraction ionizes to form H^+ and HCO_3^-, and an even smaller fraction ionizes to give CO_3^{2-}. Notice also that $[CO_3^{2-}]$ is numerically equal to K_{a2}.

Practice Exercise

What is the pH of a 0.28 M solution of ascorbic acid (Vitamin C)? (See Table 16.3 for K_{a1} and K_{a2}.)
(a) 2.04 **(b)** 2.32 **(c)** 2.82 **(d)** 4.65 **(e)** 6.17

A CLOSER LOOK Polyprotic Acids

Different protonation states of polyprotic acids exist at different pH values. Shown in **Figure 16.14** are the relative equilibrium concentrations of phosphoric acid and its successive conjugate bases as a function of pH.

We can learn many things from Figure 16.14. For instance, if the pH is greater than 4, there is essentially no H_3PO_4 left in solution. At pH > 14, the major component is the phosphate ion, PO_4^{3-}. We can also see that when the pH is equal to one of the pK_a values, the concentrations of the relevant conjugate acid-base pairs are equal. For instance, if you look at pH = 7.21, $[H_2PO_4^{2-}] = [HPO_4^-]$. This makes sense if we consider that the equilibrium reaction at that pH is:

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$

And therefore K_{a2} corresponds to

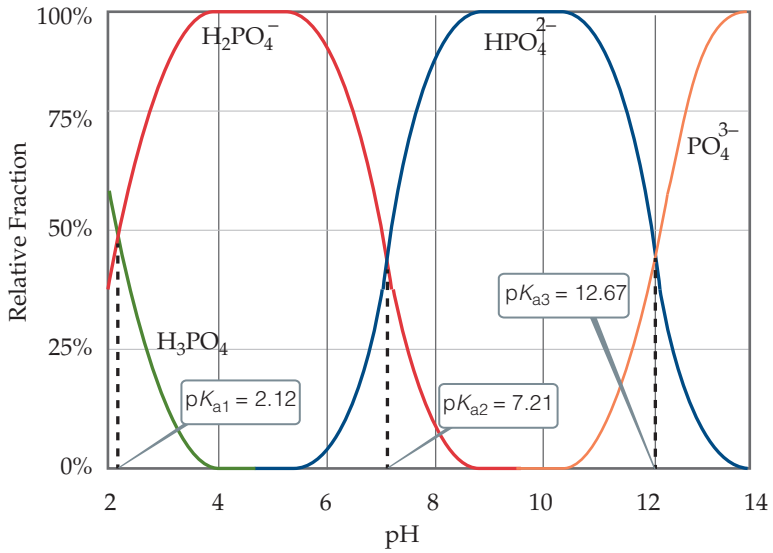
$$K_{a2} = [HPO_4^{2-}][H_3O]^+/[H_2PO_4^-]$$

Using our log rules, we can see that

$$pK_{a2} = \log([H_2PO_4^-]/[HPO_4^{2-}]) + pH$$

and therefore if pK_{a2} has the same value as the pH, the ratio of $[H_2PO_4^-]$ to $[HPO_4^{2-}]$ must be one (since the log of 1 is equal to zero).

Continued



▲ **Figure 16.14** **Relative fraction of phosphate species in water as a function of pH for phosphoric acid.**

Self-Assessment Exercise

16.24 A solution of benzoic acid has a pH of 2.63 ($K_a = 6.3 \times 10^{-5}$). What is the concentration of the solution?

(a) 0.027 *M*
(b) 0.087 *M*
(c) 11 *M*
(d) 37 *M*

Exercises

16.25 Write the chemical equation and the K_a expression for the acid dissociation of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (**a**) HSO_4^-, (**b**) C_6H_5OH.

16.26 Phenylacetic acid ($C_6H_5CH_2COOH$) is one of the substances that accumulates in the blood of people with phenylketonuria, an inherited disorder that can cause mental retardation or even death. A 0.085 *M* solution of $C_6H_5CH_2COOH$ has a pH of 2.68. Calculate the K_a value for this acid.

16.27 A 0.100 *M* solution of bromoacetic acid ($BrCH_2COOH$) is 13.2% ionized. Calculate $[H^+]$, $[BrCH_2COO^-]$, $[BrCH_2COOH]$ and K_a for bromoacetic acid.

16.28 The acid-dissociation constant for chlorous acid ($HClO_2$) is 1.1×10^{-2}. Calculate the concentrations of H_3O^+, ClO_2^-, and $HClO_2$ at equilibrium if the initial concentration of $HClO_2$ is 0.0200 *M*.

16.29 The active ingredient in aspirin is acetylsalicylic acid ($HC_9H_7O_4$), a monoprotic acid with $K_a = 3.3 \times 10^{-4}$ at 25 °C. What is the pH of a solution obtained by dissolving one regular aspirin tablet, containing 100 mg of acetylsalicylic acid, in 200 mL of water?

16.30 Calculate the percent ionization of propionic acid (C_2H_5COOH) in solutions of each of the following concentrations (K_a is given in Appendix D): (**a**) 0.250 *M*, (**b**) 0.0800 *M*, (**c**) 0.0200 *M*.

16.31 Tartaric acid is found in many fruits, including grapes, and is partially responsible for the dry texture of certain wines. Calculate the pH and the tartrate ion ($C_4H_4O_6^{2-}$) concentration for a 0.250 *M* solution of tartaric acid, for which the acid-dissociation constants are listed in Table 16.3. Did you have to make any approximations or assumptions in your calculation?

Answers to Self-Assessment Exercises

16.24 (b)

16.6 | Weak Bases



Dead tissue breaks down as a result of chemical degradation and by the action of bacteria. The latter often results in release of volatile amines and the name of two of them, cadaverine ($H_2N(CH_2)_5NH_2$) and putrescine ($H_2N(CH_2)_5NH_2$), suggest a bad smell accompanies the decomposition. The simplest amine is ammonia. The name has its origin in a mineral deposit close to a temple of the Egyptian deity Amun. The deposit was originally thought to be ammonium chloride, which has the pungent smell of ammonia associated with it. By the time it was found the deposit was likely to be common sea salt, the name was already established in the language. Amines are examples of weak bases. By the end of this section, you should be able to

- Perform calculations using K_a and K_b and determine the pH of a weak base solution

Many substances behave as weak bases in water. Weak bases react with water, abstracting protons from H_2O, thereby forming the conjugate acid of the base and OH^- ions:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq) \qquad [16.33]$$

The equilibrium expression for this reaction can be written as

$$K_b = \frac{[BH^+][OH^-]}{[B]} \qquad [16.34]$$

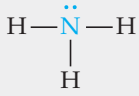
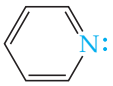
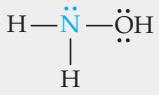
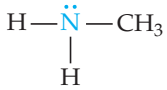
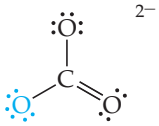
Water is the solvent, so it is omitted from the equilibrium expression. One of the most commonly encountered weak bases is ammonia, NH_3:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad [16.35]$$

As with K_w and K_a, the subscript b in K_b denotes that the equilibrium constant refers to a particular type of reaction, namely, the ionization of a weak base in water. The constant K_b, the **base-dissociation constant**, *always refers to the equilibrium in which a base reacts with H_2O to form the corresponding conjugate acid and OH^-.*

Table 16.4 lists the Lewis structures, conjugate acids, and K_b values for a number of weak bases in water. Appendix D includes a more extensive list. These bases contain one or more lone pairs of electrons because a lone pair is necessary to form the bond with H^+. Notice that in the neutral molecules in Table 16.4, the lone pairs are on nitrogen atoms. The other bases listed are anions derived from weak acids.

TABLE 16.4 Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)		NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)		$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)		$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)		$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)		H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})		HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)		HClO	3.3×10^{-7}

*The atom that accepts the proton is shown in blue.

Sample Exercise 16.15

Using K_b to Calculate $[OH^-]$

Calculate the concentration of OH^- in a 0.15 *M* solution of NH_3.

SOLUTION

Analyze We are given the concentration of a weak base and asked to determine the concentration of OH^-.

Plan We will use essentially the same procedure here as used in solving problems involving the ionization of weak acids—that is, write the chemical equation and tabulate initial and equilibrium concentrations.

Solve

The ionization reaction and equilibrium expression are:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Ignoring the concentration of H_2O because it is not involved in the equilibrium expression, we see that the equilibrium concentrations are:

	$NH_3(aq)$	+ $H_2O(l)$ ⇌	$NH_4^+(aq)$	+ OH^-
Initial concentration (*M*)	0.15	—	0	0
Change in concentration (*M*)	$-x$	—	$+x$	$+x$
Equilibrium concentration (*M*)	$(0.15 - x)$	—	x	x

Inserting these quantities into the equilibrium expression gives:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{0.15 - x} = 1.8 \times 10^{-5}$$

Continued

Because K_b is small, the amount of NH_3 that reacts with water is much smaller than the NH_3 concentration, and so we can neglect x relative to 0.15 *M*. Then we have:

$$\frac{x^2}{0.15} = 1.8 \times 10^{-5}$$

$$x^2 = (0.15)(1.8 \times 10^{-5}) = 2.7 \times 10^{-6}$$

$$x = [NH_4^+] = [OH^-] = \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3}\,M$$

Check The value obtained for x is only about 1% of the NH_3 concentration, 0.15 *M*. Therefore, neglecting x relative to 0.15 was justified.

Comment You may be asked to find the pH of a solution of a weak base. Once you have found $[OH^-]$, you can proceed as in Sample Exercise 16.9, where we calculated the pH of a strong base. In the present sample exercise, we have seen that the 0.15 *M* solution of NH_3 contains $[OH^-] = 1.6 \times 10^{-3}\,M$. Thus, pOH $= -\log(1.6 \times 10^{-3}) = 2.80$, and pH $= 14.00 - 2.80 = 11.20$. The pH of the solution is above 7 because we are dealing with a solution of a base.

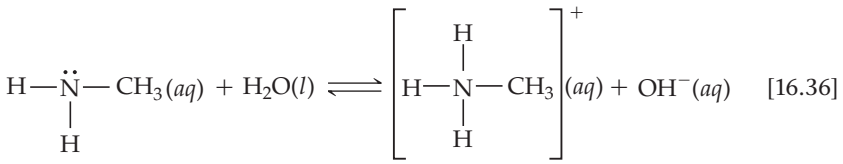
Practice Exercise

What is the pH of a 0.65 *M* solution of pyridine, C_5H_5N? (See Table 16.4 for K_b.)

(**a**) 4.48 (**b**) 8.96 (**c**) 9.52 (**d**) 9.62 (**e**) 9.71

Types of Weak Bases

Weak bases fall into two general categories. The first category is neutral substances that have an atom with a nonbonding pair of electrons that can accept a proton. Most of these bases, including all uncharged bases in Table 16.4, contain a nitrogen atom. These substances include ammonia and a related class of compounds called **amines** (Figure 16.15). In organic amines, at least one N—H bond in NH_3 is replaced with an N—C bond. Like NH_3, amines can abstract a proton from a water molecule by forming an N—H bond, as shown here for methylamine:



[16.36]

Anions of weak acids make up the second general category of weak bases. In an aqueous solution of sodium hypochlorite (NaClO), for example, NaClO dissociates to Na^+ and ClO^- ions. The Na^+ ion is always a spectator ion in acid–base reactions. The ClO^- ion, however, is the conjugate base of a weak acid, hypochlorous acid. Consequently, the ClO^- ion acts as a weak base in water:

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \qquad K_b = 3.3 \times 10^{-7} \qquad [16.37]$$

Sample Exercise 16.16

Using pH to Determine the Concentration of a Salt

A solution made by adding solid sodium hypochlorite (NaClO) to enough water to make 2.00 L of solution has a pH of 10.50. Using the information in Equation 16.37, calculate the number of moles of NaClO added to the water.

SOLUTION

Analyze NaClO is an ionic compound consisting of Na^+ and ClO^- ions. As such, it is a strong electrolyte that completely dissociates in solution into Na^+, a spectator ion, and ClO^- ion, a weak base with $K_b = 3.3 \times 10^{-7}$ (Equation 16.37). Given this information, we must calculate the number of moles of NaClO needed to increase the pH of 2.00 L of water to 10.50.

Plan From the pH, we can determine the equilibrium concentration of OH^-. We can then construct a table of initial and equilibrium concentrations in which the initial concentration of ClO^- is our unknown. We can calculate $[ClO^-]$ using the expression for K_b.

Solve

We can calculate $[OH^-]$ by using either Equation 16.16 or Equation 16.20; we will use the latter method here:

$$pOH = 14.00 - pH = 14.00 - 10.50 = 3.50$$

$$[OH^-] = 10^{-3.50} = 3.2 \times 10^{-4}\,M$$

This concentration is high enough that we can assume that Equation 16.37 is the only source of OH^-; that is, we can neglect any OH^- produced by the autoionization of H_2O. We now assume a value of x for the initial concentration of ClO^- and solve the equilibrium problem in the usual way.

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$$

Initial concentration (M)	x	—	0	0
Change in concentration (M)	-3.2×10^{-4}	—	$+3.2 \times 10^{-4}$	$+3.2 \times 10^{-4}$
Equilibrium concentration (M)	$(x - 3.2 \times 10^{-4})$	—	3.2×10^{-4}	3.2×10^{-4}

We now use the expression for the base-dissociation constant to solve for x:

$$K_b = \frac{[HClO][OH^-]}{[ClO^-]} = \frac{(3.2 \times 10^{-4})^2}{x - 3.2 \times 10^{-4}} = 3.3 \times 10^{-7}$$

$$x = \frac{(3.2 \times 10^{-4})^2}{3.3 \times 10^{-7}} + (3.2 \times 10^{-4}) = 0.31\,M$$

We say that the solution is 0.31 M in NaClO even though some of the ClO^- ions have reacted with water. Because the solution is 0.31 M in NaClO and the total volume of solution is 2.00 L, 0.62 mol of NaClO is the amount of the salt that was added to the water.

Practice Exercise

The benzoate ion, $C_6H_5COO^-$, is a weak base with $K_b = 1.6 \times 10^{-10}$. How many moles of sodium benzoate are present in 0.50 L of a solution of NaC_6H_5COO if the pH is 9.04?
(**a**) 0.38 (**b**) 0.66 (**c**) 0.76 (**d**) 1.5 (**e**) 2.9

In Figure 16.6 we saw that bleach is quite basic (pH values of 12–13). Common chlorine bleach is typically a 5% NaOCl solution.

Relationship Between K_a and K_b

We have seen in a qualitative way that the stronger an acid, the weaker its conjugate base. Let us be more quantitative and consider the NH_4^+ and NH_3 conjugate acid–base pair. Each species reacts with water. For the acid, NH_4^+, the equilibrium is

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

or written in its simpler form:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \qquad [16.38]$$

For the base, NH_3, the equilibrium is

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [16.39]$$

Each equilibrium is expressed by a dissociation constant:

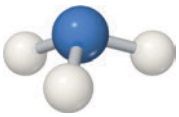
$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

When we add Equations 16.38 and 16.39, the NH_4^+ and NH_3 species cancel and we are left with the autoionization of water:

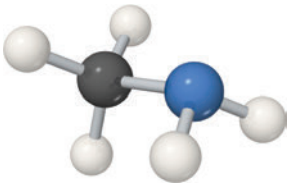
$$\begin{array}{r} NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq) \\ NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \\ \hline H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \end{array}$$

Go Figure

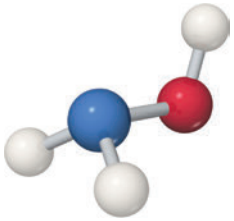
When hydroxylamine acts as a base, which atom accepts the proton?



Ammonia
NH_3



Methylamine
CH_3NH_2



Hydroxylamine
NH_2OH

▲ **Figure 16.15** **Structures of ammonia and two simple amines.**

Recall that when two equations are added to give a third, the equilibrium constant associated with the third equation equals the product of the equilibrium constants of the first two equations.

Applying this rule to our present example, we see that when we multiply K_a and K_b, we obtain

$$K_a \times K_b = \left(\frac{[\cancel{NH_3}][H^+]}{[\cancel{NH_4^+}]}\right)\left(\frac{[\cancel{NH_4^+}][OH^-]}{[\cancel{NH_3}]}\right)$$

$$= [H^+][OH^-] = K_w$$

Thus, the product of K_a and K_b is the ion-product constant for water, K_w (Equation 16.16). We expect this result because adding Equations 16.38 and 16.39 gave us the autoionization equilibrium for water, for which the equilibrium constant is K_w.

This result holds for any conjugate acid–base pair. In general, *the product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base equals the ion-product constant for water:*

$$K_a \times K_b = K_w \quad \text{(for a conjugate acid–base pair)} \qquad [16.40]$$

Note that this relationship only holds true for conjugate acid–base pairs. You should not use Equation 16.40 for any random pair of acids and bases! As the strength of an acid increases (K_a gets larger), the strength of its conjugate base must decrease (K_b gets smaller), so that the product $K_a \times K_b$ remains 1.0×10^{-14} at 25 °C. **Table 16.5** demonstrates this relationship.

By using Equation 16.40, we can calculate K_b for any weak base if we know K_a for its conjugate acid. Similarly, we can calculate K_a for a weak acid if we know K_b for its conjugate base. As a practical consequence, ionization constants are often listed for only one member of a conjugate acid–base pair. For example, Appendix D does not contain K_b values for the anions of weak acids because they can be readily calculated from the tabulated K_a values for their conjugate acids.

Recall that we often express $[H^+]$ as pH: $pH = -\log[H^+]$. This "p" nomenclature is often used for other very small numbers. For example, if you look up the values for acid- or base-dissociation constants in a chemistry handbook, you may find them expressed as pK_a or pK_b:

$$pK_a = -\log K_a \quad \text{and} \quad pK_b = -\log K_b \qquad [16.41]$$

Using this nomenclature, we can write Equation 16.40 in terms of pK_a and pK_b by taking the negative logarithm of both sides:

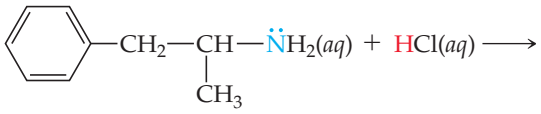
$$pK_a + pK_b = pK_w = 14.00 \quad \text{at 25 °C (conjugate acid–base pair)} \qquad [16.42]$$

TABLE 16.5 Some Conjugate Acid–Base Pairs

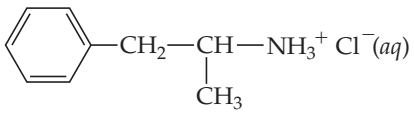
Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

CHEMISTRY PUT TO WORK Amines and Amine Hydrochlorides

Many drugs, including quinine, codeine, caffeine, and amphetamine, are amines. Like other amines, these substances are weak bases; the amine nitrogen is readily protonated upon treatment with an acid. The resulting products are called *acid salts*. If we use A as the abbreviation for an amine, the acid salt formed by reaction with hydrochloric acid can be written AH^+Cl^-. It can also be written as A · HCl and referred to as a hydrochloride. Amphetamine hydrochloride, for example, is the acid salt formed by treating amphetamine with HCl:



Amphetamine



Amphetamine hydrochloride

Acid salts are much less volatile, more stable, and generally more water soluble than the corresponding amines. For this reason, many drugs that are amines are sold and administered as acid salts. Some examples of over-the-counter medications that contain amine hydrochlorides as active ingredients are shown in Figure 16.16.

Related Exercises: 16.58, 16.92, 16.36, 16.111, 16.124, 16.134



▲ **Figure 16.16** **Some over-the-counter medications in which an amine hydrochloride is a major active ingredient.**

Sample Exercise 16.17

Calculating K_a or K_b for a Conjugate Acid–Base Pair

Calculate (**a**) K_b for the fluoride ion, (**b**) K_a for the ammonium ion.

SOLUTION

Analyze We are asked to determine dissociation constants for F^-, the conjugate base of HF, and NH_4^+, the conjugate acid of NH_3.

Plan We can use the tabulated K values for HF and NH_3 and the relationship between K_a and K_b to calculate the dissociation constants for their conjugates, F^- and NH_4^+.

Solve

(**a**) For the weak acid HF, Table 16.2 and Appendix D give $K_a = 6.8 \times 10^{-4}$. We can use Equation 16.40 to calculate K_b for the conjugate base, F^-:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

(**b**) For NH_3, Table 16.4 and Appendix D give $K_b = 1.8 \times 10^{-5}$, and this value in Equation 16.40 gives us K_a for the conjugate acid, NH_4^+:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Check The respective K values for F^- and NH_4^+ are listed in Table 16.5, where we see that the values calculated here agree with those in Table 16.5.

Practice Exercise

By using information from Appendix D, put the following three substances in order of weakest to strongest base:
(i) $(CH_3)_3N$, (ii) $HCOO^-$, (iii) BrO^-.
(**a**) i < ii < iii (**b**) ii < i < iii (**c**) iii < i < ii
(**d**) ii < iii < i (**e**) iii < ii < i

Self-Assessment Exercise

16.32 Consider the data:

	CH_3COOH	HCN	HNO_2	NH_4^+
pK_a =	4.74	9.31	3.35	9.26

Write the conjugate bases of thee four weak acids and rank them in order of increasing base strength.

(a) $CH_3COO^- < CN^- < NO_2^- < NH_3$
(b) $NO_2^- < CH_3COO^- < NH_3 < CN^-$
(c) $CN^- < NH_3 < CH_3COO^- < NO_2^-$

Exercises

16.33 The hypochlorite ion, ClO^-, acts as a weak base. (**a**) Is ClO^- a stronger or weaker base than hydroxylamine? Use Tables 16.2 and 16.4 (**b**) When ClO^- acts as a base, which atom, Cl or O, acts as the proton acceptor? (**c**) Can you use formal charges to rationalize your answer to part (b)?

16.34 Write the chemical equation and the K_b expression for the reaction of each of the following bases with water: (**a**) propylamine, $C_3H_7NH_2$; (**b**) monohydrogen phosphate ion, HPO_4^{2-}; (**c**) benzoate ion, $C_6H_5CO_2^-$.

16.35 Calculate the molar concentration of OH^- in a 0.724 *M* solution of hypobromite ion (BrO^-; $K_b = 4.0 \times 10^{-6}$). What is the pH of this solution?

16.36 Codeine ($C_{18}H_{21}NO_3$) is a weak organic base. A 5.0×10^{-3} *M* solution of codeine has a pH of 9.95. Calculate the value of K_b for this substance. What is the pK_b for this base?

16.37 Phenol, C_6H_5OH, has a K_a of 1.3×10^{-10}.

(**a**) Write out the K_a reaction for phenol.

(**b**) Calculate K_b for phenol's conjugate base.

(**c**) Is phenol a stronger or weaker acid than water?

16.38 (**a**) Given that K_b for ammonia is 1.8×10^{-5} and that for hydroxylamine is 1.1×10^{-8}, which is the stronger base? (**b**) Which is the stronger acid, the ammonium ion or the hydroxylammonium ion? (**c**) Calculate K_a values for NH_4^+ and H_3NOH^+.

Answers to Self-Assessment Exercises

16.32 (b)

16.7 Acid–Base Properties of Salt Solutions



Hydrangeas, often bred for their spectacular blooms, are sensitive to the pH of the soil they are grown in. If the soil is slightly acidic (pH ~ 5.5), the flowers will have a blue color, while alkaline soils will grow hydrangeas bearing pink flowers. Growers keen to show off

a blue flowering plant will add salts, usually aluminum sulfate, to their hydrangeas to lower the pH in the vicinity of the roots. By the end of this section, you should be able to

- Predict the pH of a water solution of any soluble salt.

Even before you began this chapter, you were undoubtedly aware of many substances that are acidic, such as HNO_3, HCl, and H_2SO_4, and others that are basic, such as NaOH and NH_3. However, our discussion up to this point in the chapter has indicated that ions can also exhibit acidic or basic properties. For example, we calculated K_a for NH_4^+ and K_b for F^- in Sample Exercise 16.17. Such behavior implies that salt solutions can be acidic or basic. Before proceeding with further discussions of acids and bases, let's examine the way dissolved salts can affect pH.

Because nearly all salts are strong electrolytes, we can assume that any salt dissolved in water is completely dissociated. Consequently, the acid–base properties of salt solutions are due to the behavior of the cations and anions. Many ions react with water to generate $H^+(aq)$ or $OH^-(aq)$ ions. This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted qualitatively by considering the salt's cations and anions.

An Anion's Ability to React with Water

In general, an anion A^- in solution can be considered the conjugate base of an acid. For example, Cl^- is the conjugate base of HCl, and CH_3COO^- is the conjugate base of CH_3COOH. Whether an anion reacts with water to produce hydroxide ions depends on the strength of the anion's conjugate acid. To identify the acid and assess its strength, we add a proton to the anion's formula. If the acid HA determined in this way is one of the seven strong acids listed at the beginning of Section 16.5, the anion has a negligible tendency to produce OH^- ions from water and does not affect the pH of the solution. The presence of Cl^- in an aqueous solution, for example, does not result in the production of any OH^- and does not affect the pH. Thus, Cl^- is always a spectator ion in acid–base chemistry.

If HA is *not* one of the seven common strong acids, it is a weak acid. In this case, the conjugate base A^- is a weak base, and it reacts to a small extent with water to produce the weak acid and hydroxide ions:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad [16.43]$$

The OH^- ion generated in this way increases the pH of the solution, making it basic. Acetate ion, for example, being the conjugate base of a weak acid, reacts with water to produce acetic acid and hydroxide ions, thereby increasing the pH of the solution:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad [16.44]$$

The situation is more complicated for salts containing anions that have ionizable protons, such as HSO_3^-. These salts are amphiprotic (Section 16.2), and how they behave in water is determined by the relative magnitudes of K_a and K_b for the ion, as shown in Sample Exercise 16.19. If $K_a > K_b$, the ion causes the solution to be acidic. If $K_b > K_a$, the solution is made basic by the ion.

A Cation's Ability to React with Water

Polyatomic cations containing one or more protons can be considered the conjugate acids of weak bases. The NH_4^+ ion, for example, is the conjugate acid of the weak base NH_3. Thus, NH_4^+ is a weak acid and will donate a proton to water, producing hydronium ions and thereby lowering the pH:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad [16.45]$$

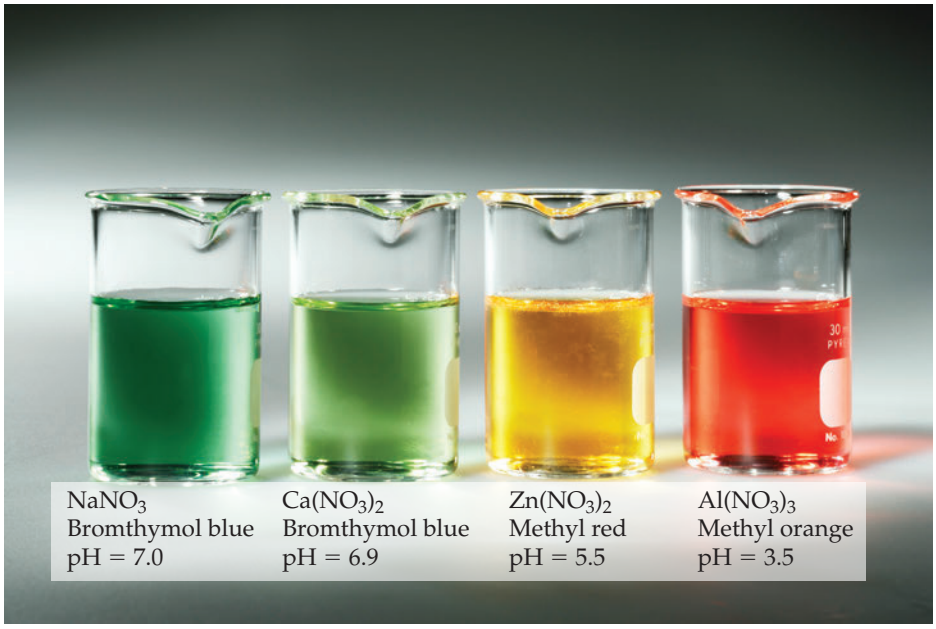
A more unusual situation is encountered with some metal salts. For instance, if you dissolve $Fe(NO_3)_3$ in water, the solution is quite acidic. Why would this be the case?

You might think that the nitrate ion is somehow producing nitric acid, but you would be wrong. Recall that nitrate is the conjugate base of a strong acid, and therefore its reaction with water is negligible. Instead, we have to consider what Fe^{3+} is doing in solution. It turns out that other small, highly charged metal cations like Fe^{3+} also create

TABLE 16.6 Acid-Dissociation Constants for Metal Cations in Aqueous Solution at 25 °C

Cation	K_a
Fe^{3+}	6.3×10^{-3}
Cr^{3+}	1.6×10^{-4}
Al^{3+}	1.4×10^{-5}
Fe^{2+}	3.2×10^{-10}
Zn^{2+}	2.5×10^{-10}
Ni^{2+}	2.5×10^{-11}

Go Figure Why do we need to use multiple acid–base indicators in this figure?

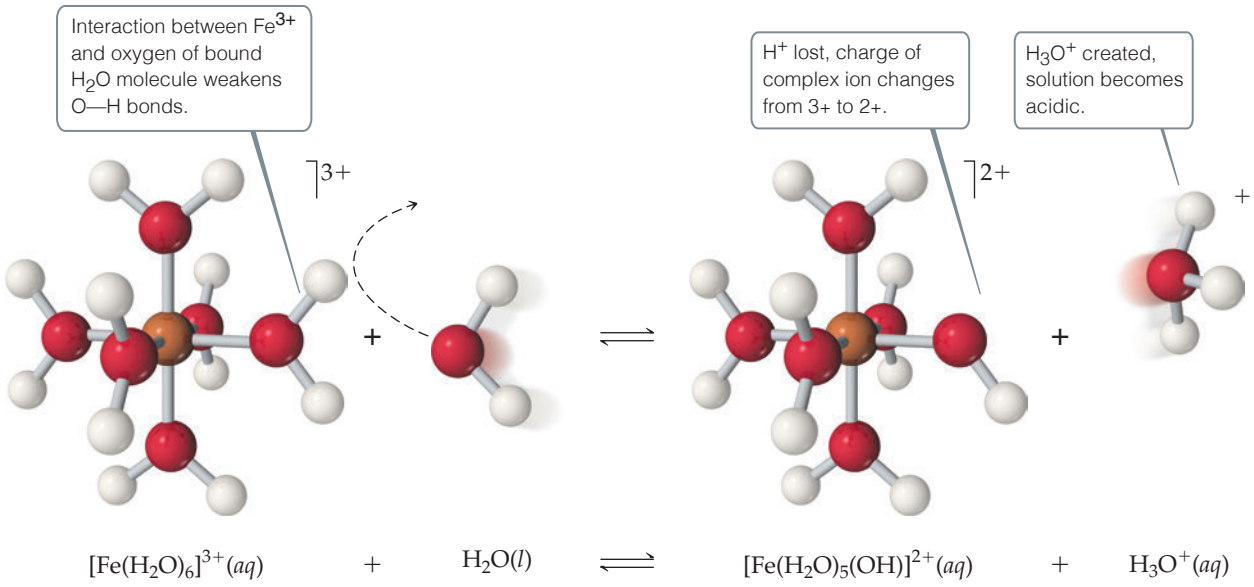


▲ **Figure 16.17 Effect of cations on solution pH.** The pH values of 1.0 *M* solutions of four nitrate salts are estimated using acid–base indicators.

surprisingly acidic solutions in water (Table 16.6). A comparison of Fe^{2+} and Fe^{3+} values in the table illustrates how acidity increases as ionic charge increases.

Notice that K_a values for the 3+ ions in Table 16.6 are comparable to the values for familiar weak acids, such as acetic acid ($K_a = 1.8 \times 10^{-5}$). In contrast, the ions of alkali and alkaline earth metals, being relatively large and not highly charged, do not react with water and therefore do not affect pH. Note that these are the same cations found in the strong bases (Section 16.5). The different tendencies of four cations to lower the pH of a solution are illustrated in Figure 16.17.

The mechanism by which metal ions produce acidic solutions is shown in Figure 16.18. Because metal ions are positively charged, they attract the unshared electron



▲ **Figure 16.18 A hydrated Fe^{3+} ion acts as an acid by donating an H^+ from a bound water molecule to a free H_2O molecule, forming H_3O^+.**

pairs of water molecules and become hydrated. The larger the charge on the metal ion, the stronger the interaction between the ion and the oxygen of its hydrating water molecules. As the strength of this interaction increases, the O—H bonds in the hydrating water molecules become weaker. This facilitates transfer of protons from the hydration water molecules to solvent water molecules.

Combined Effect of Cation and Anion in Solution

To determine whether a salt forms an acidic, a basic, or a neutral solution when dissolved in water, we must consider the action of both cation and anion. There are four possible combinations.

1. If the salt contains an anion that does not react with water and a cation that does not react with water, we expect the pH to be neutral. Such is the case when the anion is a conjugate base of a strong acid and the cation is either from Group 1 or one of the heavier members of Group 2 (Ca^{2+}, Sr^{2+}, and Ba^{2+}). *Examples*: NaCl, $Ba(NO_3)_2$, $RbClO_4$.
2. If the salt contains an anion that reacts with water to produce hydroxide ions and a cation that does not react with water, we expect the pH to be basic. Such is the case when the anion is the conjugate base of a weak acid and the cation is either from Group 1 or one of the heavier members of Group 2 (Ca^{2+}, Sr^{2+}, and Ba^{2+}). *Examples*: NaClO, RbF, $BaSO_3$.
3. If the salt contains a cation that reacts with water to produce hydronium ions and an anion that does not react with water, we expect the pH to be acidic. Such is the case when the cation is a conjugate acid of a weak base or a small cation with a charge of 2+ or greater. *Examples*: NH_4NO_3, $AlCl_3$, $Fe(NO_3)_3$.
4. If the salt contains an anion and a cation *both* capable of reacting with water, both hydroxide ions and hydronium ions are produced. Whether the solution is basic, neutral, or acidic depends on the relative abilities of the ions to react with water. *Examples*: NH_4ClO, $Al(CH_3COO)_3$, CrF_3.

Sample Exercise 16.18

Determining Whether Salt Solutions Are Acidic, Basic, or Neutral

Determine whether aqueous solutions of each of these salts are acidic, basic, or neutral: (**a**) $Ba(CH_3COO)_2$, (**b**) NH_4Cl, (**c**) CH_3NH_3Br, (**d**) KNO_3, (**e**) $Al(ClO_4)_3$.

SOLUTION

Analyze We are given the chemical formulas of five ionic compounds (salts) and asked whether their aqueous solutions will be acidic, basic, or neutral.

Plan We can determine whether a solution of a salt is acidic, basic, or neutral by identifying the ions in solution and by assessing how each ion will affect the pH.

Solve

(**a**) This solution contains barium ions and acetate ions. The cation is an ion of a heavy alkaline earth metal and will therefore not affect the pH. The anion, CH_3COO^-, is the conjugate base of the weak acid CH_3COOH and will hydrolyze to produce OH^- ions, thereby making the solution basic.

(**b**) In this solution, NH_4^+ is the conjugate acid of a weak base (NH_3) and is therefore acidic. Cl^- is the conjugate base of a strong acid (HCl) and therefore has no influence on the pH of the solution. Because the solution contains an ion that is acidic (NH_4^+) and one that has no influence on pH (Cl^-), the solution of NH_4Cl will be acidic.

(**c**) Here $CH_3NH_3^+$ is the conjugate acid of a weak base (CH_3NH_2, an amine) and is therefore acidic, and Br^- is the conjugate base of a strong acid (HBr) and therefore pH neutral. Because the solution contains one ion that is acidic and one that has no influence on pH, the solution of CH_3NH_3Br will be acidic.

(**d**) This solution contains the K^+ ion, which is a cation of group 1, and the NO_3^- ion, which is the conjugate base of the strong acid HNO_3. Neither of the ions will react with water to any appreciable extent, making the solution neutral.

(**e**) This solution contains Al^{3+} and ClO_4^- ions. Cations, such as Al^{3+}, that have a charge of 3+ or higher are acidic. The ClO_4^- ion is the conjugate base of a strong acid ($HClO_4$) and therefore does not affect pH. Thus, the solution of $Al(ClO_4)_3$ will be acidic.

Practice Exercise

Order the following solutions from lowest to highest pH: (i) 0.10 *M* NaClO, (ii) 0.10 *M* KBr, (iii) 0.10 *M* NH_4ClO_4.

(**a**) i < ii < iii (**b**) ii < i < iii (**c**) iii < i < ii
(**d**) ii < iii < i (**e**) iii < ii < i

Sample Exercise 16.19

Predicting Whether the Solution of an Amphiprotic Anion Is Acidic or Basic

Predict whether the salt Na_2HPO_4 forms an acidic solution or a basic solution when dissolved in water.

SOLUTION

Analyze We are asked to predict whether a solution of Na_2HPO_4 is acidic or basic. This substance is an ionic compound composed of Na^+ and HPO_4^{2-} ions.

Plan We need to evaluate each ion, predicting whether it is acidic or basic. Because Na^+ is a cation of Group 1, it has no influence on pH. Thus, our analysis of whether the solution is acidic or basic must focus on the behavior of the HPO_4^{2-} ion. We need to consider that HPO_4^{2-} can act as either an acid or a base:

$$\textit{As acid} \quad HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad [16.46]$$

$$\textit{As base} \quad HPO_4^{2-}(aq) + H_2O \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq) \qquad [16.47]$$

Of these two reactions, the one with the larger equilibrium constant determines whether the solution is acidic or basic.

Solve The value of K_a for Equation 16.46 is K_{a3} for H_3PO_4: 4.2×10^{-13} (Table 16.3). For Equation 16.47, we must calculate K_b for the base HPO_4^{2-} from the value of K_a for its conjugate acid, $H_2PO_4^-$, and the relationship $K_a \times K_b = K_w$ (Equation 16.40). The relevant value of K_a for $H_2PO_4^-$ is K_{a2} for H_3PO_4: 6.2×10^{-8} (from Table 16.3). We therefore have

$$K_b(HPO_4^{2-}) \times K_a(H_2PO_4^-) = K_w = 1.0 \times 10^{-14}$$

$$K_b(HPO_4^{2-}) = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}.$$

This K_b value is more than 10^5 times larger than K_a for HPO_4^{2-}; thus, the reaction in Equation 16.47 predominates over that in Equation 16.46, and the solution is basic.

Practice Exercise

How many of the following salts are expected to produce acidic solutions (see Table 16.3 for data): $NaHSO_4$, $NaHC_2O_4$, NaH_2PO_4, and $NaHCO_3$?
(**a**) 0 (**b**) 1 (**c**) 2 (**d**) 3 (**e**) 4

Self-Assessment Exercise

16.39 A dilute solution of a salt had the measured pH of 8.3. Which one of these salts is likely to be in the solution?

(a) $AlCl_3$
(b) NaBr
(c) NH_4NO_3
(d) K_2CO_3
(e) CH_3NH_3Cl

Exercises

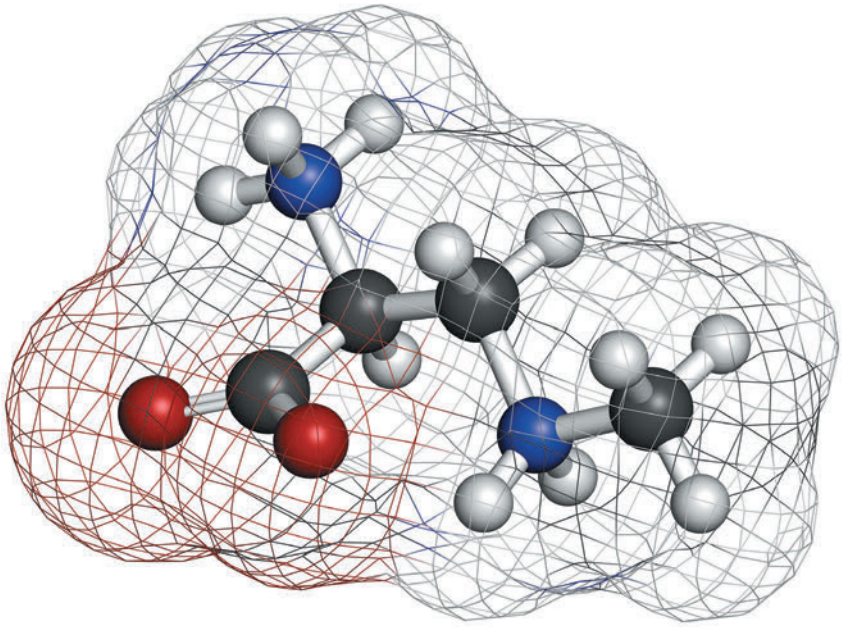
16.40 Predict whether aqueous solutions of the following substances are acidic, basic, or neutral: (**a**) $AlCl_3$, (**b**) NaBr, (**c**) NaClO, (**d**) $[CH_3NH_3]NO_3$, (**e**) Na_2SO_3.

16.41 An unknown salt is either KBr, NH_4Cl, KCN, or K_2CO_3. If a 0.100 *M* solution of the salt is neutral, what is the identity of the salt?

Answers to Self-Assessment Exercises

16.39 (d)

16.8 | Acid–Base Behavior and Chemical Structure



When a substance is dissolved in water, it may behave as an acid or a base, or exhibit no acid–base properties. How does the chemical structure of a substance determine which of these behaviors is exhibited by the substance? For example, why do some substances that contain OH groups behave as bases, releasing OH^- ions into solution, whereas others behave as acids, ionizing to release H^+ ions? Can a substance act as an acid in a solvent other than water? In this section, we discuss briefly the effects of chemical structure on acid–base behavior and broaden our definition of an acid and a base.

- Predict the relative strength of a series of acids from their molecular structures.
- Define and identify Lewis acids and bases.

Factors That Affect Acid Strength

The strength of an acid is often affected by three separate factors.

- **H—A Bond Polarity** A molecule containing H will act as a proton donor (an acid) only if the H—A bond is polarized such that the H atom has a partial positive charge. Recall that we indicate such polarization in this way:

$$\overset{+}{\longrightarrow}$$
$$H—A$$

  In ionic hydrides, such as NaH, the bond is polarized in the opposite way: The H atom possesses a negative charge and behaves as a proton acceptor (a base). Nonpolar H—A bonds, such as the H—C bond in CH_4, produce neither acidic nor basic aqueous solutions. *In general, as the H—A bond polarity increases, to draw more electron density from H, the stronger the acid.*
- **H—A Bond Strength** The strength of the bond also helps determine whether a molecule containing an H—A bond donates a proton. Very strong bonds are less easily broken than weaker ones. This factor is important, for example, in the hydrogen halides. The H—F bond is the most polar H—A bond. You therefore might expect HF to be a very strong acid if bond polarity were all that mattered. However,

the H—A bond strength increases as you move up the group: 299 kJ/mol in HI, 366 kJ/mol in HBr, 431 kJ/mol in HCl, and 567 kJ/mol in HF. Because HF has the highest bond strength among the hydrogen halides, it is a weak acid, whereas all the other hydrogen halides are strong acids in water. *In general, as the H—A bond strength decreases, the stronger the acid.*

- **Conjugate Base Stability** A third factor that affects the ease with which a hydrogen atom ionizes from HA is the stability of the conjugate base, A^-. *In general, the greater the stability of the conjugate base, the stronger the acid.*

Binary Acids

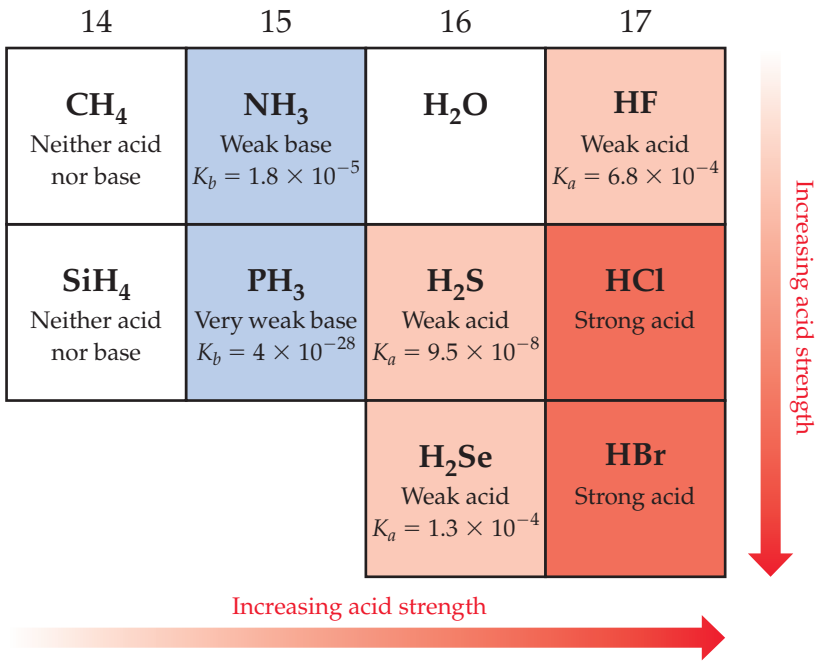
For a series of binary acids HA in which A represents members of the same *group* in the periodic table, the strength of the H—A bond is generally the most important factor determining acid strength. The strength of an H—A bond tends to decrease as the element A increases in size. As a result, the bond strength decreases and acidity increases down a group. Thus, HCl is a stronger acid than HF, and H_2S is a stronger acid than H_2O.

Bond polarity is the major factor determining acidity for binary acids HA when A represents members of the same *period*. Thus, acidity increases as the electronegativity of the element A increases, as it generally does moving from left to right across a period. For example, the difference in acidity of the Period 2 elements is $CH_4 < NH_3 \ll H_2O < HF$. Because the C—H bond is essentially nonpolar, CH_4 shows no tendency to form H^+ and CH_3^- ions. Although the N—H bond is polar, NH_3 has a nonbonding pair of electrons on the nitrogen atom that dominates its chemistry, so NH_3 acts as a base rather than an acid.

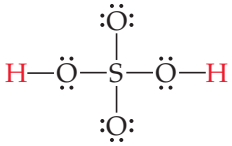
The periodic trends in the acid strengths of binary compounds of hydrogen and the nonmetals of Periods 2 and 3 are summarized in Figure 16.19.

Oxyacids

Many common acids, such as sulfuric acid, contain one or more O—H bonds:

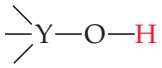


▲ **Figure 16.19** **Trends in acid strength for the binary hydrides of Periods 2–4.**



Acids in which OH groups and possibly additional oxygen atoms are bound to a central atom are called **oxyacids**. At first it may seem confusing that the OH group, which we know behaves as a base, is also present in some acids. Let's take a closer look at what factors determine whether a given OH group behaves as a base or as an acid.

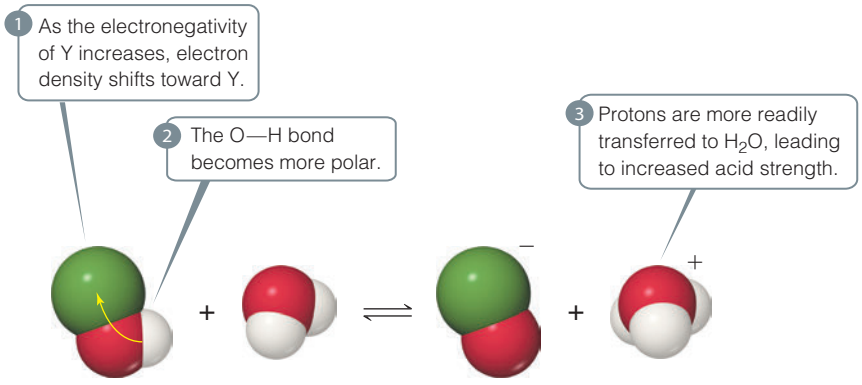
Consider an OH group bound to some atom Y, which might in turn have other groups attached to it:



At one extreme, Y might be a metal, such as Na or Mg. Because of the low electronegativity of metals, the pair of electrons shared between Y and O is completely transferred to oxygen, and an ionic compound containing OH^- is formed. Such compounds are therefore sources of OH^- ions and behave as bases, as in NaOH and $Mg(OH)_2$.

When Y is a nonmetal, the bond to O is covalent and the substance does not readily lose OH^-. Instead, these compounds are either acidic or neutral. *Generally, as the electronegativity of Y increases, so does the acidity of the substance.* This happens for two reasons: First, as electron density is drawn toward Y, the O—H bond becomes weaker and more polar, thereby favoring loss of H^+. Second, because the conjugate base of any acid YOH is usually an anion, its stability generally increases as the electronegativity of Y increases. This trend is illustrated by the K_a values of the hypohalous acids (YOH acids where Y is a halide ion), which decrease as the electronegativity of the halogen atom decreases (**Figure 16.20**).

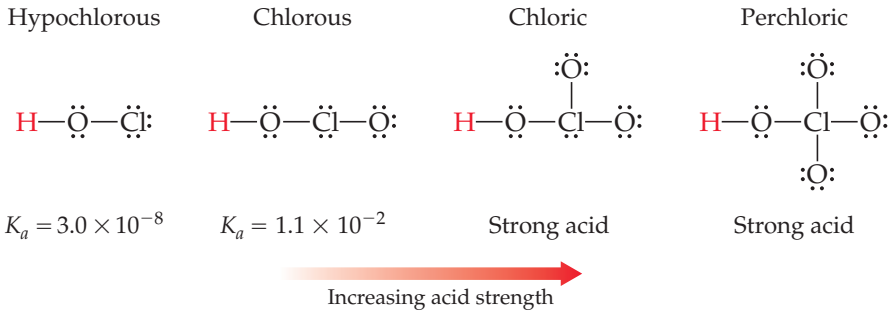
Go Figure At equilibrium, which of the two species with a halogen atom (green) is present in greater concentration?



Substance	Y—OH	Electronegativity of Y	Dissociation constant
Hypochlorous acid	Cl—OH	3.0	$K_a = 3.0 \times 10^{-8}$
Hypobromous acid	Br—OH	2.8	$K_a = 2.5 \times 10^{-9}$
Hypoiodous acid	I—OH	2.5	$K_a = 2.3 \times 10^{-11}$
Water	H—OH	2.1	$K_w = 1.0 \times 10^{-14}$

▲ **Figure 16.20** Acidity of the hypohalous oxyacids (YOH) and water as a function of electronegativity of Y.

Many oxyacids contain additional oxygen atoms bonded to the central atom Y. These atoms pull electron density from the O—H bond, further increasing its polarity. Increasing the number of oxygen atoms also helps stabilize the conjugate base by increasing its ability to "spread out" its negative charge. Thus, *the strength of an acid increases as additional electronegative atoms bond to the central atom Y*. For example, the strength of the chlorine oxyacids (Y = Cl) steadily increases as O atoms are added:



Because the oxidation number of Y increases as the number of attached O atoms increases, this correlation can be stated in an equivalent way: In a series of oxyacids, the acidity increases as the oxidation number of the central atom increases.

Sample Exercise 16.20

Predicting Relative Acidities from Composition and Structure

Arrange the compounds in each series in order of increasing acid strength: (**a**) AsH_3, HBr, KH, H_2Se; (**b**) H_2SO_4, H_2SeO_3, H_2SeO_4.

SOLUTION

Analyze We are asked to arrange two sets of compounds in order from weakest acid to strongest acid. In (a), the substances are binary compounds containing H, and in (b) the substances are oxyacids.

Plan For the binary compounds, we will consider the electronegativities of As, Br, K, and Se relative to the electronegativity of H. The higher the electronegativity of these atoms, the higher the partial positive charge on H and so the more acidic the compound.

For the oxyacids, we will consider both the electronegativities of the central atom and the number of oxygen atoms bonded to the central atom.

Solve

(**a**) Because K is on the left side of the periodic table, it has a very low electronegativity (0.8, from Figure 8.8, p. 383). As a result, the hydrogen in KH carries a negative charge. Thus, KH should be the least acidic (most basic) compound in the series.

Arsenic and hydrogen have similar electronegativities, 2.0 and 2.1, respectively. This means that the As—H bond is nonpolar, and so AsH_3 has little tendency to donate a proton in aqueous solution.

The electronegativity of Se is 2.4, and that of Br is 2.8. Consequently, the H—Br bond is more polar than the H—Se bond, giving HBr the greater tendency to donate a proton. (This expectation is confirmed by Figure 16.19, where we see that H_2Se is a weak acid and HBr a strong acid.) Thus, the order of increasing acidity is KH < AsH_3 < H_2Se < HBr.

(**b**) The acids H_2SO_4 and H_2SeO_4 have the same number of O atoms and the same number of OH groups. In such cases, the acid strength increases with increasing electronegativity of the central atom. Because S is slightly more electronegative than Se (2.5 vs 2.4), we predict that H_2SO_4 is more acidic than H_2SeO_4.

For acids with the same central atom, the acidity increases as the number of oxygen atoms bonded to the central atom increases. Thus, H_2SeO_4 should be a stronger acid than H_2SeO_3. We predict the order of increasing acidity to be H_2SeO_3 < H_2SeO_4 < H_2SO_4.

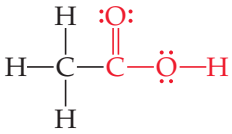
Practice Exercise

Arrange the following substances in order from weakest to strongest acid: $HClO_3$, HOI, $HBrO_2$, $HClO_2$, HIO_2.

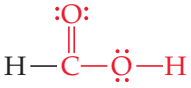
(**a**) HIO_2 < HOI < $HClO_3$ < $HBrO_2$ < $HClO_2$
(**b**) HOI < HIO_2 < $HBrO_2$ < $HClO_2$ < $HClO_3$
(**c**) $HBrO_2$ < HIO_2 < $HClO_2$ < HOI < $HClO_3$
(**d**) $HClO_3$ < $HClO_2$ < $HBrO_2$ < HIO_2 < HOI
(**e**) HOI < $HClO_2$ < $HBrO_2$ < HIO_2 < $HClO_3$

Carboxylic Acids

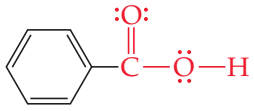
Another large group of acids is illustrated by acetic acid, a weak acid ($K_a = 1.8 \times 10^{-5}$):



The portion of the structure shown in red is called the *carboxyl group*, which is often written COOH. Thus, the chemical formula of acetic acid is written as CH_3COOH, where only the hydrogen atom in the carboxyl group can be ionized. Acids that contain a carboxyl group are called **carboxylic acids**, and they form the largest category of organic acids. Formic acid and benzoic acid are further examples of this large and important category of acids:

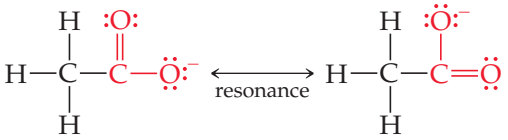


Formic acid



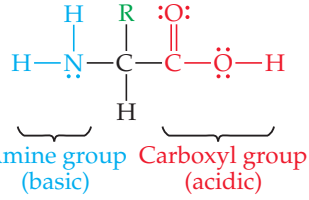
Benzoic acid

Two factors contribute to the acidic behavior of carboxylic acids. First, the additional oxygen atom attached to the carbon of the carboxyl group draws electron density from the O—H bond, increasing its polarity and helping to stabilize the conjugate base. Second, the conjugate base of a carboxylic acid (a *carboxylate anion*) can exhibit resonance, which contributes to the stability of the anion by spreading the negative charge over several atoms:

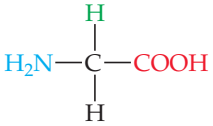


CHEMISTRY AND LIFE The Amphiprotic Behavior of Amino Acids

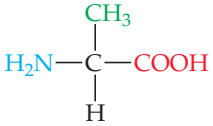
As we will discuss in greater detail in Chapter 24, *amino acids* are the building blocks of proteins. The general structure of amino acids is



where different amino acids have different R groups attached to the central carbon atom. For example, in *glycine*, the simplest amino acid, R is a hydrogen atom, and in *alanine* R is a CH_3 group:



Glycine



Alanine

Amino acids contain a carboxyl group and can therefore serve as acids. They also contain an NH_2 group, characteristic of amines (Section 16.6), and thus they can also act as bases. Amino acids, therefore, are amphiprotic. For glycine, we might expect the acid and base reactions with water to be

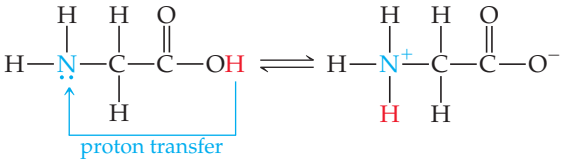
Acid: $H_2N—CH_2—COOH(aq) + H_2O(l) \rightleftharpoons H_2N—CH_2—COO^-(aq) + H_3O^+(aq)$ [16.48]

Base: $H_2N—CH_2—COOH(aq) + H_2O(l) \rightleftharpoons {}^+H_3N—CH_2—COOH(aq) + OH^-(aq)$ [16.49]

The pH of a solution of glycine in water is about 6.0, indicating that it is a slightly stronger acid than base.

The acid–base chemistry of amino acids is more complicated than shown in Equations 16.48 and 16.49, however. Because the COOH group can act as an acid and the NH_2 group can act as a base, amino acids undergo a "self-contained" Brønsted–Lowry acid–base reaction in which the proton of the carboxyl group is transferred to the basic nitrogen atom:

Continued



Neutral molecule Zwitterion

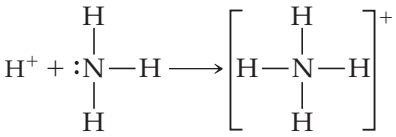
Although the form of the amino acid on the right in this equation is electrically neutral overall, it has a positively charged end and a negatively charged end. A molecule of this type is called a *zwitterion* (German for "hybrid ion").

Do amino acids exhibit any properties indicating that they behave as zwitterions? If so, their behavior should be similar to that of ionic substances. Crystalline amino acids have relatively high melting points, usually above 200 °C, which is characteristic of ionic solids. Amino acids are far more soluble in water than in nonpolar solvents. In addition, the dipole moments of amino acids are large, consistent with a large separation of charge in the molecule. Thus, the ability of amino acids to act simultaneously as acids and bases has important effects on their properties.

Related Exercise: 16.124

Lewis Acids and Bases

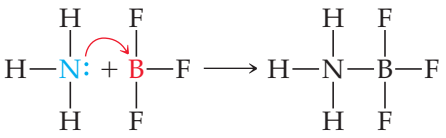
For a substance to be a proton acceptor (a Brønsted–Lowry base), it must have an unshared pair of electrons for binding the proton, as, for example, in NH_3. Using Lewis structures, we can write the reaction between H^+ and NH_3 as



G. N. Lewis was the first to notice this aspect of acid–base reactions. He proposed a more general definition of acids and bases that emphasizes the shared electron pair:

- A **Lewis acid** is an electron-pair acceptor.
- A **Lewis base** is an electron-pair donor.

Every base that we have discussed thus far—whether OH^-, H_2O, an amine, or an anion—is an electron-pair donor. Everything that is a base in the Brønsted–Lowry sense (a proton acceptor) is also a base in the Lewis sense (an electron-pair donor). In the Lewis theory, however, a base can donate its electron pair to something other than H^+. The Lewis definition therefore greatly increases the number of species that can be considered acids; in other words, H^+ is a Lewis acid but not the only one. For example, the reaction between NH_3 and BF_3 occurs because BF_3 has a vacant orbital in its valence shell. It therefore acts as an electron-pair acceptor (a Lewis acid) toward NH_3, which donates the electron pair:



Lewis base Lewis acid

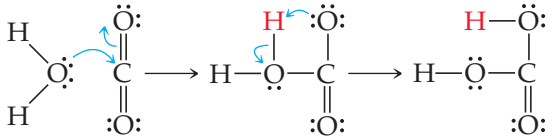
Our emphasis throughout this chapter has been on water as the solvent and on the proton as the source of acidic properties. In such cases we find the Brønsted–Lowry definition of acids and bases to be the most useful. In fact, when we speak of a substance as being acidic or basic, we are usually thinking of aqueous solutions and using these terms in the Arrhenius or Brønsted–Lowry sense. The advantage of the Lewis definitions of acid and base is that they allow us to treat a wider variety of reactions, including those that do not involve proton transfer, as acid–base reactions. To avoid confusion, a substance such as BF_3 is rarely called an acid unless it is clear from the context that we are using the term in the sense of the Lewis definition. Instead, substances that function as electron-pair acceptors are referred to explicitly as "Lewis acids."

Lewis acids include molecules that, like BF_3, have an incomplete octet of electrons. In addition, many simple cations can function as Lewis acids. For example, Fe^{3+} interacts strongly with cyanide ions to form the ferricyanide ion:

$$Fe^{3+} + 6\,[:C{\equiv}N:]^- \longrightarrow [Fe(C{\equiv}N:)_6]^{3-}$$

The Fe^{3+} ion has vacant orbitals that accept the electron pairs donated by the cyanide ions. (We will learn more in Chapter 23 about just which orbitals are used by the Fe^{3+} ion.) The metal ion is highly charged, too, which contributes to the interaction with CN^- ions.

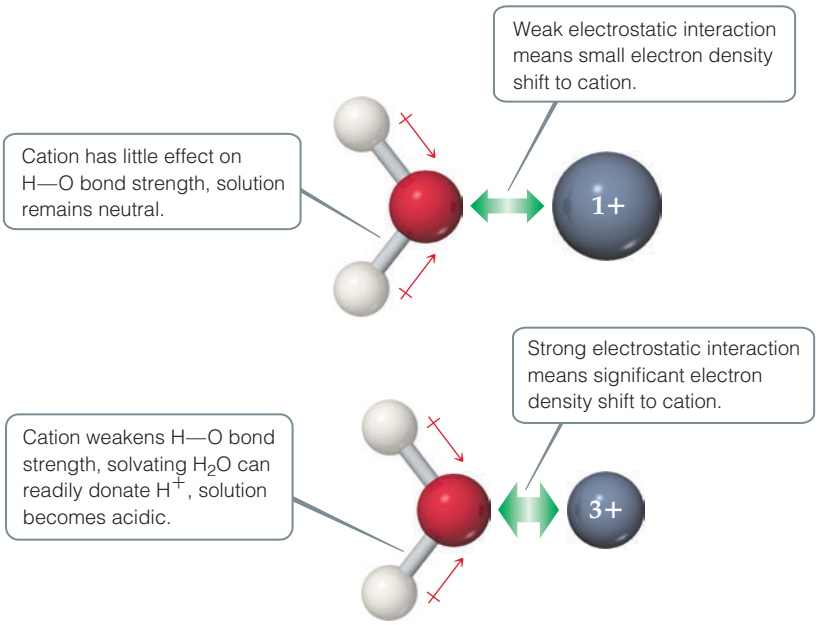
Some compounds containing multiple bonds can behave as Lewis acids. For example, the reaction of carbon dioxide with water to form carbonic acid (H_2CO_3) can be pictured as an attack by a water molecule on CO_2, in which the water acts as an electron-pair donor and the CO_2 as an electron-pair acceptor:



One electron pair of one of the carbon–oxygen double bonds is moved onto the oxygen, leaving a vacant orbital on the carbon, which means the carbon can accept an electron pair donated by H_2O. The initial acid–base product rearranges by transferring a proton from the water oxygen to a carbon dioxide oxygen, forming carbonic acid.

The hydrated cations we encountered in Section 16.7, such as $[Fe(H_2O)_6]^{3+}$ in Figure 16.18, form through the reaction between the cation acting as a Lewis acid and the water molecules acting as Lewis bases. When a water molecule interacts with the positively charged metal ion, electron density is drawn from the oxygen (**Figure 16.21**). This flow of electron density causes the O—H bond to become more polarized; as a result, water molecules bound to the metal ion are more acidic than those in the bulk solvent. This effect becomes more pronounced as the charge of the cation increases, which explains why 3+ cations are much more acidic than cations with smaller charges.

The Lewis acid–base concept allows many ideas developed in this chapter to be used more broadly in chemistry, including rections in solvents other than water. If you take a course in organic chemistry, you will see a number of important rections that require the presence of a Lewis acid in order to proceed. The interaction of lone pairs on one molecule or ion with vacant orbitals on another molecule or ion is one of the most important concepts in chemistry, as you will see throughout your studies.

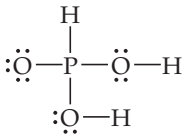


▲ **Figure 16.21** **The acidity of a hydrated cation depends on cation charge.**

Sample Integrative Exercise

Putting Concepts Together

Phosphorous acid (H_3PO_3) has the Lewis structure shown at right.



(**a**) Explain why H_3PO_3 is diprotic and not triprotic. (**b**) A 25.0 mL sample of an H_3PO_3 solution titrated with 0.102 *M* NaOH requires 23.3 mL of NaOH to neutralize both acidic protons. What is the molarity of the H_3PO_3 solution? (**c**) The original solution from part (b) has a pH of 1.59. Calculate the percent ionization and K_{a1} for H_3PO_3, assuming that $K_{a1} \gg K_{a2}$. (**d**) How does the osmotic pressure of a 0.050 *M* solution of HCl compare qualitatively with that of a 0.050 *M* solution of H_3PO_3? Explain.

SOLUTION

We will use what we have learned about molecular structure and its impact on acidic behavior to answer part (a). We will then use stoichiometry and the relationship between pH and $[H^+]$ to answer parts (b) and (c). Finally, we will consider percent ionization in order to compare the osmotic pressure of the two solutions in part (d).

(**a**) Acids have polar H—X bonds. From Figure 8.8 (p. 383) we see that the electronegativity of H is 2.1 and that of P is also 2.1. Because the two elements have the same electronegativity, the H—P bond is nonpolar. Thus, this H cannot be acidic. The other two H atoms, however, are bonded to O, which has an electronegativity of 3.5. The H—O bonds are, therefore, polar with H having a partial positive charge. These two H atoms are consequently acidic.

(**b**) The chemical equation for the neutralization reaction is:

$$H_3PO_3(aq) + 2\,NaOH(aq) \longrightarrow Na_2HPO_3(aq) + 2\,H_2O(l)$$

From the definition of molarity, M = mol/L, we see that moles = $M \times$ L. Thus, the number of moles of NaOH added to the solution is:

$$(0.0233\,\cancel{L})(0.102\,\text{mol}/\cancel{L}) = 2.38 \times 10^{-3}\,\text{mol NaOH}$$

The balanced equation indicates that 2 mol of NaOH is consumed for each mole of H_3PO_3. Thus, the number of moles of H_3PO_3 in the sample is:

$$(2.38 \times 10^{-3}\,\cancel{\text{mol NaOH}})\left(\frac{1\,\text{mol}\,H_3PO_3}{2\,\cancel{\text{mol NaOH}}}\right) = 1.19 \times 10^{-3}\,\text{mol}\,H_3PO_3$$

The concentration of the H_3PO_3 solution, therefore, equals $(1.19 \times 10^{-3}\,\text{mol})/(0.0250\,\text{L}) = 0.0476\,M$.

(**c**) From the pH of the solution, 1.59, we can calculate $[H^+]$ at equilibrium:

$$[H^+] = \text{antilog}(-1.59) = 10^{-1.59} = 0.026\,M\,\text{(two significant figures)}$$

Because $K_{a1} \gg K_{a2}$, the vast majority of the ions in solution are from the first ionization step of the acid.

Because one $H_2PO_3^-$ ion forms for each H^+ ion formed, the equilibrium concentrations of H^+ and $H_2PO_3^-$ are equal: $[H^+] = [H_2PO_3^-] = 0.026\,M$. The equilibrium concentration of H_3PO_3 equals the initial concentration minus the amount that ionizes to form H^+ and $H_2PO_3^-$: $[H_3PO_3] = 0.0476\,M - 0.026\,M = 0.022\,M$ (two significant figures). These results can be tabulated as follows:

$$H_3PO_3(aq) \rightleftharpoons H^+(aq) + H_2PO_3^-(aq)$$

Initial concentration (*M*)	0.0476	0	0
Change in concentration (*M*)	−0.026	+0.026	+0.026
Equilibrium concentration (*M*)	0.022	0.026	0.026

The percent ionization is:

$$\text{percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[H_3PO_3]_{\text{initial}}} \times 100\% = \frac{0.026\,\cancel{M}}{0.0476\,\cancel{M}} \times 100\% = 55\%$$

The first acid-dissociation constant is:

$$K_{a1} = \frac{[H^+][H_2PO_3^-]}{[H_3PO_3]} = \frac{(0.026)(0.026)}{0.022} = 0.031$$

(**d**) Osmotic pressure is a colligative property and depends on the total concentration of particles in solution. Because HCl is a strong acid, a 0.050 *M* solution will contain 0.050 *M* $H^+(aq)$ and 0.050 *M* $Cl^-(aq)$, or a total of 0.100 mol/L of particles. Because H_3PO_3 is a weak acid, it ionizes to a lesser extent than HCl and, hence, there are fewer particles in the H_3PO_3 solution. As a result, the H_3PO_3 solution will have the lower osmotic pressure.

Self-Assessment Exercises

16.42 Predict the relative strengths of the carboxylic acids: CH_3COOH and CCl_3COOH.

(a) CH_3COOH will be a stronger acid than CCl_3COOH

(b) CCl_3COOH will be a stronger acid than CH_3COOH

16.43 Review the reaction of water with carbon dioxide shown on page 803. Is the water molecule acting as a Lewis acid or a Lewis base?

(a) A Lewis acid

(b) A Lewis base

Exercises

16.44 Predict the stronger acid in each pair: (**a**) HCl or HF; (**b**) H_3PO_4 or H_3AsO_4; (**c**) $HBrO_3$ or $HBrO_2$; (**d**) $H_2C_2O_4$ or $HC_2O_4^-$; (**e**) benzoic acid (C_6H_5COOH) or phenol (C_6H_5OH).

16.45 Based on their compositions and structures and on conjugate acid–base relationships, select the stronger base in each of the following pairs: (**a**) NO_3^- or NO_2^-, (**b**) PO_4^{3-} or AsO_4^{3-}, (**c**) HCO_3^- or CO_3^{2-}.

16.46 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement to make it true. (**a**) Acid strength in a series of H—A molecules increases with increasing size of A. (**b**) For acids of the same general structure but differing electronegativities of the central atoms, acid strength decreases with increasing electronegativity of the central atom. (**c**) The strongest acid known is HF because fluorine is the most electronegative element.

16.47 Ammonia, NH_3, acts as an Arrhenius base, a Brønsted-Lowry base, and a Lewis base, in aqueous solution. Write out the reaction NH_3 undergoes with water and explain what properties of ammonia correspond to each of the three definitions of "base."

16.48 Identify the Lewis acid and Lewis base in each of the following reactions:

(a) $HNO_2(aq) + OH^-(aq) \rightleftharpoons NO_2^-(aq) + H_2O(l)$

(b) $FeBr_3(s) + Br^-(aq) \rightleftharpoons FeBr_4^-(aq)$

(c) $Zn^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$

(d) $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$

16.49 Which member of each pair produces the more acidic aqueous solution: (**a**) $ZnBr_2$ or $CdCl_2$, (**b**) CuCl or $Cu(NO_3)_2$, (**c**) $Ca(NO_3)_2$ or $NiBr_2$?

Answers to Self-Assessment Exercises

16.42 (b) **16.43** (a)

Chapter Summary and Key Terms

ACID–BASE EQUILIBRIA (SECTION 16.1) Acids and bases were first recognized by the properties of their aqueous solutions. For example, acids turn litmus red, whereas bases turn litmus blue. Arrhenius recognized that the properties of acidic solutions are due to $H^+(aq)$ ions and those of basic solutions are due to $OH^-(aq)$ ions.

The Brønsted–Lowry concept of acids and bases is more general than the Arrhenius concept and emphasizes the transfer of a proton (H^+) from an acid to a base. The H^+ ion is strongly bound to water. For this reason, the **hydronium ion**, $H_3O^+(aq)$, is often used to represent the predominant form of H^+ in water instead of the simpler $H^+(aq)$.

A **Brønsted–Lowry acid** is a substance that donates a proton to another substance; a **Brønsted–Lowry base** is a substance that accepts a proton from another substance. Water is an **amphiprotic** substance, one that can function as either a Brønsted–Lowry acid or base, depending on the substance with which it reacts.

The **conjugate base** of a Brønsted–Lowry acid is the species that remains when a proton is removed from the acid. The **conjugate acid** of a Brønsted–Lowry base is the species formed by adding a proton to the base. Together, an acid and its conjugate base (or a base and its conjugate acid) are called a **conjugate acid–base pair**.

The acid–base strengths of conjugate acid–base pairs are related: The stronger an acid, the weaker is its conjugate base; the weaker an acid, the stronger is its conjugate base. In every acid–base reaction, the position of the equilibrium favors the transfer of the proton from the stronger acid to the stronger base.

AUTOIONIZATION OF WATER (SECTION 16.2) Water ionizes to a slight degree, forming $H^+(aq)$ and $OH^-(aq)$. The extent of this **autoionization** is expressed by the **ion-product constant** for water: $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ (25 °C). This relationship holds for both pure water and aqueous solutions. The K_w expression indicates that the product of $[H^+]$ and $[OH^-]$ is a constant. Thus, as $[H^+]$ increases, $[OH^-]$ decreases. Acidic solutions are those that contain more $H^+(aq)$ than $OH^-(aq)$, whereas basic solutions contain more $OH^-(aq)$ than $H^+(aq)$. When $[H^+] = [OH^-]$, the solution is neutral.

THE pH SCALE (SECTION 16.3) The concentration of $H^+(aq)$ can be expressed in terms of **pH**: $pH = -\log[H^+]$. At 25 °C the pH of a neutral solution is 7.00, whereas the pH of an acidic solution is below 7.00, and the pH of a basic solution is above 7.00. This p notation is also used to represent the negative logarithm of other small quantities, as in pOH and pK_w. The pH of a solution can be measured using a pH meter, or it can be estimated using acid–base indicators.

STRONG ACIDS AND BASES (SECTION 16.4) Strong acids are strong electrolytes, ionizing completely in aqueous solution. The common strong acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4. The conjugate bases of strong acids have negligible basicity. Common strong bases are the ionic hydroxides of the alkali metals and the heavy alkaline earth metals.

WEAK ACIDS (SECTIONS 16.5) Weak acids are weak electrolytes; only a small fraction of the molecules exist in solution in ionized form. The extent of ionization is expressed by the **acid-dissociation constant**, K_a, which is the equilibrium constant for the reaction $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, which can also be written as $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$. The larger the value of K_a, the stronger is the acid. For solutions of the same concentration, a stronger acid also has a larger **percent ionization**. The concentration of a weak acid and its K_a value can be used to calculate the pH of a solution.

Polyprotic acids, such as H_3PO_4, have more than one ionizable proton. These acids have acid-dissociation constants that decrease in magnitude in the order $K_{a1} > K_{a2} > K_{a3}$. Because nearly all the $H^+(aq)$ in a

polyprotic acid solution comes from the first dissociation step, the pH can usually be estimated satisfactorily by considering only K_{a1}.

WEAK BASES (SECTIONS 16.6) Weak bases include NH_3, **amines**, and the anions of weak acids. The extent to which a weak base reacts with water to generate the corresponding conjugate acid and OH^- is measured by the **base-dissociation constant**, K_b. K_b is the equilibrium constant for the reaction $B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$, where B is the base.

The relationship between the strength of an acid and the strength of its conjugate base is expressed quantitatively by the equation $K_a \times K_b = K_w$, where K_a and K_b are dissociation constants for conjugate acid–base pairs. This equation explains the inverse relationship between the strength of an acid and the strength of its conjugate base.

ACID–BASE PROPERTIES OF SALTS (SECTION 16.7) The acid–base properties of salts can be ascribed to the behavior of their respective cations and anions. The reaction of ions with water, with a resulting change in pH, is called **hydrolysis**. The cations of the alkali metals and the alkaline earth metals as well as the anions of strong acids, such as Cl^-, Br^-, I^-, and NO_3^-, do not undergo hydrolysis. They are always spectator ions in acid–base chemistry. A cation that is the conjugate acid of a weak base produces H^+ upon hydrolysis. An anion that is the conjugate base of a weak acid produces OH^- upon hydrolysis. Highly charged metal cations, such as Fe^{3+}, are hydrated in water; the metal-bound water molecules undergo reaction with free water to make H_3O^+ and therefore are acidic.

ACID–BASE BEHAVIOR AND CHEMICAL STRUCTURE (SECTION 16.8) The tendency of a substance to show acidic or basic characteristics in water can be correlated with its chemical structure. Acid character requires the presence of a highly polar H—X bond. Acidity is also favored when the H—X bond is weak and when the X^- ion is very stable.

For **oxyacids** with the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom. For oxyacids with the same central atom, acid strength increases as the number of oxygen atoms attached to the central atom increases. **Carboxylic acids**, which are organic acids containing the COOH group, are the most important class of organic acids. The presence of delocalized π bonding in the conjugate base is a major factor responsible for the acidity of these compounds.

The Lewis concept of acids and bases emphasizes the shared electron pair rather than the proton. A **Lewis acid** is an electron-pair acceptor, and a **Lewis base** is an electron-pair donor. The Lewis concept is more general than the Brønsted–Lowry concept because it can apply to cases in which the acid is some substance other than H^+, and to solvents other than water.

Learning Outcomes

After studying this chapter, you should be able to:

- Define and identify Arrhenius acids and bases. (Section 16.1) *Related Exercises: 16.3, 16.62*
- Define and identify Brønsted–Lowry acids and bases and identify conjugate acid–base pairs. (Section 16.1) *Related Exercises: 16.5, 16.64*
- Correlate the strength of an acid to the strength of its conjugate base. (Section 16.1) *Related Exercises: 16.8, 16.67*
- Explain how the equilibrium position of a proton-transfer reaction relates to the strengths of the acids and bases involved. (Section 16.2) *Related Exercises: 16.9, 16.68*
- Describe the autoionization of water and explain how $[H_3O^+]$ and $[OH^-]$ are related via K_w. (Section 16.2) *Related Exercises: 16.11, 16.69*
- Calculate the pH of a solution given $[H_3O^+]$ or $[OH^-]$. (Section 16.3) *Related Exercises: 16.17, 16.74*
- Calculate the pH of a strong acid or strong base given its concentration. (Section 16.4) *Related Exercises: 16.21, 16.77*
- Calculate K_a or K_b for a weak acid or weak base given its concentration and the pH of the solution, and vice versa. (Sections 16.5 and 16.6) *Related Exercises: 16.26 , 16.34, 16.81, 16.90*
- Calculate the pH of a weak acid or weak base or its percent ionization given its concentration and K_a or K_b. (Sections 16.5 and 16.6) *Related Exercises: 16.30, 16.87*
- Calculate K_b for a weak base given K_a of its conjugate acid, and similarly calculate K_a from K_b. (Section 16.6) *Related Exercises: 16.38, 16.94*
- Predict whether an aqueous solution of a salt will be acidic, basic, or neutral. (Section 16.7) *Related Exercises: 16.40, 16.99*
- Predict the relative strength of a series of acids from their molecular structures. (Section 16.8) *Related Exercises: 16.46, 16.103*
- Define and identify Lewis acids and bases. (Section 16.8) *Related Exercises: 16.48, 16.105*

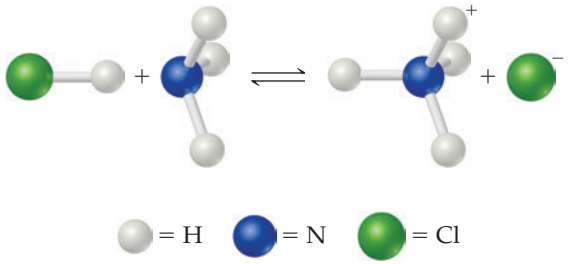
Key Equations

• $K_w = [H_3O^+][OH^-] = [H^+][OH^-] = 1.0 \times 10^{-14}$	[16.16]	Ion-product constant of water at 25 °C
• $pH = -\log[H^+]$	[16.17]	Definition of pH
• $pOH = -\log[OH^-]$	[16.18]	Definition of pOH
• $pH + pOH = 14.00$	[16.20]	Relationship between pH and pOH
• $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ or $K_a = \frac{[H^+][A^-]}{[HA]}$	[16.25]	Acid-dissociation constant for a weak acid, HA
• Percent ionization $= \frac{[H^+]_{equilibrium}}{[HA]_{initial}} \times 100\%$	[16.27]	Percent ionization of a weak acid
• $K_b = \frac{[BH^+][OH^-]}{[B]}$	[16.34]	Base-dissociation constant for a weak base, B
• $K_a \times K_b = K_w$	[16.40]	Relationship between acid- and base-dissociation constants of a conjugate acid–base pair
• $pK_a = -\log K_a$ and $pK_b = -\log K_b$	[16.41]	Definitions of pK_a and pK_b

Exercises

Visualizing Concepts

16.50 (**a**) Identify the Brønsted–Lowry acid and base in the reaction

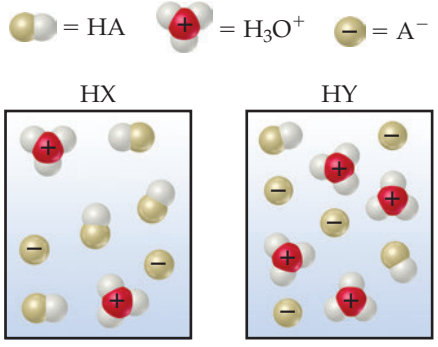


(**b**) Identify the Lewis acid and base in the reaction. [Sections 16.1 and 16.8]

16.51 The following diagrams represent aqueous solutions of two monoprotic acids, HA (A = X or Y). The water molecules have been omitted for clarity. (**a**) Which is the stronger acid, HX or HY? (**b**) Which is the stronger base, X^- or Y^-? (**c**) If you mix equal concentrations of HX and NaY, will the equilibrium

$$HX(aq) + Y^-(aq) \rightleftharpoons HY(aq) + X^-(aq)$$

lie mostly to the right ($K_c > 1$) or to the left ($K_c < 1$)? [Section 16.1]



16.52 The indicator methyl orange has been added to both of the following solutions. Based on the colors, classify each statement as true or false:

(**a**) The pH of solution A is definitely less than 7.00.

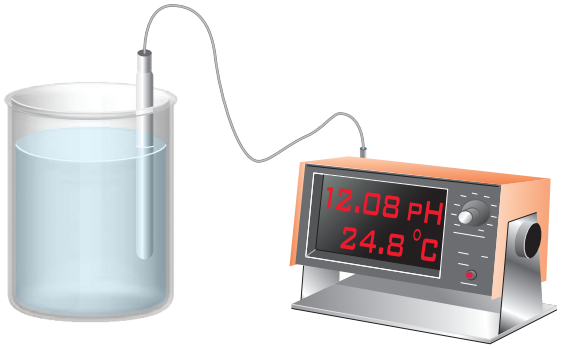
(**b**) The pH of solution B is definitely greater than 7.00.

(**c**) The pH of solution B is greater than that of solution A. [Section 16.3]

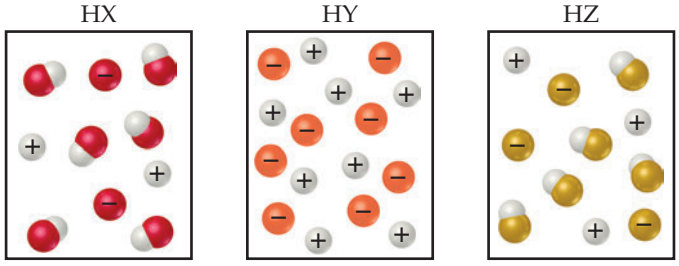


Solution A Solution B

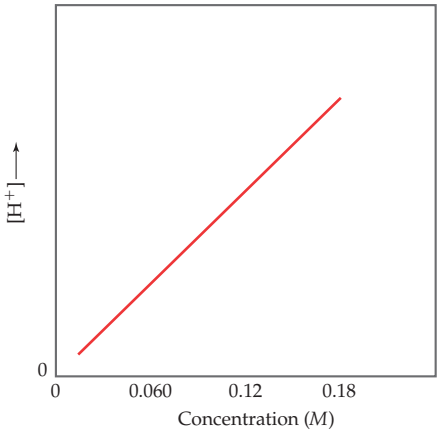
16.53 The probe of the pH meter shown here is sitting in a beaker that contains a clear liquid. (**a**) You are told the liquid is pure water, a solution of HCl(*aq*), or a solution of KOH(*aq*). Which one is it? (**b**) If the liquid is one of the solutions, what is its molarity? (**c**) Why is the temperature given on the pH meter? [Sections 16.3 and 16.4]



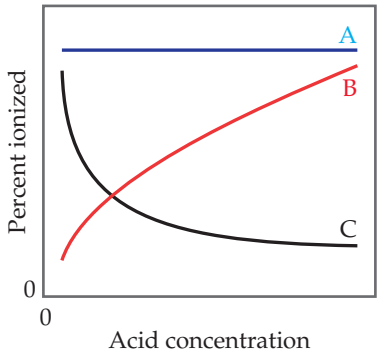
16.54 The following diagrams represent aqueous solutions of three acids, HX, HY, and HZ. The water molecules have been omitted for clarity, and the hydrated proton is represented as H^+ rather than H_3O^+. (**a**) Which of the acids is a strong acid? Explain. (**b**) Which acid would have the smallest acid-dissociation constant, K_a? (**c**) Which solution would have the highest pH? [Sections 16.4 and 16.5]



16.55 The graph given here shows $[H^+]$ versus concentration for an aqueous solution of an unknown substance. (**a**) Is the substance a strong acid, a weak acid, a strong base, or a weak base? (**b**) Based on your answer to (a), can you determine the value of the pH of the solution when the concentration is 0.18 *M*? (**c**) Would the line go exactly through the origin of the plot? [Sections 16.4 and 16.5]



16.56 Which of these statements about how the percent ionization of a weak acid depends on acid concentration is true? [Section 16.5]



(**a**) Line A is most accurate because K_a does not depend on concentration.

(**b**) Line A is the most accurate because the percent ionization of the acid does not depend on concentration.

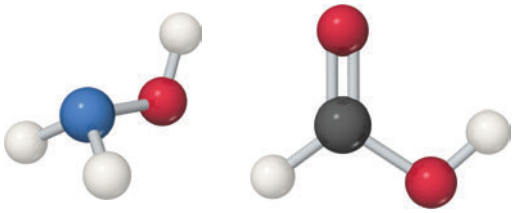
(**c**) Line B is the most accurate because as the acid concentration increases, a greater proportion of it is ionized.

(**d**) Line B is the most accurate because as the acid concentration increases, K_a increases.

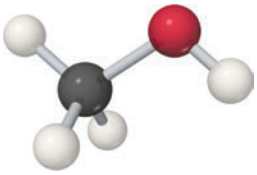
(**e**) Line C is the most accurate because as the acid concentration increases, a lesser proportion of it ionized.

(**f**) Line C is the most accurate because as the acid concentration increases, K_a decreases.

16.57 Each of the three molecules shown here contains an OH group, but one molecule acts as a base, one as an acid, and the third is neither acid nor base. (**a**) Which one acts as a base? (**b**) Which one acts as an acid? (**c**) Which one is neither acidic nor basic? [Sections 16.5 and 16.6]

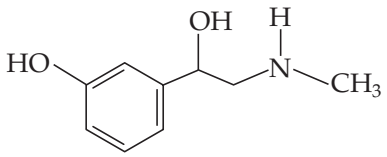


Molecule A Molecule B

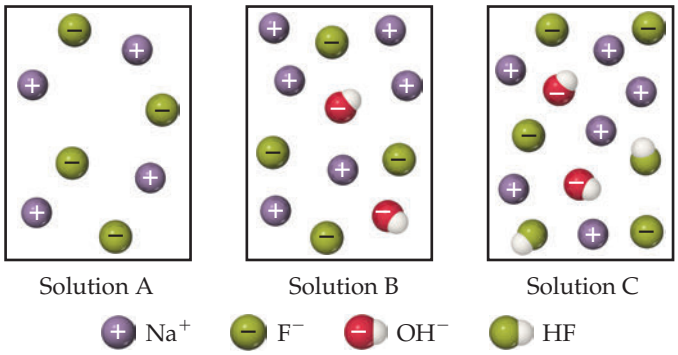


Molecule C

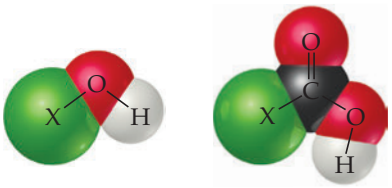
16.58 *Phenylephrine*, an organic substance with molecular formula $C_9H_{13}NO_2$, is used as a nasal decongenstant in over-the-counter medications. The molecular structure of phenylephrine is shown using the usual shortcut organic structure. (**a**) Would you expect a solution of phenylephrine to be acidic, neutral, or basic? (**b**) One of the active ingredients in Alka-Seltzer PLUS® cold medication is phenylephrine hydrochloride. How does this ingredient differ from the structure shown here? (**c**) Would you expect a solution of phenylephrine hydrochloride to be acidic, neutral, or basic? [Sections 16.6 and 16.7]



16.59 Which of the following diagrams best represents an aqueous solution of NaF? (For clarity, the water molecules are not shown.) Will this solution be acidic, neutral, or basic? [Section 16.7]



16.60 Consider the molecular models shown here, where X represents a halogen atom. (**a**) If X is the same atom in both molecules, which molecule will be more acidic? (**b**) Does the acidity of each molecule increase or decrease as the electronegativity of the atom X increases? [Section 16.8]



(a) (b)

16.61 For each of these reactions, identify the acid and base among the reactants, and state if the acids and bases are Lewis, Arrhenius, and/or Brønsted–Lowry. [Section 16.1 and 16.8]

(**a**) $PCl_4^+ + Cl^- \longrightarrow PCl_5$

(**b**) $NH_3 + BF_3 \longrightarrow H_3NBF_3$

(**c**) $[Al(H_2O)_6]^{3+} + H_2O \longrightarrow [Al(H_2O)_5OH]^{2+} + H_3O^+$

Arrhenius and Brønsted–Lowry Acids and Bases (Sections 16.1)

16.62 $NH_3(g)$ and $HCl(g)$ react to form the ionic solid $NH_4Cl(s)$. Which substance is the Brønsted–Lowry acid in this reaction? Which is the Brønsted–Lowry base?

16.63 (**a**) Give the conjugate base of the following Brønsted–Lowry acids: (**i**) $H_2PO_4^-$, (**ii**) HBr. (**b**) Give the conjugate acid of the following Brønsted–Lowry bases: (**i**) CN^-, (**ii**) HSO_4^-.

16.64 Identify the Brønsted–Lowry acid and the Brønsted–Lowry base on the left side of each of the following equations, and also identify the conjugate acid and conjugate base of each on the right side:

(**a**) $NH_4^+(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NH_3(aq)$

(**b**) $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

(**c**) $HCOOH(aq) + PO_4^{3-}(aq) \rightleftharpoons HCOO^-(aq) + HPO_4^{2-}(aq)$

16.65 (**a**) The hydrogen carbonate ion (HCO_3^-) is amphiprotic. Write a balanced chemical equation showing how it acts as an acid toward water and another equation showing how it acts as a base toward water.

16.66 Label each of the following as being a strong base, a weak base, or a species with negligible basicity. In each case write the formula of its conjugate acid, and indicate whether the conjugate acid is a strong acid, a weak acid, or a species with negligible acidity: (**a**) F^- (**b**) Br^- (**c**) HS^- (**d**) ClO_4^- (**e**) $HCOO^-$

16.67 (**a**) Which of the following is the stronger Brønsted–Lowry acid, HBrO or HBr? (**b**) Which is the stronger Brønsted–Lowry base, F^- or Cl^-?

16.68 Predict the products of the following acid–base reactions, and predict whether the equilibrium lies to the left or to the right of the reaction arrow:

(**a**) $O^{2-}(aq) + H_2O(l) \rightleftharpoons$

(**b**) $CH_3COOH(aq) + HS^-(aq) \rightleftharpoons$

(**c**) $NO_2^-(aq) + H_2O(l) \rightleftharpoons$

Autoionization of Water (Section 16.2)

16.69 If a neutral solution of water, with pH = 7.00, is cooled to 10 °C, the pH rises to 7.27. Which of the following three statements is correct for the cooled water: (i) $[H^+] > [OH^-]$, (ii) $[H^+] = [OH^-]$, or (iii) $[H^+] < [OH^-]$?

16.70 Calculate $[H^+]$ for each of the following solutions, and indicate whether the solution is acidic, basic, or neutral: (**a**) $[OH^-] = 7.3 \times 10^{-10}\,M$ (**b**) $[OH^-] = 0.015\,M$; (**c**) a solution in which $[H^+]$ is 10 times greater than $[OH^-]$.

16.71 At the boiling point of water (100 °C), $K_w = 5.6 \times 10^{-13}$. Calculate $[H^+]$ and $[OH^-]$ for a neutral solution at this temperature.

The pH Scale (Section 16.3)

16.72 By what factor does $[H^+]$ change for a pH change of (**a**) 3.0 units, (**b**) 0.3 units?

16.73 Complete the following table by calculating the missing entries and indicating whether the solution is acidic or basic. Consider the temperature to be 25 °C.

$[H^+]$	$[OH^-]$	pH	pOH	Acidic or Basic?
$5.7 \times 10^{-3}\,M$				
	$6.3 \times 10^{-10}\,M$			
		9.95		
			4.20	

16.74 The average pH of normal arterial blood is 7.40. At normal body temperature (37 °C), $K_w = 2.4 \times 10^{-14}$. Calculate $[H^+]$, $[OH^-]$, and pOH for blood at this temperature.

16.75 Addition of the indicator methyl orange to an unknown solution leads to a yellow color. The addition of bromthymol blue to the same solution also leads to a yellow color. (**a**) Is the solution acidic, neutral, or basic? (**b**) What is the range (in whole numbers) of possible pH values for the solution? (**c**) Is there another indicator you could use to narrow the range of possible pH values for the solution?

Strong Acids and Bases (Section 16.4)

16.76 Is each of the following statements true or false? (**a**) All strong acids contain one or more H atoms. (**b**) A strong acid is a strong electrolyte. (**c**) A 1.0-*M* solution of a strong acid will have pH = 1.0.

16.77 Calculate the pH of each of the following strong acid solutions: (**a**) $8.3 \times 10^{-4}\,M$ HCl, (**b**) 1.20 g of HNO_3 in 500 mL of solution, (**c**) 2.0 mL of 0.250 *M* $HClO_4$ diluted to 40.0 mL, (**d**) a solution formed by mixing 25.0 mL of 0.100 *M* HBr with 25.0 mL of 0.200 *M* HCl.

16.78 Calculate $[OH^-]$ and pH for (**a**) $1.5 \times 10^{-3}\,M$ $Sr(OH)_2$, (**b**) 2.250 g of LiOH in 250.0 mL of solution, (**c**) 1.00 mL of 0.175 *M* NaOH diluted to 2.00 L, (**d**) a solution formed by adding 5.00 mL of 0.105 *M* KOH to 15.0 mL of $9.5 \times 10^{-2}\,M$ $Ca(OH)_2$.

16.79 Calculate the concentration of an aqueous solution of NaOH that has a pH of 12.70.

Weak Acids (Section 16.5)

16.80 Write the chemical equation and the K_a expression for the dissociation of each of the following acids in aqueous solution. First show the reaction with $H^+(aq)$ as a product and then with the hydronium ion: (**a**) HNO_2, (**b**) ClH_2CCOOH.

16.81 Lactic acid ($CH_3CH(OH)COOH$) has one acidic hydrogen. A 0.10 *M* solution of lactic acid has a pH of 2.44. Calculate K_a.

16.82 A 0.100 *M* solution of cyanic acid (HCNO) is 5.9% ionized. Using this information, calculate $[CNO^-]$, $[H^+]$, [HCNO], and K_a for cyanic acid.

16.83 A particular sample of vinegar has a pH of 2.20. If acetic acid is the only acid that vinegar contains ($K_a = 1.8 \times 10^{-5}$), calculate the concentration of acetic acid in the vinegar.

16.84 If a solution of hydrofluoric acid (HF; $K_a = 6.8 \times 10^{-4}$) has a pH of 2.12, calculate the concentration of hydrofluoric acid.

16.85 The acid-dissociation constant for benzoic acid (C_6H_5COOH) is 6.3×10^{-5}. Calculate the equilibrium concentrations of H_3O^+, $C_6H_5COO^-$, and C_6H_5COOH in the solution if the initial concentration of C_6H_5COOH is 0.100 *M*.

16.86 Saccharin, a sugar substitute, is a weak acid with $pK_a = 2.32$ at 25 °C. It ionizes in aqueous solution as follows:

$$HNC_7H_4SO_3(aq) \rightleftharpoons H^+(aq) + NC_7H_4SO_3^-(aq)$$

What is the pH of a 0.25 *M* solution of this substance?

16.87 Calculate the percent ionization of hydrazoic acid (HN_3) in solutions of each of the following concentrations (K_a is given in Appendix D): (**a**) 0.400 *M*, (**b**) 0.100 *M*, (**c**) 0.0400 *M*.

16.88 Citric acid, which is present in citrus fruits, is a triprotic acid (Table 16.3). (**a**) Calculate the pH of a 0.040 *M* solution of citric acid. (**b**) Did you have to make any approximations or assumptions in completing your calculations? (**c**) Is the concentration of citrate ion ($C_6H_5O_7^{3-}$) equal to, less than, or greater than the H^+ ion concentration?

Weak Bases (Section 16.6)

16.89 Consider the base hydroxylamine, NH_2OH. (**a**) What is the conjugate acid of hydroxylamine? (**b**) When it acts as a base, which atom in hydroxylamine accepts a proton? (**c**) There are two atoms in hydroxylamine that have nonbonding electron pairs that could act as proton acceptors. Use Lewis structures and formal charges to rationalize why one of these two atoms is a much better proton acceptor than the other.

16.90 Write the chemical equation and the K_b expression for the reaction of each of the following bases with water: (**a**) trimethylamine, $(CH_3)_3N$; (**b**) sulfite, SO_3^{2-}; (**c**) cyanide, CN^-.

16.91 Calculate the molar concentration of OH^- in a 0.050 *M* solution of ethylamine ($C_2H_5NH_2$; $K_b = 6.4 \times 10^{-4}$). Calculate the pH of this solution.

16.92 Ephedrine, a central nervous system stimulant, is used in nasal sprays as a decongestant. This compound is a weak organic base:

$$C_{10}H_{15}ON(aq) + H_2O(l) \rightleftharpoons C_{10}H_{15}ONH^+(aq) + OH^-(aq)$$

A 0.035 *M* solution of ephedrine has a pH of 11.33. (**a**) What are the equilibrium concentrations of $C_{10}H_{15}ON$, $C_{10}H_{15}ONH^+$, and OH^-? (**b**) Calculate K_b for ephedrine.

Acid–Base Properties of Salts (Sections 16.7)

16.93 Use the acid-dissociation constants in Table 16.3 to arrange these oxyanions from strongest base to weakest: SO_4^{2-}, CO_3^{2-}, SO_3^{2-}, and PO_4^{3-}.

16.94 (**a**) Given that K_a for cyanic acid is 3.5×10^{-4} and that for hydrofluoric acid is 6.8×10^{-4}, which is the stronger acid? (**b**) Which is the stronger base, the cyanate ion or the fluoride ion? (**c**) Calculate K_b values for NCO^- and F^-.

16.95 Using data from Appendix D, calculate pOH and pH for each of the following solutions: (**a**) 0.080 *M* potassium hypobromite (KBrO), (**b**) 0.150 *M* potassium hydrosulfide (KHS), (**c**) a mixture that is 0.25 *M* in potassium nitrite (KNO_2) and 0.15 *M* in magnesium nitrite ($Mg(NO_2)_2$).

16.96 Using data from Appendix D, calculate $[OH^-]$ and pH for each of the following solutions: (**a**) 0.105 *M* NaF, (**b**) 0.035 *M* Na_2S, (**c**) a mixture that is 0.045 *M* in $NaCH_3COO$ and 0.055 *M* in $Ba(CH_3COO)_2$.

16.97 A solution of potassium (KCH_3COO) has a pH of 8.90. What is the molarity of the solution?

16.98 Pyridinium bromide (C_5H_5NHBr) is a strong electrolyte that dissociates completely into $C_5H_5NH^+$ and Br^-. An aqueous solution of pyridinium bromide has a pH of 2.95.

(**a**) Write out the reaction that leads to this acidic pH.

(**b**) Using Appendix D, calculate the K_a for pyridinium bromide.

(**c**) A solution of pyridinium bromide has a pH of 2.95. What is the concentration of the pyridinium cation at equilibrium, in units of molarity?

16.99 Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral: (**a**) NH_4Br, (**b**) $FeCl_3$, (**c**) Na_2CO_3, (**d**) $KClO_4$, (**e**) $NaHC_2O_4$.

16.100 An unknown salt is either NaF, NaCl, or NaOCl. When 0.050 mol of the salt is dissolved in water to form 0.500 L of solution, the pH of the solution is 8.08. What is the identity of the salt?

Acid–Base Character and Chemical Structure (Section 16.8)

16.101 Predict the stronger acid in each pair: (**a**) HNO_3 or HNO_2; (**b**) H_2S or H_2O; (**c**) H_2SO_4 or H_2SeO_4; (**d**) CH_3COOH or CCl_3COOH.

16.102 Based on their compositions and structures and on conjugate acid–base relationships, select the stronger base in each of the following pairs: (**a**) BrO^- or ClO^-, (**b**) BrO^- or BrO_2^-, (**c**) HPO_4^{2-} or $H_2PO_4^-$.

16.103 Indicate whether each of the following statements is true or false. For each statement that is false, correct the statement to make it true. (**a**) In general, the acidity of binary acids increases from left to right in a given row of the periodic table. (**b**) In a series of acids that have the same central atom, acid strength increases with the number of hydrogen atoms bonded to the central atom. (**c**) Hydrotelluric acid (H_2Te) is a stronger acid than H_2S because Te is more electronegative than S.

Lewis Acids and Bases (Section 16.9)

16.104 The fluoride ion reacts with water to produce HF.

(**a**) Write out the chemical equation for this reaction.

(**b**) Will a concentrated solution of NaF in water be acidic, basic, or neutral?

(**c**) Is fluoride acting as a Lewis acid or as a Lewis base when reacting with water?

16.105 Identify the Lewis acid and Lewis base among the reactants in each of the following reactions:

(**a**) $Fe(ClO_4)_3(s) + 6\,H_2O(l) \rightleftharpoons [Fe(H_2O)_6]^{3+}(aq) + 3\,ClO_4^-(aq)$

(**b**) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$

(**c**) $(CH_3)_3N(g) + BF_3(g) \rightleftharpoons (CH_3)_3NBF_3(s)$

(**d**) $HIO(lq) + NH_2^-(lq) \rightleftharpoons NH_3(lq) + IO^-(lq)$
(lq denotes liquid ammonia as solvent)

16.106 Predict which member of each pair produces the more acidic aqueous solution: (**a**) K^+ or Cu^{2+}, (**b**) Fe^{2+} or Fe^{3+}, (**c**) Al^{3+} or Ga^{3+}.

Additional Exercises

16.107 Calculate the pH of each of the following solutions (K_a and K_b values are given in Appendix D): (**a**) 0.150 *M* propionic acid (C_2H_5COOH), (**b**) 0.250 *M* hydrogen chromate ion ($HCrO_4^-$), (**c**) 0.750 *M* pyridine (C_5H_5N).

16.108 Determine the pH of each of the following solutions (K_a and K_b values are given in Appendix D): (**a**) 0.095 *M* hypochlorous acid, (**b**) 0.0085 *M* hydrazine, (**c**) 0.165 *M* hydroxylamine.

16.109 Indicate whether each of the following statements is correct or incorrect.

(**a**) Every Brønsted–Lowry acid is also a Lewis acid.

(**b**) Every Lewis acid is also a Brønsted–Lowry acid.

(**c**) Conjugate acids of weak bases produce more acidic solutions than conjugate acids of strong bases.

(**d**) K^+ ion is acidic in water because it causes hydrating water molecules to become more acidic.

(**e**) The percent ionization of a weak acid in water increases as the concentration of acid decreases.

16.110 A solution is made by adding 1.000 g $Ca(OH)_2(s)$, 100.0 mL of 0.10 *M* H_2SO_4, and enough water to make a final volume of 350.0 mL. Assuming that all of the solid dissolves, what is the pH of the final solution?

16.111 The odor of fish is due primarily to amines, especially methylamine (CH_3NH_2). Fish is often served with a wedge of lemon, which contains citric acid. The amine and the acid react forming a product with no odor, thereby making the less-than-fresh fish more appetizing. Using data from Appendix D, calculate the equilibrium constant for the reaction of citric acid with methylamine, if only the first proton of the citric acid (K_{a1}) is important in the neutralization reaction.

16.112 Which, if any, of the following statements are true?

(**a**) The stronger the base, the smaller the pK_b.

(**b**) The stronger the base, the larger the pK_b.

(**c**) The stronger the base, the smaller the K_b.

(**d**) The stronger the base, the larger the K_b.

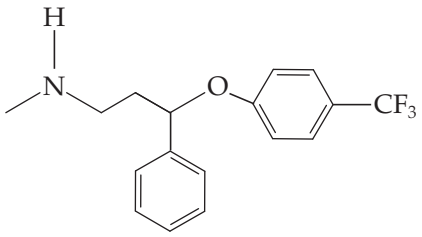
(**e**) The stronger the base, the smaller the pK_a of its conjugate acid.

(**f**) The stronger the base, the larger the pK_a of its conjugate acid.

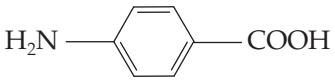
16.113 Predict how each molecule or ion would act, in the Brønsted–Lowry sense, in aqueous solution by writing "acid," "base," "both," or "neither" on the line provided.

(**a**) HCO_3^-, the bicarbonate ion: _____

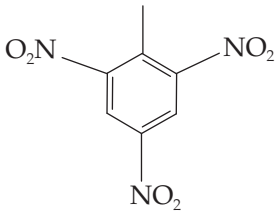
(**b**) Prozac: _____



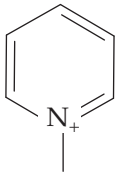
(**c**) PABA (formerly on sunscreen): _____



(**d**) TNT, trinitrotoluene: _____

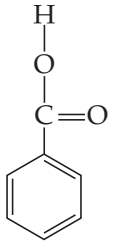


(**e**) *N*-Methylpyridinium: _____

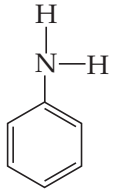


16.114 Calculate the pH of a solution made by adding 1.00 g potassium oxide (K_2O) to enough water to make 2.00 L of solution.

16.115 Benzoic acid (C_6H_5COOH) and aniline ($C_6H_5NH_2$) are both derivatives of benzene. Benzoic acid is an acid with $K_a = 6.3 \times 10^{-5}$ and aniline is a base with $K_a = 4.3 \times 10^{-10}$.



Benzoic acid



Aniline

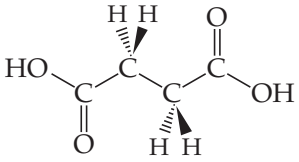
(a) What are the conjugate base of benzoic acid and the conjugate acid of aniline? **(b)** Anilinium chloride ($C_6H_5NH_3Cl$) is a strong electrolyte that dissociates into anilinium ions ($C_6H_5NH_3^+$) and chloride ions. Which will be more acidic, a 0.10 *M* solution of benzoic acid or a 0.10 *M* solution of anilinium chloride? **(c)** What is the value of the equilibrium constant for the following equilibrium?

$$C_6H_5COOH(aq) + C_6H_5NH_2(aq) \rightleftharpoons C_6H_5COO^-(aq) + C_6H_5NH_3^+(aq)$$

16.116 What is the pH of a solution that is 1.2×10^{-8} *M* in KOH? Does your answer make sense? What assumption do we normally make that is not valid in this case?

16.117 Oxalic acid ($H_2C_2O_4$) is a diprotic acid. By using data in Appendix D as needed, determine whether each of the following statements is true: **(a)** $H_2C_2O_4$ can serve as both a Brønsted–Lowry acid and a Brønsted–Lowry base. **(b)** $C_2O_4^{2-}$ is the conjugate base of $HC_2O_4^-$. **(c)** An aqueous solution of the strong electrolyte KHC_2O_4 will have pH < 7.

16.118 Succinic acid ($H_2C_4H_6O_4$), which we will denote H_2Suc, is a biologically relevant diprotic acid with the structure shown here. At 25 °C, the acid-dissociation constants for succinic acid are $K_{a1} = 6.9 \times 10^{-5}$ and $K_{a2} = 2.5 \times 10^{-6}$. **(a)** Determine the pH of a 0.32 *M* solution of H_2Suc at 25 °C, assuming that only the first dissociation is relevant. **(b)** Determine the molar concentration of Suc^{2-} in the solution in part (a). **(c)** Is the assumption you made in part (a) justified by the result from part (b)? **(d)** Will a solution of the salt NaHSuc be acidic, neutral, or basic?



16.119 Butyric acid is responsible for the foul smell of rancid butter. The pK_b of the butyrate ion is 9.16. **(a)** Calculate the K_a for butyric acid. **(b)** Calculate the pH of a 0.075 *M* solution of butyric acid. **(c)** Calculate the pH of a 0.075 *M* solution of sodium butyrate.

16.120 Arrange the following 0.10 *M* solutions in order of increasing acidity: (i) $HCOONH_4$, (ii) NH_4Br, (iii) $NaNO_3$, (iv) HCOOK, (v) KF.

16.121 A 0.25 *M* solution of a salt NaA has pH = 9.29. What is the value of K_a for the parent acid HA?

16.122 The following observations are made about a diprotic acid H_2A: (i) A 0.10 *M* solution of H_2A has pH = 3.30. (ii) A 0.10 *M* solution of the salt NaHA is acidic. Which of the following could be the value of pK_{a2} for H_2A: (i) 3.22, (ii) 5.30, (iii) 7.47, or (iv) 9.82?

16.123 Many moderately large organic molecules containing basic nitrogen atoms are not very soluble in water as neutral molecules, but they are frequently much more soluble as their acid salts. Assuming that pH in the stomach is 2.5, indicate whether each of the following compounds would be present in the stomach as the neutral base or in the protonated form: nicotine, $K_b = 7 \times 10^{-7}$; caffeine, $K_b = 4 \times 10^{-14}$; strychnine, $K_b = 1 \times 10^{-6}$; quinine, $K_b = 1.1 \times 10^{-6}$.

16.124 The amino acid glycine ($H_2N—CH_2—COOH$) can participate in the following equilibria in water:

$$H_2N—CH_2—COOH + H_2O \rightleftharpoons H_2N—CH_2—COO^- + H_3O^+ \quad K_a = 4.3 \times 10^{-3}$$

$$H_2N—CH_2—COOH + H_2O \rightleftharpoons {}^+H_3N—CH_2—COOH + OH^- \quad K_b = 6.0 \times 10^{-5}$$

(**a**) Use the values of K_a and K_b to estimate the equilibrium constant for the intramolecular proton transfer to form a zwitterion:

$$H_2N—CH_2—COOH \rightleftharpoons {}^+H_3N—CH_2—COO^-$$

(**b**) What is the pH of a 0.050 *M* aqueous solution of glycine?

(**c**) What would be the predominant form of glycine in a solution with pH 13? With pH 1?

16.125 The pK_b of water is _____.

(**a**) 1 (**b**) 7 (**c**) 14 (**d**) not defined (**e**) none of these

Integrative Exercises

16.126 Calculate the number of $H^+(aq)$ ions in 1.0 mL of pure water at 25 °C.

16.127 How many milliliters of concentrated hydrochloric acid solution (36.0% HCl by mass, density = 1.18 g/mL) are required to produce 10.0 L of a solution that has a pH of 2.05?

16.128 The volume of an adult's stomach ranges from about 50 mL when empty to 1 L when full. If the stomach volume is 400 mL and its contents have a pH of 2, how many moles of H^+ does the stomach contain? Assuming that all the H^+ comes from HCl, how many grams of sodium hydrogen carbonate will totally neutralize the stomach acid?

16.129 Atmospheric CO_2 levels have risen by nearly 20% over the past 40 years from 320 ppm to 400 ppm. **(a)** Given that the average pH of clean, unpolluted rain today is 5.4, determine the pH of unpolluted rain 40 years ago. Assume that carbonic acid (H_2CO_3) formed by the reaction of CO_2 and water is the only factor influencing pH.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

(b) What volume of CO_2 at 25 °C and 101.3 kPa is dissolved in a 20.0 L bucket of today's rainwater?

16.130 At 50 °C, the ion-product constant for H_2O has the value $K_w = 5.48 \times 10^{-14}$. **(a)** What is the pH of pure water at 50 °C? **(b)** Based on the change in K_w with temperature, predict whether ΔH is positive, negative, or zero for the autoionization reaction of water:

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

16.131 In many reactions, the addition of $AlCl_3$ produces the same effect as the addition of H^+.

(a) Draw a Lewis structure for $AlCl_3$ in which no atoms carry formal charges, and determine its structure using the VSEPR method.

(b) What characteristic is notable about the structure in part (a) that helps us understand the acidic character of $AlCl_3$?

(c) Predict the result of the reaction between $AlCl_3$ and NH_3 in a solvent that does not participate as a reactant.

(d) Which acid–base theory is most suitable for discussing the similarities between $AlCl_3$ and H^+?

16.132 What is the boiling point of a 0.10 *M* solution of $NaHSO_4$ if the solution has a density of 1.002 g/mL?

16.133 Use average bond enthalpies from Table 8.4 to estimate the enthalpies of the following gas-phase reactions:

Reaction 1: $HF(g) + H_2O(g) \rightleftharpoons F^-(g) + H_3O^+(g)$

Reaction 2: $HCl(g) + H_2O(g) \rightleftharpoons Cl^-(g) + H_3O^+(g)$

Are both reactions exothermic? How do these values relate to the different strengths of hydrofluoric and hydrochloric acid?

16.134 Cocaine is a weak organic base whose molecular formula is $C_{17}H_{21}NO_4$. An aqueous solution of cocaine was found to have a pH of 8.53 and an osmotic pressure of 7.03 kPa at 15 °C. Calculate K_b for cocaine.

16.135 The iodate ion is reduced by sulfite according to the following reaction:

$$IO_3^-(aq) + 3\,SO_3^{2-}(aq) \longrightarrow I^-(aq) + 3\,SO_4^{2-}(aq)$$

The rate of this reaction is found to be first order in IO_3^-, first order in SO_3^{2-}, and first order in H^+.

(a) Write the rate law for the reaction.

(b) By what factor will the rate of the reaction change if the pH is lowered from 5.00 to 3.50? Does the reaction proceed more quickly or more slowly at the lower pH?

(c) By using the concepts discussed in Section 14.6, explain how the reaction can be pH-dependent even though H^+ does not appear in the overall reaction.

16.136 (**a**) Using dissociation constants from Appendix D, determine the value for the equilibrium constant for each of the following reactions.

(i) $HCO_3^-(aq) + OH^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H_2O(l)$

(ii) $NH_4^+(aq) + CO_3^{2-}(aq) \rightleftharpoons NH_3(aq) + HCO_3^-(aq)$

(**b**) We usually use single arrows for reactions when the forward reaction is appreciable (*K* much greater than 1) or when products escape from the system, so that equilibrium is never established. If we follow this convention, which of these equilibria might be written with a single arrow?

Design an Experiment

Your professor gives you a bottle that contains a clear liquid. You are told that the liquid is a pure substance that is volatile, soluble in water, and might be an acid or a base. Design experiments to elucidate the following about this unknown sample. (**a**) Determine whether the substance in the sample is an acid or a base. (**b**) Suppose the substance is an acid. How would you determine whether it is a strong acid or a weak acid? (**c**) If the substance is a weak acid, how would you determine the value of K_a for the substance? (**d**) Suppose the substance were a weak acid and that you are also given a solution of NaOH(*aq*) of known molarity. What procedure would you use to isolate a pure sample of the sodium salt of the substance? (**e**) Now suppose that the substance were a base rather than an acid. How would you adjust the procedures in parts (b) and (c) to determine if the substance were a strong or weak base, and, if weak, the value of K_b?

17

ADDITIONAL ASPECTS OF AQUEOUS EQUILIBRIA

WHAT'S AHEAD

17.1 ▶ The Common-Ion Effect

17.2 ▶ Buffers

17.3 ▶ Acid–Base Titrations

17.4 ▶ Solubility Equilibria

17.5 ▶ Factors That Affect Solubility

17.6 ▶ Precipitation and Separation of Ions

17.1 | The Common-Ion Effect



Water, the most common and most important solvent on Earth, occupies its position of importance because of its abundance and its exceptional ability to dissolve a wide variety of substances. In this chapter, we take a step toward understanding such complex solutions by looking first at further applications of acid–base equilibria. The idea is to consider not only solutions in which there is a single solute but also those containing a mixture of solutes. We then broaden our discussion to include two additional types of aqueous equilibria: those involving slightly soluble salts and those involving the formation of metal complexes in solution. The discussions and calculations in this chapter are extensions of those in Chapters 15 and 16. We start our

examination with what we call the common-ion effect. By the end of this section, you should be able to

- Describe the common-ion effect.

In Chapter 16, we examined the equilibrium concentrations of ions in solutions containing a weak acid or a weak base. We now consider solutions that contain a weak acid, such as acetic acid (CH_3COOH), and a soluble salt of that acid, such as sodium acetate (CH_3COONa). Notice that these solutions contain two substances that share a *common ion*, CH_3COO^-. It is instructive to view these solutions from the perspective of Le Châtelier's principle.

Sodium acetate is a soluble ionic compound and therefore a strong electrolyte. Consequently, it dissociates completely in aqueous solution to form Na^+ and CH_3COO^- ions:

$$CH_3COONa(aq) \longrightarrow Na^+(aq) + CH_3COO^-(aq)$$

In contrast, CH_3COOH is a weak electrolyte that ionizes only partially, represented by the dynamic equilibrium

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad [17.1]$$

The equilibrium constant for Equation 17.1 is $K_a = 1.8 \times 10^{-5}$ at 25 °C (Table 16.2). If we add sodium acetate to a solution of acetic acid in water, the CH_3COO^- from CH_3COONa causes the equilibrium concentrations of the substances in Equation 17.1 to shift to the left as expected from Le Châtelier's principle, thereby decreasing the equilibrium concentration of $H^+(aq)$:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

In other words, the presence of the added acetate ion causes the acetic acid to ionize less than it normally would. We call this observation the **common-ion effect**.

> *Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution.*

Note that the equilibrium constant itself does not change; it is the relative concentrations of products and reactants in the equilibrium expression that change.

Sample Exercise 17.1

Calculating the pH When a Common Ion Is Involved

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

SOLUTION

Analyze We are asked to determine the pH of a solution of a weak electrolyte (CH_3COOH) and a strong electrolyte (CH_3COONa) that share a common ion, CH_3COO^-.

Plan In any problem in which we must determine the pH of a solution containing a mixture of solutes, it is helpful to proceed by a series of logical steps:

(**1**) Consider which solutes are strong electrolytes and which are weak electrolytes, and identify the major species in solution.

(**2**) Identify the important equilibrium reaction that is the source of H^+ and therefore determines pH.

(**3**) Tabulate the concentrations of ions involved in the equilibrium.

(**4**) Use the equilibrium-constant expression to calculate $[H^+]$ and then pH.

Solve

First, because CH_3COOH is a weak electrolyte and CH_3COONa is a strong electrolyte, the major species in the solution are CH_3COOH (a weak acid), Na^+ (which is neither acidic nor basic and is therefore a spectator in the acid–base chemistry), and CH_3COO^- (which is the conjugate base of CH_3COOH).

Second, $[H^+]$ and, therefore, the pH are controlled by the dissociation equilibrium of CH_3COOH:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

(We have written the equilibrium using $H^+(aq)$ rather than $H_3O^+(aq)$, but both representations of the hydrated hydrogen ion are equally valid.)

Third, we tabulate the initial and equilibrium concentrations as we did in solving other equilibrium problems in Chapters 15 and 16:

The equilibrium concentration of CH_3COO^- (the common ion) is the initial concentration that is due to CH_3COONa (0.30 *M*) plus the change in concentration (x) that is due to the ionization of CH_3COOH.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Initial (*M*)	0.30	0	0.30
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$(0.30 - x)$	x	$(0.30 + x)$

Now we can use the equilibrium expression:

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

The dissociation constant for CH_3COOH at 25 °C is from Table 16.2, or Appendix D; addition of CH_3COONa does not change the value of this constant. Substituting the equilibrium concentrations from our table into the equilibrium expression gives:

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x}$$

Because K_a is small, we assume that x is small compared to the original concentrations of CH_3COOH and CH_3COO^- (0.30 *M* each). Thus, we can ignore the very small x relative to 0.30 *M*, giving:

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$

The resulting value of x is indeed small relative to 0.30, justifying the approximation made in simplifying the problem.

$$x = 1.8 \times 10^{-5}\,M = [H^+]$$

Finally, we calculate the pH from the equilibrium concentration of $H^+(aq)$:

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

Comment In Section 16.5, we calculated that a 0.30 *M* solution of CH_3COOH has a pH of 2.64, corresponding to $[H^+] = 2.3 \times 10^{-3}\,M$. Thus, the addition of CH_3COONa has substantially decreased $[H^+]$, as we expect from Le Châtelier's principle.

Practice Exercise

For the generic equilibrium $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$, which of these statements is true?

(**a**) The equilibrium constant for this reaction changes as the pH changes.

(**b**) If you add the soluble salt KA to a solution of HA that is at equilibrium, the concentration of HA would decrease.

(**c**) If you add the soluble salt KA to a solution of HA that is at equilibrium, the concentration of A^- would decrease.

(**d**) If you add the soluble salt KA to a solution of HA that is at equilibrium, the pH would increase.

Sample Exercise 17.2

Calculating Ion Concentrations When a Common Ion Is Involved

Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl.

SOLUTION

Analyze We are asked to determine the concentration of F^- and the pH in a solution containing the weak acid HF and the strong acid HCl. In this case the common ion is H^+.

Plan We can again use the four steps outlined in Sample Exercise 17.1.

Solve

Because HF is a weak acid and HCl is a strong acid, the major species in solution are HF, H^+, and Cl^-. The Cl^-, which is the conjugate base of a strong acid, is merely a spectator ion in any acid–base chemistry. The problem asks for $[F^-]$, which is formed by ionization of HF. Thus, this is the important equilibrium:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

The common ion in this problem is the hydrogen (or hydronium) ion. Now we can tabulate the initial and equilibrium concentrations of each species involved in this equilibrium:

	$HF(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$F^-(aq)$
Initial (*M*)	0.20		0.10		0
Change (*M*)	$-x$		$+x$		$+x$
Equilibrium (*M*)	$(0.20 - x)$		$(0.10 + x)$		x

The equilibrium constant for the ionization of HF, from Appendix D, is 6.8×10^{-4}. Substituting the equilibrium-constant concentrations into the equilibrium expression gives:

$$K_a = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(0.10 + x)(x)}{0.20 - x}$$

If we assume that x is small relative to 0.10 or 0.20 *M*, this expression simplifies to:

$$\frac{(0.10)(x)}{0.20} = 6.8 \times 10^{-4}$$

$$x = \frac{0.20}{0.10}(6.8 \times 10^{-4}) = 1.4 \times 10^{-3}\,M = [F^-]$$

This F^- concentration is substantially smaller than it would be in a 0.20 *M* solution of HF with no added HCl. The common ion, H^+, suppresses the ionization of HF. The concentration of $H^+(aq)$ is:

$$[H^+] = (0.10 + x)\,M \simeq 0.10\,M$$

Thus,

$$pH = 1.00$$

Comment Notice that for all practical purposes, the hydrogen ion concentration is due entirely to the HCl; the HF makes a negligible contribution by comparison.

Practice Exercise

Calculate the concentration of the lactate ion in a solution that is 0.100 *M* in lactic acid ($CH_3CH(OH)COOH$, $pK_a = 3.86$) and 0.080 *M* in HCl.

(**a**) 4.83 *M* (**b**) 0.0800 *M*
(**c**) $7.3 \times 10^{-3}\,M$ (**d**) $3.65 \times 10^{-3}\,M$
(**e**) $1.73 \times 10^{-4}\,M$

Sample Exercises 17.1 and 17.2 both involve weak acids. The ionization of a weak base is also decreased by the addition of a common ion. For example, the addition of NH_4^+ (as from the strong electrolyte NH_4Cl) causes the equilibrium concentrations of the reagents in Equation 17.2 to shift to the left, decreasing the equilibrium concentration of OH^- and lowering the pH:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad [17.2]$$

Addition of NH_4^+ shifts equilibrium concentrations, lowering $[OH^-]$

Self-Assessment Exercise

17.1 In a solution made from the weak base ammonia, NH_3, and the soluble salt $Ca(OH)_2$, which is the common ion?

(a) NH_3

(b) NH_4^+

(c) Ca^{2+}

(d) OH^-

Exercises

17.2 Consider the equilibrium

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq).$$

Suppose that a salt of $HB^+(aq)$ is added to a solution of $B(aq)$ at equilibrium. (**a**) Will the equilibrium constant for the reaction increase, decrease, or stay the same? (**b**) Will the concentration of $B(aq)$ increase, decrease, or stay the same? (**c**) Will the pH of the solution increase, decrease, or stay the same?

17.3 Use information from Appendix D to calculate the pH of (**a**) a solution that is 0.250 *M* in sodium methanoate (HCOONa) and 0.150 *M* in methanoic acid (HCOOH), (**b**) a solution that is 0.490 *M* in pyridine (C_5H_5N) and 0.450 *M* in pyridinium chloride (C_5H_5NHCl), (**c**) a solution that is made by combining 80 mL of 0.050 *M* hydrofluoric acid with 100 mL of 0.10 *M* sodium fluoride.

17.4 (**a**) Calculate the percent ionization of 0.250 *M* lactic acid ($K_a = 1.4 \times 10^{-4}$). (**b**) Calculate the percent ionization of 0.250 *M* lactic acid in a solution containing 0.050 *M* sodium lactate.

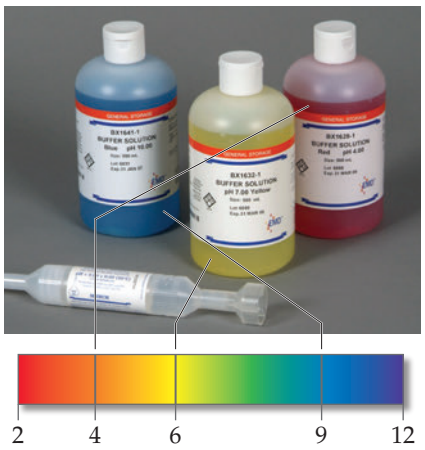
Answers to Self-Assessment Exercises

17.1 (d)

17.2 Buffers



Buffers are used in many areas of industry. For example, to control the pH of a dying process, in fermentation to counter the acidity resulting from CO_2 release, in the culture medium used in microbiology labs, and in the manufacture of pharmaceuticals. Buffers are used in processed food to maintain color and flavor and delay spoilage. For example, sodium citrate (assigned the number E331 on food packaging) is added to fruit products such as jams and jellies to act with the naturally present citric acid as a buffer, maintaining color and helping preserve the fruit.



▲ **Figure 17.1 Standard buffers.** For laboratory work, prepackaged buffers at specific pH values can be purchased.

By the end of this section, you should be able to

- Explain how a buffer functions and calculate the pH of a buffered solution.
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base.
- Calculate the appropriate quantities of compounds to make a buffer at a given pH.

Solutions that contain high concentrations ($10^{-3}\ M$ or more) of a weak conjugate acid–base pair and that resist drastic changes in pH when small amounts of strong acid or strong base are added to them are called **buffered solutions** (or merely **buffers**). Human blood, for example, is a complex buffered solution that maintains the blood pH at about 7.4 (The *Chemistry and Life* box, "Blood as a Buffered Solution" later in this section). Much of the chemical behavior of seawater is determined by its pH, buffered at about 8.1 to 8.3 near the surface due to the HCO_3^-/CO_3^{2-} acid-base pair. Buffers find many important applications in the laboratory and in medicine (**Figure 17.1**). Many biological reactions occur at the optimal rates only when properly buffered. If you ever work in a biochemistry lab, you will very likely have to prepare specific buffers in which to run your biochemical reactions.

Composition and Action of Buffers

A buffer resists changes in pH because it contains both an acid to neutralize added OH^- ions and a base to neutralize added H^+ ions. The acid and base that make up the buffer, however, must not consume each other through a neutralization reaction. These requirements are fulfilled by a weak acid–base conjugate pair, such as CH_3COOH/CH_3COO^- or NH_4^+/NH_3. The key is to have roughly equal concentrations of both the weak acid and its conjugate base. There are two ways to make a buffer.

- Mix a weak acid or a weak base with a salt of that acid or base. For example, the CH_3COOH/CH_3COO^- buffer can be prepared by adding CH_3COONa to a solution of CH_3COOH. Similarly, the NH_4^+/NH_3 buffer can be prepared by adding NH_4Cl to a solution of NH_3.
- Make the conjugate acid or base from a solution of weak base or acid by the addition of a strong acid or base. For example, to make the CH_3COOH/CH_3COO^- buffer, you could start with a solution of CH_3COOH and add some NaOH to the solution—enough to neutralize about half of CH_3COOH according to the reaction

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

Neutralization reactions have very large equilibrium constants, and so the amount of acetate formed will only be limited by the relative amounts of the acid and strong base that are mixed. The resulting solution is the same as if you added sodium acetate to the acetic acid solution: You will have comparable quantities of both acetic acid and its conjugate base in solution.

By choosing appropriate components and adjusting their relative concentrations, we can buffer a solution at virtually any pH.

To understand how a buffer works, let's consider one composed of a weak acid HA and one of its salts MA, where M^+ could be Na^+, K^+, or any other cation that does not react with water. The acid-dissociation equilibrium in this buffered solution involves both the acid and its conjugate base:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad [17.3]$$

The corresponding acid-dissociation-constant expression is

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad [17.4]$$

Solving this expression for $[H^+]$, we have

$$[H^+] = K_a\frac{[HA]}{[A^-]} \qquad [17.5]$$

We see from this expression that $[H^+]$ and, thus, the pH are determined by two factors:

- the value of K_a for the weak-acid component of the buffer;
- the ratio of the concentrations of the conjugate acid–base pair, $[HA]/[A^-]$.

If OH^- ions are added to this buffered solution, they react with the buffer acid component to produce water and A^-:

$$\underset{\text{added base}}{OH^-(aq)} + HA(aq) \longrightarrow H_2O(l) + A^-(aq) \qquad [17.6]$$

This neutralization reaction causes $[HA]$ to decrease and $[A^-]$ to increase. As long as the amounts of HA and A^- in the buffer are large relative to the amount of OH^- added, the ratio $[HA]/[A^-]$ does not change much and, thus, the change in pH is small.

If H^+ ions are added, they react with the base component of the buffer:

$$\underset{\text{added acid}}{H^+(aq)} + A^-(aq) \longrightarrow HA(aq) \qquad [17.7]$$

This reaction can also be represented using H_3O^+:

$$H_3O^+(aq) + A^-(aq) \longrightarrow HA(aq) + H_2O(l)$$

Using either equation, we see that this reaction causes $[A^-]$ to decrease and $[HA]$ to increase. As long as the change in the ratio $[HA]/[A^-]$ is small, the change in pH will be small.

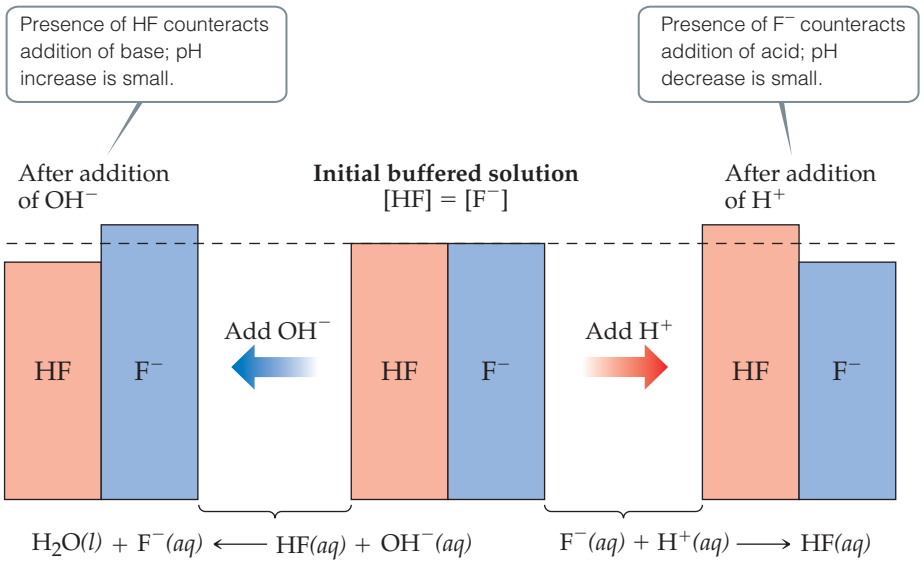
An example of an HA/A^- buffer is the HF/F^- buffered solution shown in **Figure 17.2**. The buffer consists of equal concentrations of hydrofluoric acid, HF, and fluoride ion, F^- (center). The addition of OH^- reduces $[HF]$ and slightly increases $[F^-]$, whereas the addition of H^+ reduces $[F^-]$ and slightly increases $[HF]$.

It is possible to overwhelm a buffer by adding too much strong acid or strong base. We will examine this in more detail a little later in this chapter.

Calculating the pH of a Buffer

Because conjugate acid–base pairs share a common ion, we can use the same procedures to calculate the pH of a buffer that we used to treat the common-ion effect in Sample Exercise 17.1. Alternatively, we can take an approach based on an equation derived from Equation 17.5. Taking the negative logarithm of both sides of Equation 17.5, we have

$$-\log[H^+] = -\log\left(K_a\frac{[HA]}{[A^-]}\right) = -\log K_a - \log\frac{[HA]}{[A^-]}$$



▲ **Figure 17.2 Buffer action.** The pH of an HF/F^- buffered solution changes by only a small amount in response to addition of an acid or base.

Because $-\log[H^+] = pH$ and $-\log K_a = pK_a$, we have

$$pH = pK_a - \log\frac{[HA]}{[A^-]} = pK_a + \log\frac{[A^-]}{[HA]} \qquad [17.8]$$

(Remember the logarithm rules in Appendix A.2, if you are not sure how this calculation works.)

In general,

$$pH = pK_a + \log\frac{[base]}{[acid]} \qquad [17.9]$$

where [acid] and [base] refer to the equilibrium concentrations of the *conjugate acid–base pair*. Note that when [base] = [acid], we have $pH = pK_a$.

Equation 17.9 is known as the **Henderson–Hasselbalch equation**. Biologists, biochemists, and others who work frequently with buffers often use this equation to calculate the pH of buffers. In doing equilibrium calculations, we have seen that we can normally neglect the amounts of the acid and base of the buffer that ionize. Therefore, we can usually use the initial concentrations of the acid and base components of the buffer directly in Equation 17.9, as seen in Sample Exercise 17.3. However, the assumption that the initial concentrations of the acid and base components in the buffer are equal to the equilibrium concentrations is just that: an assumption. There may be times when you will need to be more careful, as seen in Sample Exercise 17.4.

Sample Exercise 17.3

Calculating the pH of a Buffer

What is the pH of a buffer that is 0.12 *M* in lactic acid [$CH_3CH(OH)COOH$, or $HC_3H_5O_3$] and 0.10 *M* in sodium lactate [$CH_3CH(OH)COONa$ or $NaC_3H_5O_3$]? For lactic acid, $K_a = 1.4 \times 10^{-4}$.

SOLUTION

Analyze We are asked to calculate the pH of a buffer containing lactic acid ($HC_3H_5O_3$) and its conjugate base, the lactate ion ($C_3H_5O_3^-$).

Plan We will first determine the pH using the method described in Section 17.1. Because $HC_3H_5O_3$ is a weak electrolyte and $NaC_3H_5O_3$ is a strong electrolyte, the major species in solution are $HC_3H_5O_3$, Na^+, and $C_3H_5O_3^-$. The Na^+ ion is a spectator ion. The $HC_3H_5O_3/C_3H_5O_3^-$ conjugate acid–base pair determines $[H^+]$ and, thus, pH; $[H^+]$ can be determined using the acid-dissociation equilibrium of lactic acid.

Solve

The initial and equilibrium concentrations of the species involved in this equilibrium are:

$$CH_3CH(OH)COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH(OH)COO^-(aq)$$

Initial (*M*)	0.12	0	0.10
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$(0.12 - x)$	x	$(0.10 + x)$

The equilibrium concentrations are governed by the equilibrium expression:

$$K_a = 1.4 \times 10^{-4} = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{x(0.10 + x)}{0.12 - x}$$

Because K_a is small and a common ion is present, we expect x to be small relative to either 0.12 or 0.10 *M*. Thus, our equation can be simplified to give:

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

Solving for x gives a value that justifies our approximation:

$$[H^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4}\,M$$

Then, we can solve for pH:

$$pH = -\log(1.7 \times 10^{-4}) = 3.77$$

Alternatively, we can use the Henderson–Hasselbalch equation with the initial concentrations of acid and base to calculate pH directly:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 3.85 + \log\left(\frac{0.10}{0.12}\right)$$
$$= 3.85 + (-0.08) = 3.77$$

Practice Exercise

If the pH of a buffer solution is equal to the pK_a of the acid in the buffer, what does this tell you about the relative concentrations of the acid and conjugate base forms of the buffer components?

(**a**) The acid concentration must be zero. (**b**) The base concentration must be zero. (**c**) The acid and base concentrations must be equal. (**d**) The acid and base concentrations must be equal to the K_a. (**e**) The base concentration must be 2.3 times as large as the acid concentration.

Sample Exercise 17.4

Calculating pH When the Henderson–Hasselbalch Equation May Not Be Accurate

Calculate the pH of a buffer that initially contains 1.00×10^{-3} *M* CH_3COOH and 1.00×10^{-4} *M* CH_3COONa in the following two ways: (i) using the Henderson–Hasselbalch equation and (ii) making no assumptions about quantities (which means you will need to use the quadratic equation). The K_a of CH_3COOH is 1.80×10^{-5}.

SOLUTION

Analyze We are asked to calculate the pH of a buffer two different ways. We know the initial concentrations of the weak acid and its conjugate base, and the K_a of the weak acid.

Plan We will first use the Henderson–Hasselbalch equation, which relates pK_a and ratio of acid–base concentrations to the pH. This will be straightforward. Then, we will redo the calculation making no assumptions about any quantities, which means we will need to write out the initial/change/equilibrium concentrations, as we have done before. In addition, we will need to solve for quantities using the quadratic equation (since we cannot make assumptions about unknowns being small).

Solve

(**i**) The Henderson–Hasselbalch equation is:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

We know the K_a of the acid (1.8×10^{-5}), so we know pK_a ($pK_a = -\log K_a = 4.74$). We know the initial concentrations of the base, sodium acetate, and the acid, acetic acid, which we will assume are the same as the equilibrium concentrations.

Therefore, we have:

$$\text{pH} = 4.74 + \log\frac{(1.00 \times 10^{-4})}{(1.00 \times 10^{-3})}$$
$$= 4.74 - 1.00 = 3.74$$

(**ii**) Now we will redo the calculation, without making any assumptions at all. We will solve for x, which represents the H^+ concentration at equilibrium, in order to calculate pH.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

	CH_3COOH	CH_3COO^-	H^+
Initial (*M*)	1.00×10^{-3}	1.00×10^{-4}	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$(1.00 \times 10^{-3} - x)$	$(1.00 \times 10^{-4} + x)$	x

$$\frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = K_a$$

$$\frac{(1.00 \times 10^{-4} + x)(x)}{(1.00 \times 10^{-3} - x)} = 1.8 \times 10^{-5}$$

$$1.00 \times 10^{-4}x + x^2 = 1.8 \times 10^{-5}(1.00 \times 10^{-3} - x)$$

$$x^2 + 1.00 \times 10^{-4}x = 1.8 \times 10^{-8} - 1.8 \times 10^{-5}x$$

$$x^2 + 1.18 \times 10^{-4}x - 1.8 \times 10^{-8} = 0$$

$$x = \frac{-1.18 \times 10^{-4} \pm \sqrt{(1.18 \times 10^{-4})^2 - 4(1)(-1.8 \times 10^{-8})}}{2(1)}$$

$$= \frac{-1.18 \times 10^{-4} \pm \sqrt{8.5924 \times 10^{-8}}}{2}$$

$$= 8.76 \times 10^{-5} = [H^+]$$

$$\text{pH} = 4.06$$

Continued

Comment In Sample Exercise 17.3, the calculated pH is the same whether we solve exactly using the quadratic equation or make the simplifying assumption that the equilibrium concentrations of acid and base are equal to their initial concentrations. The simplifying assumption works because the concentrations of the acid–base conjugate pair are both a thousand times larger than K_a. In this Sample Exercise, the acid–base conjugate pair concentrations are only 10–100 as large as K_a. Therefore, we cannot assume that x is small compared to the initial concentrations (that is, that the initial concentrations are essentially equal to the equilibrium concentrations). The best answer to this Sample Exercise is pH = 4.06, obtained without assuming x is small. Therefore, we see that the assumptions behind the Henderson–Hasselbalch equation are not valid when the initial concentration of the weak acid (or base) is small compared to its K_a (or K_b).

Practice Exercise

A buffer is made with sodium acetate (CH_3COONa) and acetic acid (CH_3COOH); the K_a for acetic acid is 1.80×10^{-5}. The pH of the buffer is 3.98. What is the ratio of the equilibrium concentration of sodium acetate to that of acetic acid? (**a**) −0.760 (**b**) 0.174 (**c**) 0.840 (**d**) 5.75 (**e**) Not enough information is given to answer this question.

In Sample Exercise 17.3 we calculated the pH of a buffered solution. Often we will need to work in the opposite direction by calculating the amounts of the acid and its conjugate base needed to achieve a specific pH. This calculation is illustrated in Sample Exercise 17.5.

Sample Exercise 17.5

Preparing a Buffer

How many moles of NH_4Cl must be added to 2.0 L of 0.10 *M* NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

SOLUTION

Analyze We are asked to determine the amount of NH_4^+ ion required to prepare a buffer of a specific pH.

Plan The major species in the solution will be NH_4^+, Cl^-, and NH_3. Of these, the Cl^- ion is a spectator (it is the conjugate base of a strong acid). Thus, the NH_4^+/NH_3 conjugate acid–base pair will determine the pH of the buffer. The equilibrium relationship between NH_4^+ and NH_3 is given by the base-dissociation reaction for NH_3:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

The key to this exercise is to use this K_b expression to calculate $[NH_4^+]$.

Solve

We obtain $[OH^-]$ from the given pH:

$$pOH = 14.00 - pH = 14.00 - 9.00 = 5.00$$

and so:

$$[OH^-] = 1.0 \times 10^{-5}\,M$$

Because K_b is small and the common ion $[NH_4^+]$ is present, the equilibrium concentration of NH_3 essentially equals its initial concentration:

$$[NH_3] = 0.10\,M$$

We now use the expression for K_b to calculate $[NH_4^+]$:

$$[NH_4^+] = K_b\frac{[NH_3]}{[OH^-]} = (1.8 \times 10^{-5})\frac{(0.10)}{(1.0 \times 10^{-5})} = 0.18\,M$$

Thus, for the solution to have pH = 9.00, $[NH_4^+]$ must equal 0.18 *M*. The number of moles of NH_4Cl needed to produce this concentration is given by the product of the volume of the solution and its molarity:

$$(2.0\,\text{L})(0.18\ \text{mol}\ NH_4Cl/\text{L}) = 0.36\ \text{mol}\ NH_4Cl$$

Comment Because NH_4^+ and NH_3 are a conjugate acid–base pair, we could use the Henderson–Hasselbalch equation (Equation 17.9) to solve this problem. To do so requires first using Equation 16.41 to calculate pK_a for NH_4^+ from the value of pK_b for NH_3. We suggest you try this approach to convince yourself that you can use the Henderson–Hasselbalch equation for buffers for which you are given K_b for the conjugate base rather than K_a for the conjugate acid.

Practice Exercise

Calculate the number of grams of ammonium chloride that must be added to 2.00 L of a 0.500 *M* ammonia solution to obtain a buffer of pH = 9.20. Assume the volume of the solution does not change as the solid is added. K_b for ammonia is 1.80×10^{-5}.
(**a**) 60.7 g (**b**) 30.4 g (**c**) 1.52 g (**d**) 0.568 g
(**e**) 1.59×10^{-5} g

Buffer Capacity and pH Range

Two important characteristics of a buffer are its capacity and its effective pH range. **Buffer capacity** is the amount of acid or base the buffer can neutralize before the pH begins to change to an appreciable degree. The buffer capacity depends on the amount of acid and base used to prepare the buffer. According to Equation 17.5, for example, the pH of a 1 L solution that is 1 *M* in CH_3COOH and 1 *M* in CH_3COONa is the same as the pH of a 1 L solution that is 0.1 *M* in CH_3COOH and 0.1 *M* in CH_3COONa. The first solution has a greater buffering capacity, however, because it contains more CH_3COOH and CH_3COO^-.

The pH range of any buffer is the pH range over which the buffer acts effectively. Buffers most effectively resist a change in pH in *either* direction when the concentrations of weak acid and conjugate base are about the same. From Equation 17.9 we see that when the concentrations of weak acid and conjugate base are equal, $pH = pK_a$. This relationship gives the optimal pH of any buffer. Thus, we usually try to select a buffer whose acid form has a pK_a close to the desired pH. In practice, we find that if the concentration of one component of the buffer is more than 10 times the concentration of the other component, the buffering action is poor. Because $\log 10 = 1$, *buffers usually have a usable range within* ± 1 *pH unit of* pK_a (that is, a range of $pH = pK_a \pm 1$).

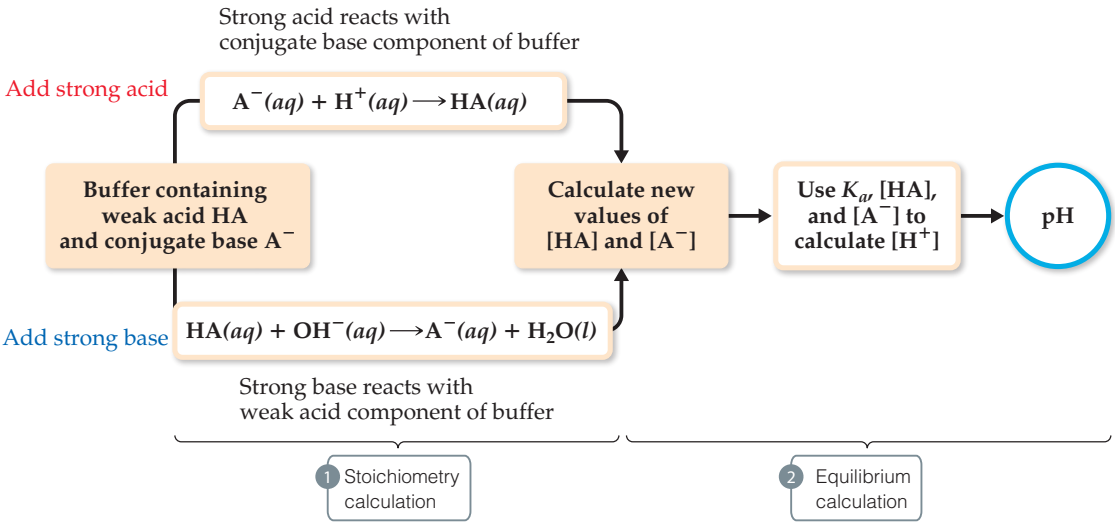
Addition of Strong Acids or Bases to Buffers

Let's now consider in a more quantitative way how a buffered solution responds to addition of a strong acid or base. In this discussion, it is important to understand that *neutralization reactions between strong acids and weak bases proceed essentially to completion, as do those between strong bases and weak acids*. This is because water is a product of the reaction, and you have an equilibrium constant of $1/K_w = 10^{14}$ in your favor when making water. Thus, as long as we do not exceed the buffering capacity of the buffer, we can assume that the strong acid or strong base is completely consumed by reaction with the buffer.

Consider a buffer that contains a weak acid HA and its conjugate base A^-. When a strong acid is added to this buffer, the added H^+ is consumed by A^- to produce HA; thus, $[HA]$ increases and $[A^-]$ decreases. (See Equation 17.7.) Upon addition of a strong base, the added OH^- is consumed by HA to produce A^-; in this case $[HA]$ decreases and $[A^-]$ increases. (See Equation 17.6.) These two situations are summarized in Figure 17.2.

To calculate how the pH of the buffer responds to the addition of a strong acid or a strong base, we follow the strategy outlined in **Figure 17.3**:

1. Consider the acid–base neutralization reaction and determine its effect on $[HA]$ and $[A^-]$. This step is a *limiting reactant stoichiometry calculation*.
2. Use the calculated values of $[HA]$ and $[A^-]$ along with K_a to calculate $[H^+]$. This step is an *equilibrium calculation* and is most easily done using the Henderson–Hasselbalch equation (if the concentrations of the weak acid–base pair are very large compared to K_a for the acid).



▲ **Figure 17.3** **Calculating the pH of a buffer after addition of a strong acid or strong base.**

Sample Exercise 17.6

Calculating pH Changes in Buffers

A buffer is made by adding 0.300 mol CH_3COOH and 0.300 mol CH_3COONa to enough water to make 1.000 L of solution. The pH of the buffer is 4.74 (Sample Exercise 17.1). (**a**) Calculate the pH of this solution after 5.0 mL of 4.0 *M* NaOH(*aq*) solution is added. (**b**) For comparison, calculate the pH of a solution made by adding 5.0 mL of 4.0 *M* NaOH(*aq*) solution to 1.000 L of pure water.

SOLUTION

Analyze We are asked to determine the pH of a buffer after addition of a small amount of strong base and to compare the pH change with the pH that would result if we were to add the same amount of strong base to pure water.

Plan Solving this problem involves the two steps outlined in Figure 17.3. First we do a stoichiometry calculation to determine how the added OH^- affects the buffer composition. Then we use the resulting buffer composition and either the Henderson–Hasselbalch equation or the equilibrium-constant expression for the buffer to determine the pH.

Solve

(a) *Stoichiometry Calculation*: The OH^- provided by NaOH reacts with CH_3COOH, the weak acid component of the buffer. Since volumes are changing, it is prudent to figure out how many moles of reactants and products would be produced, then divide by the final volume later to obtain concentrations. Prior to this neutralization reaction, there are 0.300 mol each of CH_3COOH and CH_3COO^-. The amount of base added is $0.0050\ L \times 4.0\ mol/L = 0.020$ mol. Neutralizing the 0.020 mol OH^- requires 0.020 mol of CH_3COOH. Consequently, the amount of CH_3COOH *decreases* by 0.020 mol, and the amount of the product of the neutralization, CH_3COO^-, *increases* by 0.020 mol. We can create a table to see how the composition of the buffer changes as a result of its reaction with OH^-:

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)	0.300	0.020	—	0.300
Change (limiting reactant) (mol)	−0.020	−0.020	—	+0.020
After reaction (mol)	0.280	0	—	0.320

Equilibrium Calculation: We now turn our attention to the equilibrium for the ionization of acetic acid, the relationship that determines the buffer pH:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Using the quantities of CH_3COOH and CH_3COO^- remaining in the buffer after the reaction with strong base, we determine the pH using the Henderson–Hasselbalch equation. The volume of the solution is now 1.000 L + 0.0050 L = 1.005 L due to addition of the NaOH solution:

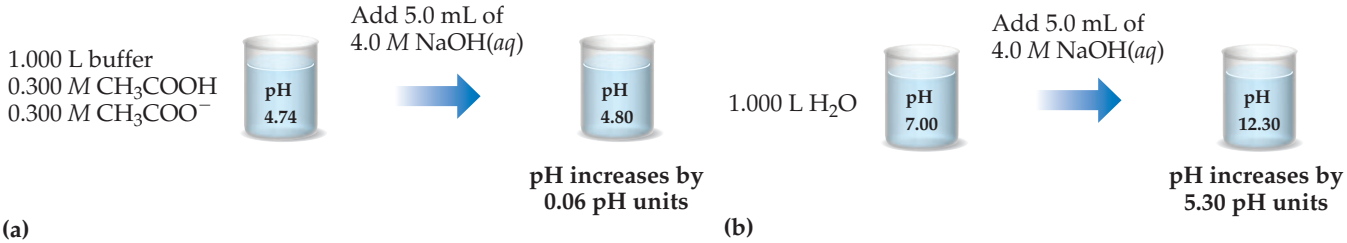
$$pH = 4.74 + \log\frac{0.320\ \cancel{mol}/1.005\ \cancel{L}}{0.280\ \cancel{mol}/1.005\ \cancel{L}} = 4.80$$

(b) To determine the pH of a solution made by adding 0.020 mol of NaOH to 1.000 L of pure water, we first determine the concentration of OH^- ions in solution:

$$[OH^-] = 0.020\ mol/1.005\ L = 0.020\ M$$

We use this value in Equation 16.18 to calculate pOH and then use our calculated pOH value to obtain pH:

$$pOH = -\log[OH^-] = -\log(0.020) = +1.70$$
$$pH = 14 - (+1.70) = 12.30$$



▲ **Figure 17.4** Effect of adding a strong base to (a) a buffered solution and to (b) water.

Comment Note that the small amount of added NaOH changes the pH of water significantly. In contrast, the pH of the buffer changes very little when the NaOH is added, as summarized in Figure 17.4.

Practice Exercise

Which of these statements is true? (**a**) If you add strong acid or base to a buffer, the pH will never change. (**b**) In order to do calculations in which strong acid or base is added to a buffer, you only need to use the Henderson–Hasselbalch equation. (**c**) Strong bases react with strong acids, but not weak acids. (**d**) If you add a strong acid or base to a buffer, the buffer's pK_a or pK_b will change. (**e**) In order to do calculations in which a strong acid or base is added to a buffer, you need to calculate the amounts of substances from the neutralization reaction and then equilibrate.

CHEMISTRY AND LIFE Blood as a Buffered Solution

Chemical reactions that occur in living systems are often extremely sensitive to pH. Many of the enzymes that catalyze important biochemical reactions are effective only within a narrow pH range. For this reason, the human body maintains a remarkably intricate system of buffers, both within cells and in the fluids that transport cells. Blood, the fluid that transports oxygen to all parts of the body, is one of the most prominent examples of the importance of buffers in living beings.

Human blood has a normal pH of 7.35 to 7.45. Any deviation from this range can have extremely disruptive effects on the stability of cell membranes, the structures of proteins, and the activities of enzymes. Death may result if the blood pH falls below 6.8 or rises above 7.8. When the pH falls below 7.35, the condition is called *acidosis*; when it rises above 7.45, the condition is called *alkalosis*. Acidosis is the more common tendency because metabolism generates several acids in the body.

The major buffer system used to control blood pH is the *carbonic acid–bicarbonate buffer system*. Carbonic acid (H_2CO_3) and bicarbonate ion (HCO_3^-) are a conjugate acid–base pair. In addition, carbonic acid decomposes into carbon dioxide gas and water. The important equilibria in this buffer system are

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g) \qquad [17.10]$$

Several aspects of these equilibria are notable. First, although carbonic acid is diprotic, the carbonate ion (CO_3^{2-}) is unimportant in this system. Second, one component of this equilibrium, CO_2, is a gas, which provides a mechanism for the body to adjust the equilibria. Removal of CO_2 via exhalation shifts the equilibria to the right, consuming H^+ ions. Third, the buffer system in blood operates at pH 7.4, which is fairly far removed from the pK_{a1} value of H_2CO_3 (6.1 at physiological temperatures). For the buffer to have a pH of 7.4, the ratio [base]/[acid] must be about 20. In normal blood plasma, the concentrations of HCO_3^- and H_2CO_3 are about 0.024 *M* and 0.0012 *M*, respectively. Consequently, the buffer has a high capacity to neutralize additional acid but only a low capacity to neutralize additional base.

The principal organs that regulate the pH of the carbonic acid–bicarbonate buffer system are the lungs and kidneys. When the concentration of CO_2 rises, the equilibrium concentrations in Equation 17.10 shift to the left, which leads to the formation of more H^+ and a drop in pH. This change is detected by receptors in the brain that trigger a reflex to breathe faster and deeper, increasing the rate at which CO_2 is expelled from the lungs and thereby shifting the equilibrium concentrations back to the right. When the blood pH becomes too high, the kidneys remove HCO_3^- from the blood. This shifts the equilibrium concentrations to the left, increasing the concentration of H^+. As a result, the pH decreases.

Regulation of blood pH relates directly to the effective transport of O_2 throughout the body. The protein hemoglobin, found in red blood cells (Figure 17.5), carries oxygen. Hemoglobin (Hb) reversibly binds both O_2 and H^+. These two substances compete for the Hb, which can be represented approximately by the equilibrium

$$HbH^+(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) + H^+(aq) \qquad [17.11]$$

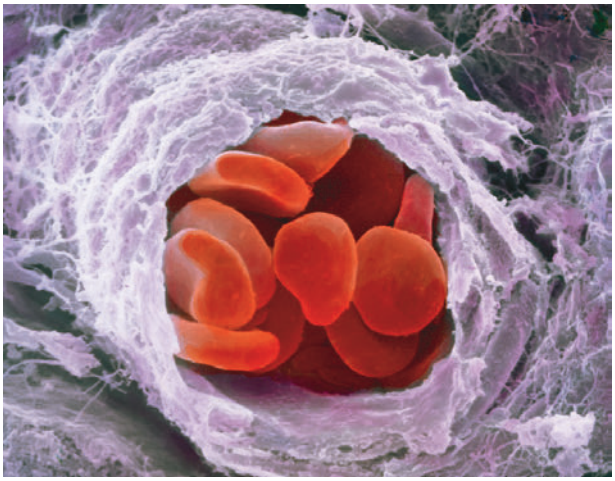
Oxygen enters the blood through the lungs, where it passes into the red blood cells and binds to Hb. When the blood reaches tissue in which the concentration of O_2 is low, the equilibrium concentrations in Equation 17.11 shift to the left and O_2 is released.

During periods of strenuous exertion, three factors work together to ensure delivery of O_2 to active tissues. The role of each factor can be understood by applying Le Châtelier's principle to Equation 17.11:

1. O_2 is consumed, causing the equilibrium concentrations to shift to the left, releasing more O_2.
2. Large amounts of CO_2 are produced by metabolism, which increases $[H^+]$ and causes the equilibrium concentrations to shift to the left, releasing O_2.
3. Body temperature rises. Because Equation 17.11 is exothermic, the increase in temperature shifts the equilibrium concentrations to the left, releasing O_2.

In addition to the factors causing release of O_2 to tissues, the decrease in pH stimulates an increase in breathing rate, which furnishes more O_2 and eliminates CO_2. Without this elaborate series of equilibrium shifts and pH changes, the O_2 in tissues would be rapidly depleted, making further activity impossible. Under such conditions, the buffering capacity of the blood and the exhalation of CO_2 through the lungs are essential to keep the pH from dropping too low, thereby triggering acidosis.

Related Exercise: 17.66



▲ **Figure 17.5 Red blood cells.** A scanning electron micrograph of red blood cells traveling through a small branch of an artery. The red blood cells are approximately 0.010 mm in diameter.

Self-Assessment Exercises

17.5 Which of the following pairs of substances will function as a buffer?

(a) HBr and Br^-

(b) H_3PO_4 and PO_4^{3-}

(c) CH_3COOH and NO_3^-

(d) CH_3NH_2 and $CH_3NH_3^+$

17.6 The K_a values for methanoic acid (HCOOH) and carbonic acid (H_2CO_3) are 1.77×10^{-4} and 4.3×10^{-7}, respectively. Which one would be more suitable for use in a solution buffered at pH = 7.00?

(a) HCOOH

(b) H_2CO_3

17.7 Starting with the same buffer as that used in sample exercise 17.6 (1.000 L that is 0.300 *M* in both CH_3COOH and CH_3COONa. $pK_a = 4.74$), calculate the pH after the addition of 0.020 mol of HCl (*g*). Assume there is no change in volume of the buffer as the HCl dissolves.

(a) 1.70

(b) 4.68

(c) 4.80

(d) 5.62

Exercises

17.8 Which of the following solutions is a buffer? (**a**) A solution made by mixing 50 mL of 0.200 *M* formic acid (HCOOH) and 250 mL of 0.200 *M* KOH, (**b**) A solution made by mixing 50 mL of 0.200 *M* formic acid (HCOOH) and 25 mL of 0.200 *M* nitric acid (HNO_3), (**c**) A solution made by mixing 50 mL of 0.200 *M* potassium formate (HCOOK) and 25 mL of 0.200 *M* KNO_3, (**d**) A solution made by mixing 50 mL of 0.200 *M* formic acid (HCOOH), and 25 mL of 0.200 *M* KOH.

17.9 (**a**) Calculate the pH of a buffer that is 0.125 *M* in $NaHCO_3$ and 0.095 *M* in Na_2CO_3. (**b**) Calculate the pH of a solution formed by mixing 25 mL of 0.25 *M* $NaHCO_3$ with 75 mL of 0.15 *M* Na_2CO_3.

17.10 A buffer is prepared by adding 3.5 g of ammonium chloride (NH_4Cl) to 100 mL of 1.00 *M* NH_3 solution. (**a**) What is the pH of this buffer? (**b**) Write the complete ionic equation for the reaction that occurs when a few drops of hydrochloric acid are added to the buffer. (**c**) Write the complete ionic equation for the reaction that occurs when a few drops of sodium hydroxide solution are added to the buffer.

17.11 You are asked to prepare a pH = 3.00 buffer starting from 2.00 L of 0.025 *M* solution of benzoic acid (C_6H_5COOH) and any amount you need of sodium benzoate (C_6H_5COONa). (**a**) What is the pH of the benzoic acid solution prior to adding sodium benzoate? (**b**) How many grams of sodium benzoate should be added to prepare the buffer? Neglect the small volume change that occurs when the sodium benzoate is added.

17.12 A buffer contains 0.30 mol of propanoic acid (C_2H_5COOH) and 0.25 mol of potassium propanoate (C_2H_5COOK) in 1.80 L. (**a**) What is the pH of this buffer? (**b**) What is the pH of the buffer after the addition of 0.10 mol of NaOH? (**c**) What is the pH of the buffer after the addition of 0.10 mol of HCl?

17.13 A buffer, consisting of $H_2PO_4^-$ and HPO_4^{2-}, helps control the pH of physiological fluids. Many carbonated soft drinks also use this buffer system. What is the pH of a soft drink in which the major buffer ingredients are 10.0 g of KH_2PO_4 and 10.0 g of K_2HPO_4 per 0.500 L of solution?

17.14 You have to prepare a pH = 4.00 buffer, and you have the following 0.20 *M* solutions available: HCOOH, CH_3COOH, HCN, KCH_3COO, KHCOO, and KCN. Which solutions would you use? How many milliliters of each solution would you use to make approximately 2 L of the buffer?

Answers to Self-Assessment Exercises

17.5 (d) **17.6** (a) **17.7** (b)

17.3 Acid–Base Titrations



The word *titration* originated in mid-sixteenth century France, where it referred to the proportion of gold or silver in coins. While the technique may seem old fashioned in these days of instrumental analysis, it can be an accurate and quick way to determine the concentration of a solution. In addition, plotting a titration curve can give the K_a of the analyte, and the shape of the curve tells us if we have a weak or strong acid/base present.

By the end of this section, you should be able to

- Calculate the pH at any point for an acid–base titration curve.
- Estimate the pK_a for monoprotic or polyprotic acids from their titration curves.

Titrations are procedures in which one reactant is slowly added into a solution of another reactant, while equilibrium concentrations along the way are monitored. There are two main reasons to do titrations:

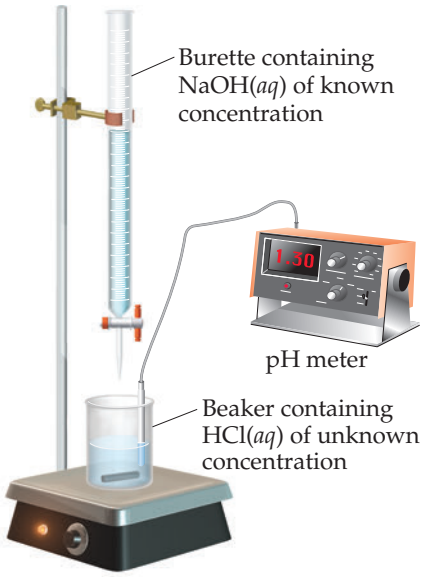
- to determine the concentration of one of the reactants
- to determine the equilibrium constant for the reaction

In an acid–base titration, a solution containing a known concentration of base is slowly added to an acid (or the acid is added to the base). Acid–base indicators can be used to signal the *equivalence point* of a titration (the point at which stoichiometrically equivalent quantities of acid and base have been brought together). Alternatively, a pH meter can be used to monitor the progress of the reaction (**Figure 17.6**), producing a **pH titration curve**, a graph of the pH as a function of the volume of titrant added. The shape of the titration curve makes it possible to determine the equivalence point. The curve can also be used to select suitable indicators and to determine the K_a of the weak acid or the K_b of the weak base being titrated.

To understand why titration curves have certain characteristic shapes, we will examine the curves for three kinds of titrations: (1) strong acid–strong base, (2) weak acid–strong base, and (3) polyprotic acid–strong base. We will also briefly consider how these curves relate to those involving weak bases.

Go Figure

In which direction do you expect the pH to change as NaOH is added to the HCl solution?



▲ **Figure 17.6** **Measuring pH during a titration.**

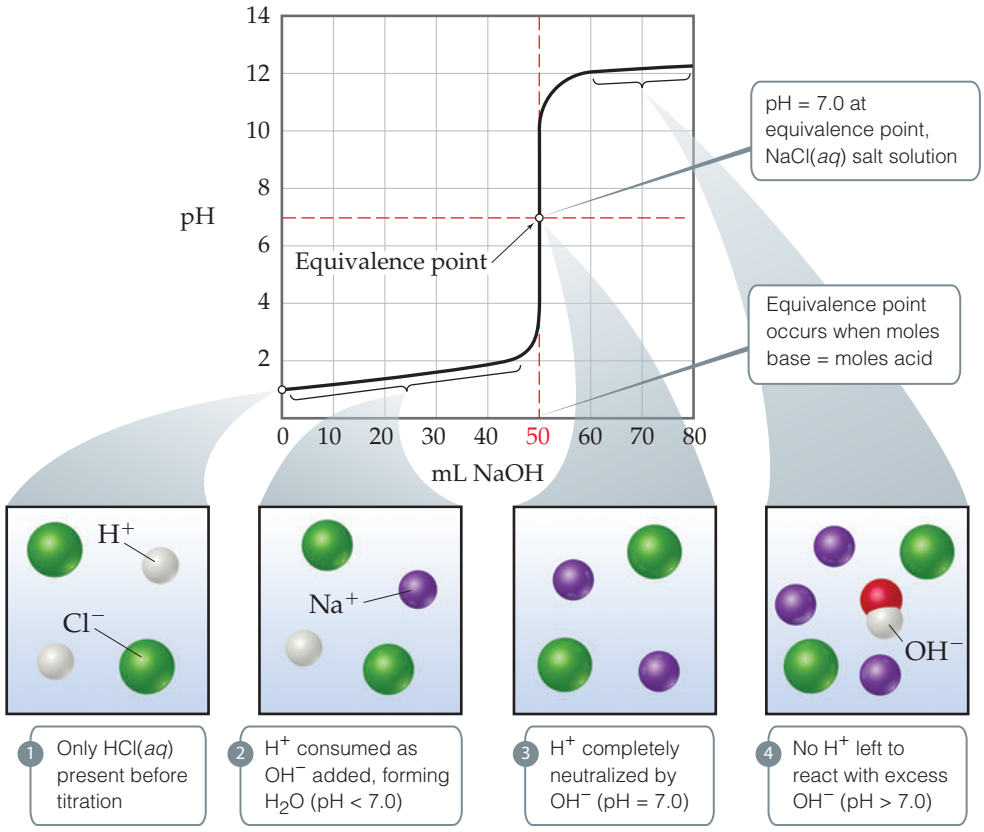
Strong Acid–Strong Base Titrations

The titration curve produced when a strong base is added to a strong acid has the general shape shown in **Figure 17.7**, which depicts the pH change that occurs as 0.100 *M* NaOH is added to 50.0 mL of 0.100 *M* HCl. The pH can be calculated at various stages of the titration. To help understand these calculations, we can divide the curve into four regions:

1. **Initial pH:** The pH of the solution before the addition of any base is determined by the initial concentration of the strong acid. For a solution of 0.100 *M* HCl, $[H^+] = 0.100\ M$ and $pH = -\log(0.100) = 1.000$. Thus, the initial pH is low.
2. **Between initial pH and equivalence point:** As NaOH is added, the pH increases slowly at first and then rapidly in the vicinity of the equivalence point. The pH before the equivalence point is determined by the concentration of acid not yet neutralized. This calculation is illustrated in Sample Exercise 17.7(a).
3. **Equivalence point:** At the equivalence point an equal number of moles of NaOH and HCl have reacted, leaving only a solution of their salt, NaCl. The pH of the solution is 7.00 because the cation of a strong base (in this case Na^+) and the anion of a strong acid (in this case Cl^-) are neither acids nor bases and, therefore, have no appreciable effect on pH.
4. **After equivalence point:** The pH of the solution after the equivalence point is determined by the concentration of excess NaOH in the solution. This calculation is illustrated in Sample Exercise 17.7(b).

Titration of a solution of a strong base with a solution of a strong acid yields an analogous curve of pH versus added acid. In this case, however, the pH is high at the outset

Go Figure What volume of NaOH(*aq*) would be needed to reach the equivalence point if the concentration of the added base were 0.200 *M*?



▲ **Figure 17.7 Titration of a strong acid with a strong base.** The pH curve for titration of 50.0 mL of a 0.100 *M* solution of hydrochloric acid with a 0.100 *M* solution of NaOH(*aq*). For clarity, water molecules have been omitted from the molecular art.

Sample Exercise 17.7

Calculations for a Strong Acid–Strong Base Titration

Calculate the pH when (**a**) 49.0 mL and (**b**) 51.0 mL of 0.100 *M* NaOH solution have been added to 50.0 mL of 0.100 *M* HCl solution.

SOLUTION

Analyze We are asked to calculate the pH at two points in the titration of a strong acid with a strong base. The first point is just before the equivalence point, so we expect the pH to be determined by the small amount of strong acid that has not yet been neutralized. The second point is just after the equivalence point, so we expect this pH to be determined by the small amount of excess strong base.

Plan (**a**) As the NaOH solution is added to the HCl solution, $H^+(aq)$ reacts with $OH^-(aq)$ to form H_2O. Both Na^+ and Cl^- are spectator ions, having negligible effect on the pH. To determine the pH of the solution, we must first determine how many moles of H^+ were originally present and how many moles of OH^- were added. We can then calculate how many moles of each ion remain after the neutralization reaction. To calculate $[H^+]$, and hence pH, we must also remember that the volume of the solution increases as we add titrant, thus diluting the concentration of all solutes present. Therefore, it is best to deal with moles first, and then convert to molarities using total solution volumes (volume of acid plus volume of base). (**b**) We proceed in the same way as in part (a) except we are now past the equivalence point and have more OH^- in the solution than H^+.

Solve

(**a**) The number of moles of H^+ in the original HCl solution is given by the product of the volume of the solution and its molarity:

$$(0.0500\ \text{L soln})\left(\frac{0.100\ \text{mol H}^+}{1\ \text{L soln}}\right) = 5.00 \times 10^{-3}\ \text{mol H}^+$$

Likewise, the number of moles of OH^- in 49.0 mL of 0.100 *M* NaOH is:

$$(0.0490\ \text{L soln})\left(\frac{0.100\ \text{mol OH}^-}{1\ \text{L soln}}\right) = 4.90 \times 10^{-3}\ \text{mol OH}^-$$

Because we have not reached the equivalence point, there are more moles of H^+ present than OH^-. Therefore, OH^- is the limiting reactant. Each mole of OH^- reacts with 1 mol of H^+. Using the convention introduced in Sample Exercise 17.6, we have:

	$H^+(aq)$	+ $OH^-(aq)$	⟶ $H_2O(l)$
Before reaction (mol)	5.00×10^{-3}	4.90×10^{-3}	—
Change (limiting reactant) (mol)	-4.90×10^{-3}	-4.90×10^{-3}	—
After reaction (mol)	0.10×10^{-3}	0	—

The volume of the reaction mixture increases as the NaOH solution is added to the HCl solution. Thus, at this point in the titration, the volume in the titration flask is:

$$50.0\text{ mL} + 49.0\text{ mL} = 99.0\text{ mL} = 0.0990\text{ L}$$

Thus, the concentration of $H^+(aq)$ in the flask is:

$$[H^+] = \frac{\text{moles } H^+(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3}\text{ mol}}{0.09900\text{ L}} = 1.0 \times 10^{-3}\,M$$

The corresponding pH is:

$$-\log(1.0 \times 10^{-3}) = 3.00$$

(**b**) As before, the initial number of moles of each reactant is determined from their volumes and concentrations. The reactant present in smaller stoichiometric amount (the limiting reactant) is consumed completely, leaving an excess of hydroxide ion.

	$H^+(aq)$	+ $OH^-(aq)$	⟶ $H_2O(l)$
Before reaction (mol)	5.00×10^{-3}	5.10×10^{-3}	—
Change (limiting reactant) (mol)	-5.00×10^{-3}	-5.00×10^{-3}	—
After reaction (mol)	0	0.10×10^{-3}	—

In this case, the volume in the titration flask is:

$$50.0\text{ mL} + 51.0\text{ mL} = 101.0\text{ mL} = 0.1010\text{ L}$$

Hence, the concentration of $OH^-(aq)$ in the flask is:

$$[OH^-] = \frac{\text{moles } OH^-(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3}\text{ mol}}{0.1010\text{ L}} = 1.0 \times 10^{-3}\,M$$

and we have:

$$\text{pOH} = -\log(1.0 \times 10^{-3}) = 3.00$$
$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.00 = 11.00$$

Comment Note that the pH increased by only two pH units, from 1.00 (Figure 17.7) to 3.00, after the first 49.0 mL of NaOH solution was added, but jumped by eight pH units, from 3.00 to 11.00, as 2.0 mL of base solution was added near the equivalence point. Such a rapid rise in pH near the equivalence point is a characteristic of titrations involving strong acids and strong bases.

▶ Practice Exercise

An acid–base titration is performed: 250.0 mL of an unknown concentration of HCl (*aq*) is titrated to the equivalence point with 36.7 mL of a 0.1000 *M* aqueous solution of NaOH. Which of the following statements is *not* true of this titration?

(**a**) The HCl solution is less concentrated than the NaOH solution. (**b**) The pH is less than 7 after adding 25 mL of NaOH solution. (**c**) The pH at the equivalence point is 7.00. (**d**) If an additional 1.00 mL of NaOH solution is added beyond the equivalence point, the pH of the solution is more than 7.00. (**e**) At the equivalence point, the OH^- concentration in the solution is $3.67 \times 10^{-3}\,M$.

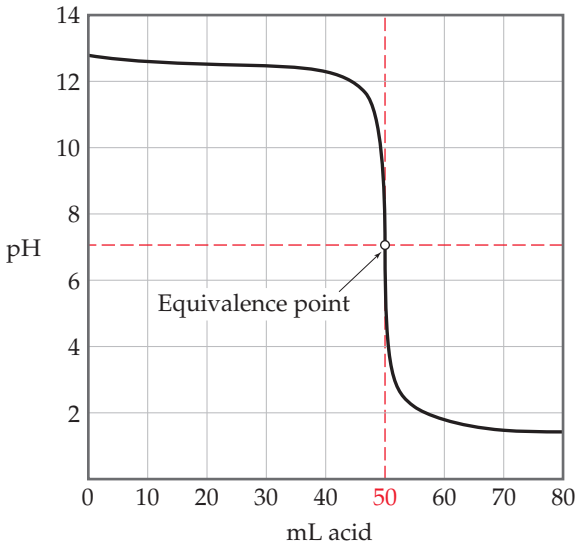
of the titration and low at its completion (**Figure 17.8**). The pH at the equivalence point is still 7.0 (at 25 °C), just like the strong acid–strong base titration.

Weak Acid–Strong Base Titrations

The curve for titration of a weak acid by a strong base is similar to the curve in Figure 17.7. Consider, for example, the curve for titration of 50.0 mL of 0.100 *M* acetic acid with 0.100 *M* NaOH shown in **Figure 17.9**. We can calculate the pH at points along this curve, using principles we discussed earlier, which means again dividing the curve into four regions:

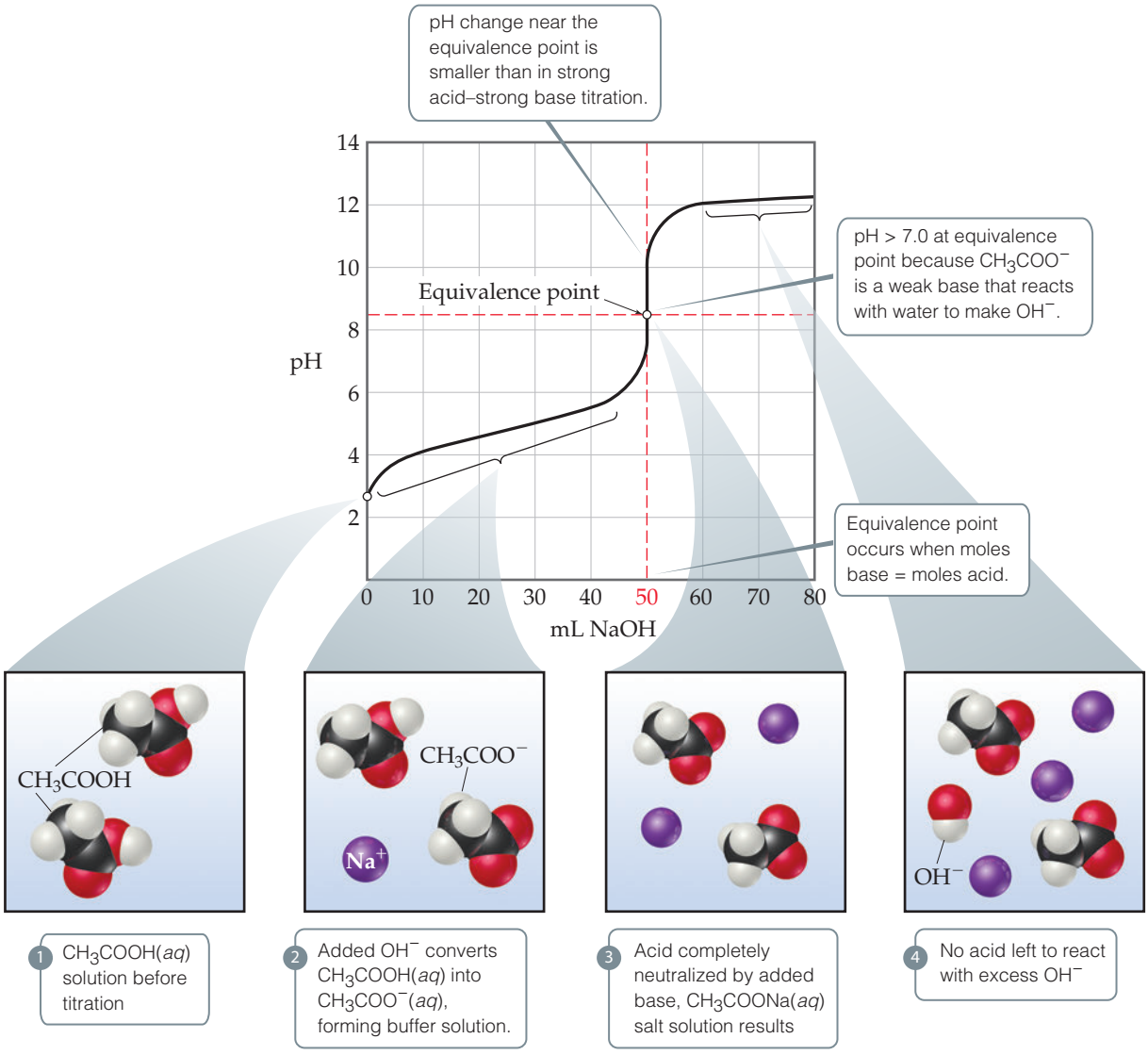
1. **Initial pH:** We use K_a to calculate this pH, as shown in Section 16.5. The calculated pH of 0.100 *M* CH_3COOH is 2.89.
2. **Between initial pH and equivalence point:** Prior to reaching the equivalence point, the acid is being neutralized, and its conjugate base is being formed:

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l) \qquad [17.12]$$



▲ **Figure 17.8 Titration of a strong base with a strong acid.** The pH curve for titration of 50.0 mL of a 0.100 *M* solution of a strong base with a 0.100 *M* solution of a strong acid.

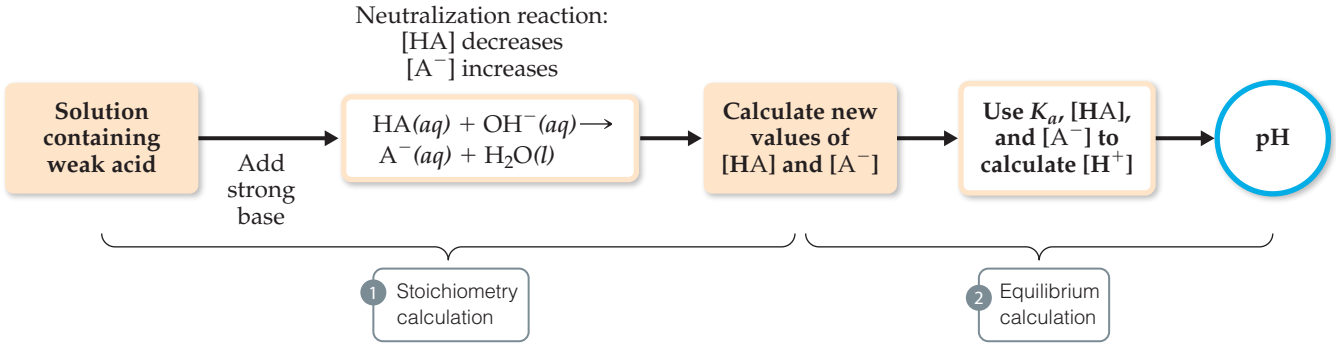
Go Figure If the acetic acid being titrated here were replaced by hydrochloric acid, would the amount of base needed to reach the equivalence point change? Would the pH at the equivalence point change?



▲ **Figure 17.9 Titration of a weak acid with a strong base.** The pH curve for titration of 50.0 mL of a 0.100 *M* solution of acetic acid with a 0.100 *M* solution of NaOH(*aq*). For clarity, water molecules have been omitted from the molecular art.

Thus, the solution contains a mixture of CH_3COOH and CH_3COO^-. Calculating the pH in this region involves two steps. First, we consider the neutralization reaction between CH_3COOH and OH^- to determine $[CH_3COOH]$ and $[CH_3COO^-]$. Next, we calculate the pH of this buffer pair using procedures developed in Sections 17.1 and 17.2. The general procedure is diagrammed in **Figure 17.10** and illustrated in Sample Exercise 17.8.

3. **Equivalence point:** The equivalence point is reached when 50.0 mL of 0.100 *M* NaOH has been added to the 50.0 mL of 0.100 *M* CH_3COOH. At this point, the 5.00×10^{-3} mol of NaOH completely reacts with the 5.00×10^{-3} mol of CH_3COOH to form 5.00×10^{-3} mol of CH_3COONa. The Na^+ ion of this salt has no significant effect on the pH. The CH_3COO^- ion, however, is a weak base whose reaction with water cannot be neglected, and the pH at the equivalence point is therefore greater than 7. In general, the pH at the equivalence point is always above 7 in a weak acid–strong base titration because the anion of the salt formed is a weak base.



▲ **Figure 17.10** **Procedure for calculating pH when a weak acid is partially neutralized by a strong base.**

Sample Exercise 17.8

Calculations for a Weak Acid–Strong Base Titration

Calculate the pH of the solution formed when 45.0 mL of 0.100 *M* NaOH is added to 50.0 mL of 0.100 *M* CH_3COOH ($K_a = 1.8 \times 10^{-5}$).

SOLUTION

Analyze We are asked to calculate the pH before the equivalence point of the titration of a weak acid with a strong base.

Plan We first must determine the number of moles of CH_3COOH and CH_3COO^- present after the neutralization reaction (the stoichiometry calculation). We then calculate pH using K_a, $[CH_3COOH]$, and $[CH_3COO^-]$ (the equilibrium calculation).

Solve

Stoichiometry Calculation: The product of the volume and concentration of each solution gives the number of moles of each reactant present before the neutralization:

$$(0.0500\ \text{L soln})\left(\frac{0.100\ \text{mol } CH_3COOH}{1\ \text{L soln}}\right) = 5.00 \times 10^{-3}\ \text{mol } CH_3COOH$$

$$(0.0450\ \text{L soln})\left(\frac{0.100\ \text{mol NaOH}}{1\ \text{L soln}}\right) = 4.50 \times 10^{-3}\ \text{mol NaOH}$$

The 4.50×10^{-3} mol of NaOH consumes 4.50×10^{-3} mol of CH_3COOH:

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

Before reaction (mol)	5.00×10^{-3}	4.50×10^{-3}	0	—
Change (limiting reactant) (mol)	-4.50×10^{-3}	-4.50×10^{-3}	$+4.50 \times 10^{-3}$	
After reaction (mol)	0.50×10^{-3}	0	4.50×10^{-3}	—

The total volume of the solution is:

$$45.0\ \text{mL} + 50.0\ \text{mL} = 95.0\ \text{mL} = 0.0950\ \text{L}$$

The resulting molarities of CH_3COOH and CH_3COO^- after the reaction are therefore:

$$[CH_3COOH] = \frac{0.50 \times 10^{-3}\ \text{mol}}{0.0950\ \text{L}} = 0.0053\ M$$

$$[CH_3COO^-] = \frac{4.50 \times 10^{-3}\ \text{mol}}{0.0950\ \text{L}} = 0.0474\ M$$

Equilibrium Calculation: The equilibrium between CH_3COOH and CH_3COO^- must obey the equilibrium expression for CH_3COOH:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Solving for $[H^+]$ gives:

$$[H^+] = K_a \times \frac{[CH_3COOH]}{[CH_3COO^-]} = (1.8 \times 10^{-5}) \times \left(\frac{0.0053}{0.0474}\right) = 2.0 \times 10^{-6}\ M$$

$$\text{pH} = -\log(2.0 \times 10^{-6}) = 5.70$$

Continued

Comment We could have solved for pH equally well using the Henderson–Hasselbalch equation in the last step.

Practice Exercise

If you think carefully about what happens during the course of a weak acid–strong base titration, you can learn some very interesting things. For example, let's look back at Figure 17.9 and pretend you did not know that acetic acid was the acid being titrated. You can figure out the pK_a of a weak acid just by thinking about the definition of K_a and looking at the right place on the titration curve! Which of the following choices is the best way to do this?

(**a**) At the equivalence point, pH = pK_a. (**b**) Halfway to the equivalence point, pH = pK_a. (**c**) Before any base is added, pH = pK_a. (**d**) At the top of the graph with excess base added, pH = pK_a.

The procedure for calculating the pH of the solution of a weak base is described in Section 16.6 and is shown in Sample Exercise 17.9.

4. **After equivalence point (excess base):** In this region, $[OH^-]$ from the reaction of CH_3COO^- with water is negligible relative to $[OH^-]$ from the excess NaOH. Thus, the pH is determined by the concentration of OH^- from the excess NaOH. The method for calculating pH in this region is therefore like that illustrated in Sample Exercise 17.7(b). Thus, the addition of 51.0 mL of 0.100 *M* NaOH to 50.0 mL of

Sample Exercise 17.9

Calculating the pH at the Equivalence Point

Calculate the pH at the equivalence point in the titration of 50.0 mL of 0.100 *M* CH_3COOH with 0.100 *M* NaOH.

SOLUTION

Analyze We are asked to determine the pH at the equivalence point of the titration of a weak acid with a strong base. Because the neutralization of a weak acid produces its anion, a conjugate base that can react with water, we expect the pH at the equivalence point to be greater than 7.

Plan The initial number of moles of acetic acid equals the number of moles of acetate ion at the equivalence point. We use the volume of the solution at the equivalence point to calculate the concentration of acetate ion. Because the acetate ion is a weak base, we can calculate the pH using K_b and $[CH_3COO^-]$.

Solve

The number of moles of acetic acid in the initial solution is obtained from the volume and molarity of the solution:

$$\text{Moles} = M \times V = (0.100\ \text{mol}/\cancel{\text{L}})(0.0500\ \cancel{\text{L}}) = 5.00 \times 10^{-3}\ \text{mol}\ CH_3COOH$$

Hence, 5.00×10^{-3} mol of CH_3COO^- is formed. It will take 50.0 mL of NaOH to reach the equivalence point (Figure 17.9). The volume of this salt solution at the equivalence point is the sum of the volumes of the acid and base, 50.0 mL + 50.0 mL = 100.0 mL = 0.1000 L. Thus, the concentration of CH_3COO^- is:

$$[CH_3COO^-] = \frac{5.00 \times 10^{-3}\ \text{mol}}{0.1000\ \text{L}} = 0.0500\ M$$

The CH_3COO^- ion is a weak base:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The K_b for CH_3COO^- can be calculated from the K_a value of its conjugate acid, $K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$. Using the K_b expression, we have:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

Making the approximation that $0.0500 - x \simeq 0.0500$, and then solving for x, we have:

$x = [OH^-] = 5.3 \times 10^{-6}\ M$, which gives pOH = 5.28 and pH = 8.72

Check The pH is above 7, as expected for the salt of a weak acid and strong base.

Practice Exercise

Why is pH at the equivalence point larger than 7 when you titrate a weak acid with a strong base? (**a**) There is excess strong base at the equivalence point. (**b**) There is excess weak acid at the equivalence point. (**c**) The conjugate base that is formed at the equivalence point is a strong base. (**d**) The conjugate base that is formed at the equivalence point reacts with water. (**e**) This statement is false: the pH is always 7 at an equivalence point in a pH titration.

either 0.100 *M* HCl or 0.100 *M* CH_3COOH yields the same pH, 11.00. Notice by comparing Figures 17.7 and 17.9 that the titration curves for a strong acid and a weak acid are the same after the equivalence point.

In order to further monitor the evolution of pH as a function of added base, we can calculate the pH at the equivalence point.

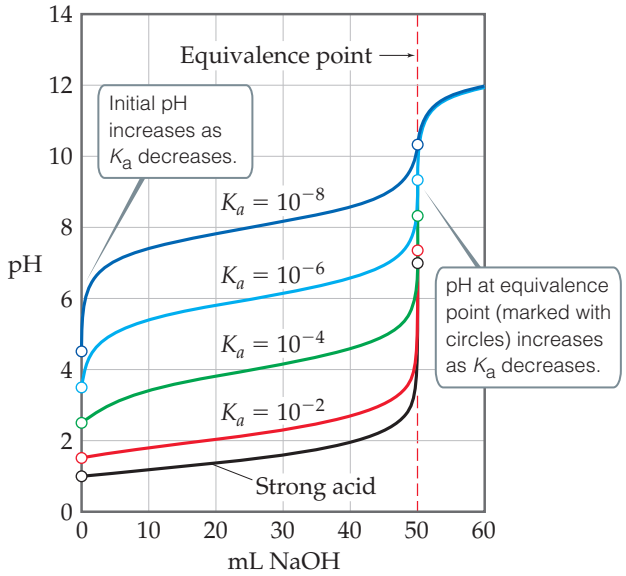
The titration curve for a weak acid–strong base titration (Figure 17.9) differs from the curve for a strong acid–strong base titration (Figure 17.7) in three noteworthy ways:

1. The solution of the weak acid has a higher initial pH than a solution of a strong acid of the same concentration.
2. The pH change in the rapid-rise portion of the curve near the equivalence point is smaller for the weak acid than for the strong acid.
3. The pH at the equivalence point is above 7.00 for the weak acid titration.

The weaker the acid, the more pronounced these differences become. To illustrate this consider the family of titration curves shown in **Figure 17.11**. Notice that as the acid becomes weaker (that is, as K_a becomes smaller), the initial pH increases and the pH change near the equivalence point becomes less marked. Furthermore, the pH at the equivalence point steadily increases as K_a decreases, because the strength of the conjugate base of the weak acid increases. It is virtually impossible to determine the equivalence point when pK_a is 10 or higher because the pH change is too small and gradual.

Go Figure

How does the pH at the equivalence point change as the acid being titrated becomes weaker? How does the volume of NaOH(*aq*) needed to reach the equivalence point change?



▲ **Figure 17.11 A set of curves showing the effect of acid strength on the characteristics of the titration curve when a weak acid is titrated by a strong base.** Each curve represents titration of 50.0 mL of 0.10 *M* acid with 0.10 *M* NaOH.

pH titration experiments are an excellent way to measure the pK_a of a weak acid. Look at Figure 17.11. Notice that for each acid solution, 50 mL of strong base is required to reach the equivalence point. This means, of course, that 50 mL of base is required to convert the HA molecules into A^- conjugate base anions. Also notice that halfway to each equivalence point (at 25 mL base added), the pH of the solution is nearly equal to the pK_a of the acid. Is this a coincidence? No! Recall that $K_a = [H^+][A^-]/[HA]$, where all concentrations are those at equilibrium. Halfway to the equivalence point, half of [HA] has been converted to $[A^-]$. In other words, $[HA] = [A^-]$. Therefore, $[HA]/[A^-] = 1$. In which case, $K_a = [H^+]$, and therefore $pK_a = pH$.

It becomes possible, then, to determine the pK_a of a weak acid from its pH titration curve. Once you identify the amount of base needed to reach the equivalence point, find the pH on the curve at halfway to the equivalence point. The pH you read off the graph at that point corresponds to the pK_a of the weak acid. If the acid's concentration is too low, however, the autoionization of water becomes significant, and this graphical way of measuring pK_a is not as accurate.

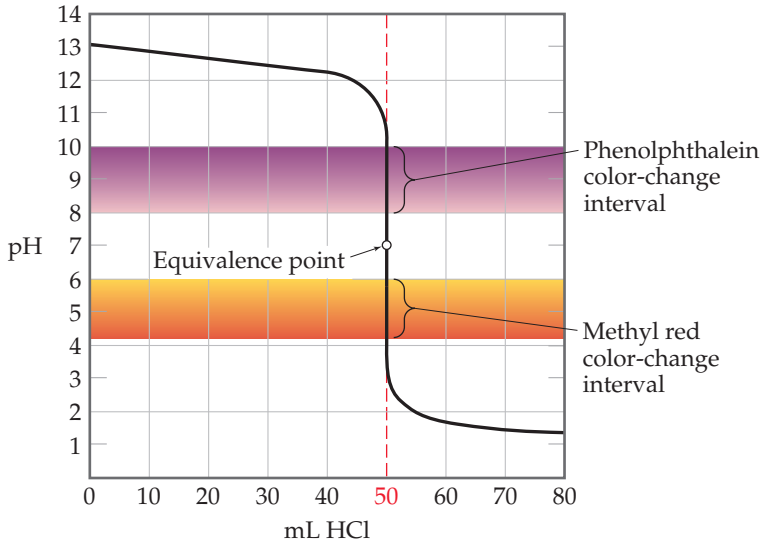
Titrating with an Acid–Base Indicator

Often in an acid–base titration, an indicator is used rather than a pH meter. An indicator is a compound that changes color in solution over a specific pH range. Optimally, an indicator should change color at the equivalence point in a titration. In practice, however, an indicator need not precisely mark the equivalence point. The pH changes very rapidly near the equivalence point, and in this region one drop of titrant can change the pH by several units. Thus, an indicator beginning and ending its color change anywhere on the rapid-rise portion of the titration curve gives a sufficiently accurate measure of the titrant volume needed to reach the equivalence point. The point in a titration where the indicator changes color is called the *end point* to distinguish it from the equivalence point that it closely approximates.

Figure 17.12 shows the curve for titration of a strong base (NaOH) with a strong acid (HCl). We see from the vertical part of the curve that the pH changes rapidly

Go Figure

Is methyl red a suitable indicator when you are titrating a strong acid with a strong base? Explain your answer.

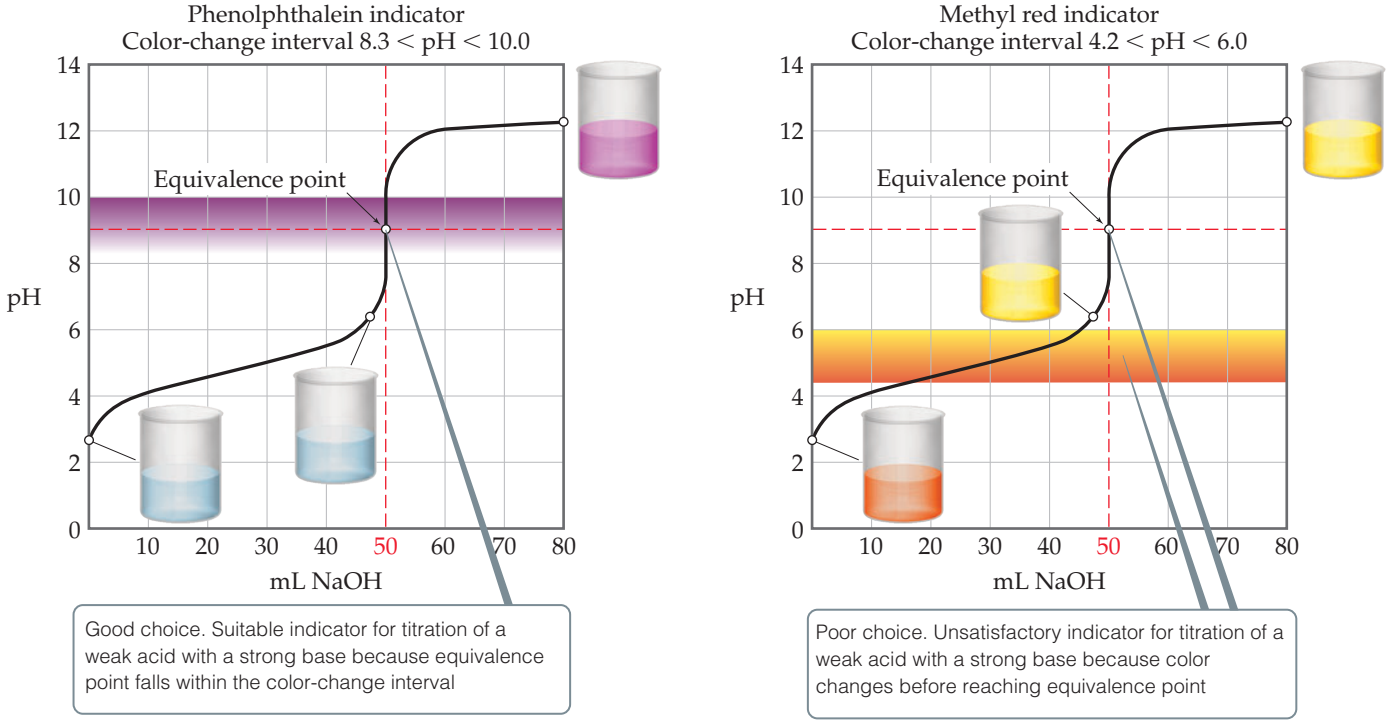


▲ **Figure 17.12 Using color indicators for titration of a strong base with a strong acid.** Both phenolphthalein and methyl red change color in the rapid-change portion of the titration curve.

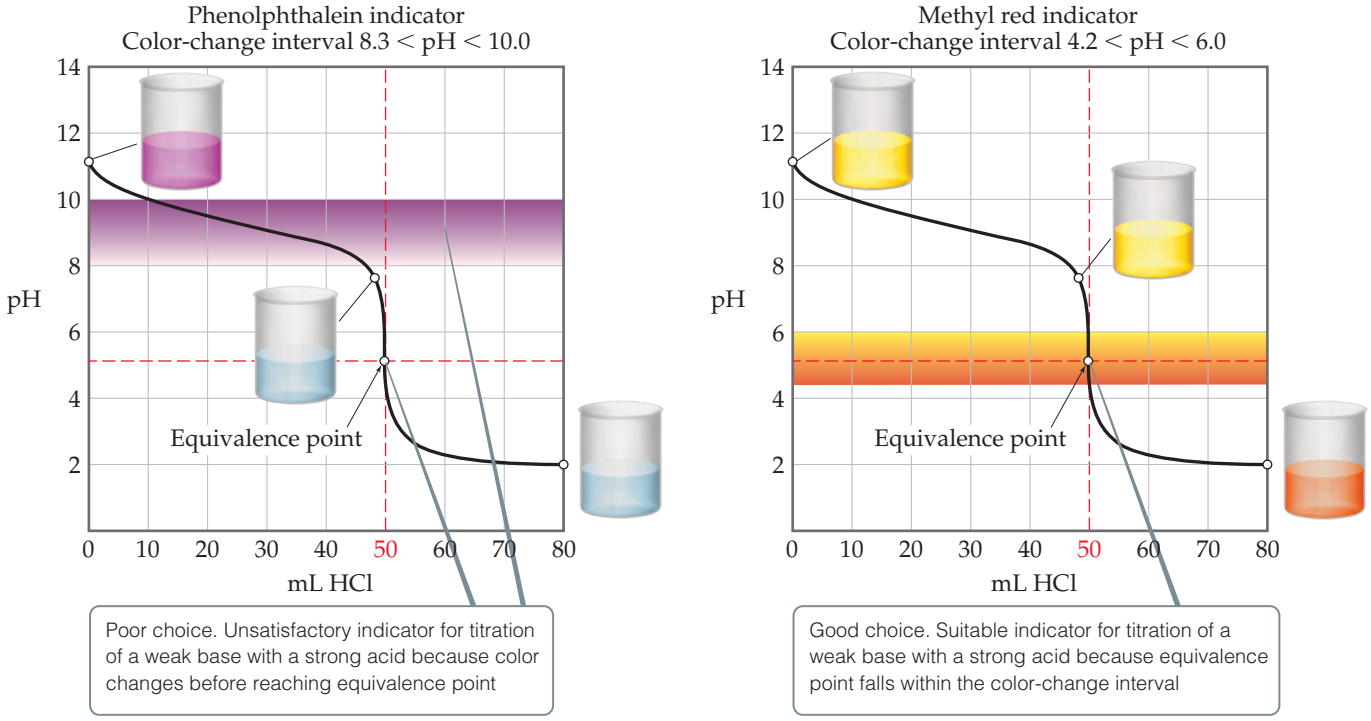
from roughly 11 to 3 near the equivalence point. Consequently, an indicator for this titration can change color anywhere in this range. Most strong acid–strong base titrations are carried out using phenolphthalein as an indicator because it changes color in this range (see Figure 16.7, p. 771). Several other indicators would also be satisfactory, including methyl red, which, as the lower color band in Figure 17.12 shows, changes color in the pH range from about 4.2 to 6.0.

As noted in our discussion of Figure 17.11, because the pH change near the equivalence point becomes smaller as K_a decreases, the choice of indicator for a weak acid–strong base titration is more critical than it is for titrations where both acid and base are strong. When 0.100 M CH_3COOH ($K_a = 1.8 \times 10^{-5}$) is titrated with 0.100 M NaOH, for example, the pH increases rapidly only over the pH range from about 7 to 11 (**Figure 17.13**). Phenolphthalein is therefore an ideal indicator because it changes color from pH 8.3 to 10.0, close to the pH at the equivalence point. Methyl red is a poor choice, however, because its color change, from 4.2 to 6.0, begins well before the equivalence point is reached.

Titration of a weak base (such as 0.100 M NH_3) with a strong acid solution (such as 0.100 M HCl) leads to the titration curve shown in **Figure 17.14**. In this example, the equivalence point occurs at pH 5.28. Thus, methyl red is an ideal indicator, but phenolphthalein would be a poor choice.



▲ **Figure 17.13 Good and poor indicators for titration of a weak acid with a strong base.**



▲ **Figure 17.14** **Good and poor indicators for titration of a weak base with a strong acid.**

Titrations of Polyprotic Acids

When weak acids contain more than one ionizable H atom, the reaction with OH^- occurs in a series of steps. Neutralization of phosphorous acid, H_3PO_3, for example, proceeds in two steps (the third H is bonded to the P and does not ionize):

$$H_3PO_3(aq) + OH^-(aq) \longrightarrow H_2PO_3^-(aq) + H_2O(l) \qquad [17.13]$$

$$H_2PO_3^-(aq) + OH^-(aq) \longrightarrow HPO_3^{2-}(aq) + H_2O(l) \qquad [17.14]$$

When the neutralization steps of a polyprotic acid or polybasic base are sufficiently separated, the titration has multiple equivalence points. **Figure 17.15** shows the two equivalence points corresponding to Equations 17.13 and 17.14.

You can use titration data such as that shown in Figure 17.15 to figure out the pK_as of the weak polyprotic acid. For example, let's write the K_{a1} and K_{a2} reactions for phosphorous acid:

$$H_3PO_3(aq) \rightleftharpoons H_2PO_3^-(aq) + H^+(aq) \qquad K_{a1} = \frac{[H_2PO_3^-][H^+]}{[H_3PO_3]}$$

$$H_2PO_3^-(aq) \rightleftharpoons HPO_3^{2-}(aq) + H^+(aq) \qquad K_{a2} = \frac{[HPO_3^{2-}][H^+]}{[H_2PO_3^-]}$$

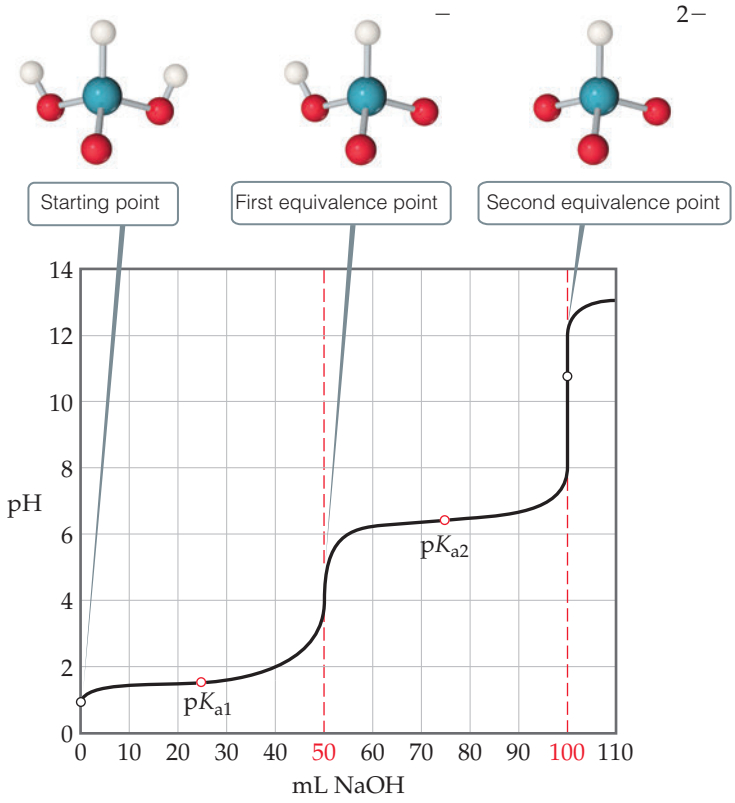
If we rearrange these equilibrium expressions, you see that we obtain Henderson–Hasselbalch equations:

$$pH = pK_{a1} + \log\frac{[H_2PO_3^-]}{[H_3PO_3]}$$

$$pH = pK_{a2} + \log\frac{[HPO_3^{2-}]}{[H_2PO_3^-]}$$

Therefore, if the concentrations of each acid and base conjugate pair are identical for each equilibrium, log (1) = 0 and so pH = pK_a. When does this happen during the titration? At the beginning of the titration, the acid is H_3PO_3 initially; at the first equivalence point, it is all converted to $H_2PO_3^-$. Therefore, halfway to the first equivalence point, half of the H_3PO_3 is converted to $H_2PO_3^-$. Thus, halfway to the equivalence point,

Go Figure What is/are the dominant species in solution at pH = 4: H_3PO_3, $H_2PO_3^-$, HPO_3^{2-}, and/or PO_3^{3-}? At pH = 11?



▲ **Figure 17.15 Titration curve for a diprotic acid.** The curve shows the pH change when 50.0 mL of 0.10 *M* H_3PO_3 is titrated with 0.10 *M* NaOH.

the concentration of H_3PO_3 is equal to that of $H_2PO_3^-$, and at that point, pH = pK_{a1}. Similar logic is true for the second equilibrium reaction: halfway toward its equivalence point, pH = pK_{a2}.

We can then just look at titration data and estimate the pK_as for the polyprotic acid directly from the titration curve. This procedure is especially useful if you are trying to identify an unknown polyprotic acid. In Figure 17.15, for instance, the first equivalence point occurs for 50 mL NaOH added. Halfway to the equivalence point corresponds to 25 mL NaOH. Because the pH at 25 mL NaOH is about 1.5 we may estimate pK_{a1} = 1.5 for phosphorous acid. The second equivalence point occurs at 100 mL NaOH added; halfway there (from the first equivalence point) is at 75 mL NaOH added. The graph indicates the pH at 75 mL NaOH added is about 6.5, and we therefore estimate that pK_{a2} for phosphorous acid is 6.5. The actual values for the two pK_as are pK_{a1} = 1.3 and pK_{a2} = 6.7 (close to our estimates).

Self-Assessment Exercises

17.15 A titration involves the addition of a strong acid (0.100 *M*) to 50.0 mL of a strong base (0.100 *M*). What is the pH after the addition of 40.0 mL of acid?

(a) 13.00

(b) 12.05

(c) 11.95

17.16 Estimate the pK_a of the weak base illustrated in figure 17.14.

(a) 11.0

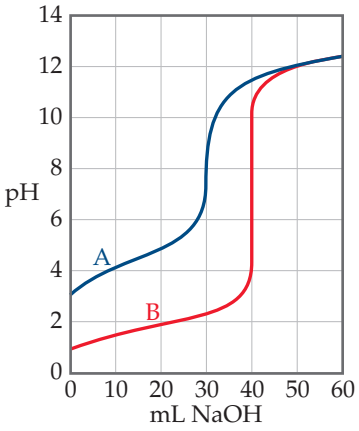
(b) 9.4

(c) 5.2

(d) 2.0

Exercises

17.17 The accompanying graph shows the titration curves for two monoprotic acids. (**a**) Which curve is that of a strong acid? (**b**) What is the approximate pH at the equivalence point of each titration? (**c**) 40.0 mL of each acid was titrated with a 0.100 *M* base. Which acid is more concentrated? (**d**) Estimate the pK_a of the weak acid.



17.18 Determine whether each of the following statements concerning titration of 25.0 mL 1.0 *M* HNO_3 (*aq*) and 25.0 mL 1.0 *M* CH_3COOH (*aq*) against 0.100 *M* solution of NaOH (*aq*) is true or false.

(**a**) The pH at the beginning of the two titrations will be the same.

(**b**) The titration curves will both be essentially the same after passing the equivalence point.

(**c**) Methyl red would be a suitable indicator for both titrations.

17.19 Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: (**a**) benzoic acid titrated with KOH, (**b**) ammonia titrated with iodic acid, (**c**) hydroxylamine with hydrochloric acid.

17.20 Assume that 30.0 mL of a 0.10 *M* solution of a weak base B that accepts one proton is titrated with a 0.10 *M* solution of the monoprotic strong acid HA. (**a**) How many moles of HA have been added at the equivalence point? (**b**) What is the predominant form of B at the equivalence point? (**a**) Is the pH 7, less than 7, or more than 7 at the equivalence point? (**d**) Which indicator, phenolphthalein or methyl red, is likely to be the better choice for this titration?

17.21 How many milliliters of 0.105 *M* HCl are needed to titrate each of the following solutions to the equivalence point: (**a**) 45.0 mL of 0.0950 *M* NaOH, (**b**) 22.5 mL of 0.118 *M* NH_3, (**c**) 125.0 mL of a solution that contains 1.35 g of NaOH per liter?

17.22 A 20.0 mL sample of 0.150 *M* KOH is titrated with 0.125 *M* $HClO_4$ solution. Calculate the pH after the following volumes of acid have been added: (**a**) 20.0 mL, (**b**) 23.0 mL, (**c**) 24.0 mL, (**d**) 25.0 mL, (**e**) 30.0 mL.

17.23 Consider the titration of 30.0 mL of 0.050 *M* NH_3 with 0.025 *M* HCl. Calculate the pH after the following volumes of titrant have been added: (**a**) 0 mL, (**b**) 20.0 mL, (**c**) 59.0 mL, (**d**) 60.0 mL, (**e**) 61.0 mL, (**f**) 65.0 mL.

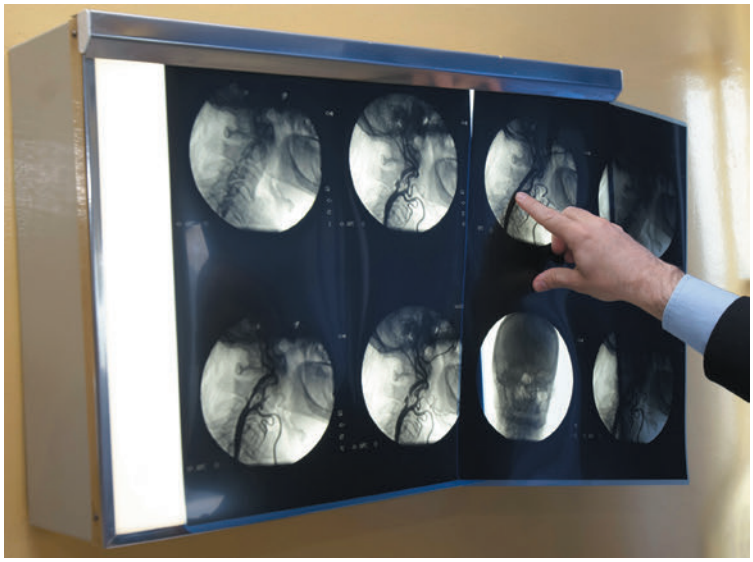
17.24 Calculate the pH at the equivalence point in titrating 0.100 *M* solutions of each of the following with 0.080 *M* NaOH: (**a**) hydrobromic acid (HBr), (**b**) chlorous acid ($HClO_2$), (**c**) benzoic acid (C_6H_5COOH).

Answers to Self-Assessment Exercises

17.15 (a)

17.16 (a)

17.4 Solubility Equilibria



For over one hundred years, X-rays have been used in medical diagnosis and provide a non-invasive way to see inside a patient. While they are useful for highlighting broken bones and displaced joints, they are not so good at imaging soft tissue. A way around this, at least for imaging the gastrointestinal tract, is to use a contrast agent or 'radio opaque'

compound such as barium sulfate. A slurry of barium sulfate in water is swallowed and coats the inside of the upper digestive tract. The barium ions scatter the X-rays and prevent them from passing through the body to the detector on the other side. In this way, the images of the throat, stomach, and small intestine are obtained. Barium ions are toxic to humans; however, the solubility of barium sulfate is so low that it is considered safe to use.

By the end of this section, you should be able to

- Calculate K_{sp} from molar solubility and molar solubility from K_{sp}.

The equilibria we have considered thus far in this chapter have involved acids and bases. Furthermore, they have been homogeneous; that is, all the species have been in the same phase. Through the rest of the chapter, we will consider the equilibria involved in the dissolution or precipitation of ionic compounds. These reactions are heterogeneous.

Dissolution and precipitation occur both within us and around us. Tooth enamel dissolves in acidic solutions, for example, causing tooth decay, and the precipitation of certain salts in our kidneys produces kidney stones. The waters of Earth contain salts dissolved as water passes over and through the ground. Precipitation of $CaCO_3$ from groundwater is responsible for the formation of stalactites and stalagmites within limestone caves.

In our earlier discussion of precipitation reactions, we considered general rules for predicting the solubility of common salts in water. These rules give us a qualitative sense of whether a compound has a low or high solubility in water. By considering solubility equilibria, however, we can make quantitative predictions about solubility.

The Solubility-Product Constant, K_{sp}

Recall that a *saturated solution* is one in which the solution is in contact with undissolved solute. Consider, for example, a saturated aqueous solution of $BaSO_4$ in contact with solid $BaSO_4$. Because the solid is an ionic compound, it is a strong electrolyte and yields $Ba^{2+}(aq)$ and $SO_4^{2-}(aq)$ ions when dissolved in water, readily establishing the equilibrium

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad [17.15]$$

As with any other equilibrium, the extent to which this dissolution reaction occurs is expressed by the magnitude of the equilibrium constant. Because this equilibrium equation describes the dissolution of a solid, the equilibrium constant indicates how soluble the solid is in water and is referred to as the **solubility-product constant** (or simply the **solubility product**). It is denoted K_{sp}, where *sp* stands for solubility product.

The equilibrium expression for the equilibrium between a solid and an aqueous solution of its component ions (K_{sp}) is written according to the rules that apply to any other equilibrium expression. Remember, however, that solids do not appear in the equilibrium expressions for heterogeneous equilibrium.

Thus, the solubility-product expression for $BaSO_4$, which is based on Equation 17.15, is

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] \qquad [17.16]$$

Sample Exercise 17.10

Writing Solubility-Product (K_{sp}) Expressions

Write the expression for the solubility-product constant for CaF_2, and look up the corresponding K_{sp} value in Appendix D.

SOLUTION

Analyze We are asked to write an equilibrium expression for the process by which CaF_2 dissolves in water.

Plan We apply the general rules for writing an equilibrium-constant expression, excluding the solid reactant from the expression. We assume that the compound dissociates completely into its component ions:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Solve The expression for K_{sp} is

$$K_{sp} = [Ca^{2+}][F^-]^2$$

Appendix D gives 3.9×10^{-11} for this K_{sp}.

Practice Exercise

Which of these expressions correctly expresses the solubility-product constant for Ag_3PO_4 in water?
(**a**) $[Ag][PO_4]$ (**b**) $[Ag^+][PO_4^{3-}]$ (**c**) $[Ag^+]^3[PO_4^{3-}]$
(**d**) $[Ag^+][PO_4^{3-}]^3$ (**e**) $[Ag^+]^3[PO_4^{3-}]^3$

The coefficient for each ion in the equilibrium equation also equals its subscript in the compound's chemical formula.

In general, the solubility product K_{sp} of a compound equals the product of the concentration of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation.

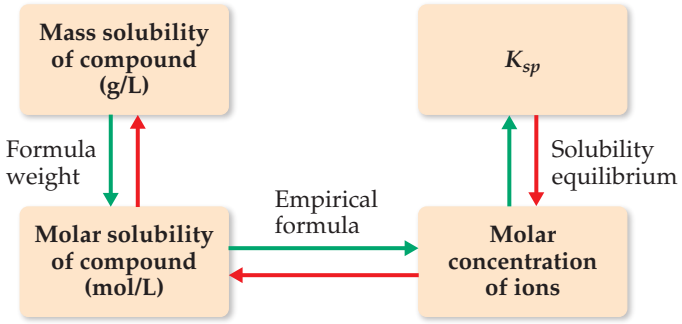
The values of K_{sp} at 25 °C for many ionic solids are tabulated in Appendix D. The value of K_{sp} for $BaSO_4$ is 1.1×10^{-10}, a very small number indicating that only a very small amount of the solid dissolves in 25 °C water.

Solubility and K_{sp}

It is important to distinguish carefully between solubility and the solubility-product constant. The solubility of a substance is the quantity that dissolves to form a saturated solution. Solubility is often expressed as grams of solute per liter of solution (g/L). *Molar solubility* is the number of moles of solute that dissolve in forming 1 L of saturated solution of the solute (mol/L). The solubility-product constant (K_{sp}) is the equilibrium constant for the equilibrium between an ionic solid and its saturated solution and is a unitless number. Thus, the magnitude of K_{sp} is a measure of how much of the solid dissolves to form a saturated solution.

The solubility of a substance can change considerably in response to a number of factors. For example, the solubilities of hydroxide salts, like $Mg(OH)_2$, are dependent upon the pH of the solution. The solubility is also affected by concentrations of other ions in solution, especially common ions. In other words, the numeric value of the solubility of a given solute does change as the other species in solution change. In contrast, the solubility-product constant, K_{sp}, has only one value for a given solute at any specific temperature.* **Figure 17.16** summarizes the relationships among various expressions of solubility and K_{sp}.

In principle, it is possible to use the K_{sp} value of a salt to calculate solubility under a variety of conditions. In practice, great care must be taken in doing so for the reasons indicated in "A Closer Look: Limitations of Solubility Products" at the end of this section. Agreement between the measured solubility and that calculated from K_{sp} is usually best for salts whose ions have low charges (1+ and 1–) and do not react with water.



▲ **Figure 17.16 Procedure for converting between solubility and K_{sp}.** Starting from the mass solubility, follow the green arrows to determine K_{sp}. Starting from K_{sp}, follow the red arrows to determine either molar solubility or mass solubility.

Sample Exercise 17.11

Calculating K_{sp} from Solubility

Solid silver chromate is added to pure water at 25 °C, and some of the solid remains undissolved. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved $Ag_2CrO_4(s)$ and the solution. Analysis of the equilibrated solution shows that its silver ion concentration is 1.3×10^{-4} *M*. Assuming that the Ag_2CrO_4 solution is saturated and that there are no other important equilibria involving Ag^+ or CrO_4^{2-} ions in the solution, calculate K_{sp} for this compound.

SOLUTION

Analyze We are given the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CrO_4 and asked to determine the value of K_{sp} for Ag_2CrO_4.

Plan The equilibrium equation and the expression for K_{sp} are

$$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

To calculate K_{sp}, we need the equilibrium concentrations of Ag^+ and CrO_4^{2-}. We know that at equilibrium $[Ag^+] = 1.3 \times 10^{-4}\,M$. All the Ag^+ and CrO_4^{2-} ions in the solution come from the Ag_2CrO_4 that dissolves. Thus, we can use $[Ag^+]$ to calculate $[CrO_4^{2-}]$.

Solve From the chemical formula of silver chromate, we know that there must be two Ag^+ ions in solution for each CrO_4^{2-} ion in solution. Consequently, the concentration of CrO_4^{2-} is half the concentration of Ag^+:

Continued

*This is strictly true only for very dilute solutions, for K_{sp} values change somewhat when the concentration of ionic substances in water is increased. However, we will ignore these effects, which are taken into consideration only for work that requires exceptional accuracy.

$$[CrO_4^{2-}] = \left(\frac{1.3 \times 10^{-4}\ \text{mol Ag}^+}{\text{L}}\right)\left(\frac{1\ \text{mol } CrO_4^{2-}}{2\ \text{mol Ag}^+}\right) = 6.5 \times 10^{-5}\ M$$

and K_{sp} is

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

Check We obtain a small value, as expected for a slightly soluble salt. Furthermore, the calculated value agrees well with the one given in Appendix D, 1.2×10^{-12}.

Practice Exercise

You add 10.0 grams of solid copper(II) phosphate, $Cu_3(PO_4)_2$, to a beaker and then add 100.0 mL of water to the beaker at $T = 298$ K. The solid does not appear to dissolve. You wait a long time, with occasional stirring and eventually measure the equilibrium concentration of $Cu^{2+}(aq)$ in the water to be $5.01 \times 10^{-8}\ M$. What is the K_{sp} of copper(II) phosphate?

(**a**) 5.01×10^{-8} (**b**) 2.50×10^{-15} (**c**) 4.20×10^{-15}
(**d**) 3.16×10^{-37} (**e**) 1.40×10^{-37}

Sample Exercise 17.12

Calculating Solubility from K_{sp}

The K_{sp} for CaF_2 is 3.9×10^{-11} at 25 °C. Assuming equilibrium is established between solid and dissolved CaF_2, and that there are no other important equilibria affecting its solubility, calculate the solubility of CaF_2 in grams per liter.

SOLUTION

Analyze We are given K_{sp} for CaF_2 and asked to determine solubility. Recall that the solubility of a substance is the quantity that can dissolve in solvent, whereas the solubility-product constant, K_{sp}, is an equilibrium constant.

Plan To go from K_{sp} to solubility, we follow the steps indicated by the red arrows in Figure 17.16. We first write the chemical equation for the dissolution and set up a table of initial and equilibrium concentrations. We then use the equilibrium expression. In this case we know K_{sp}, and so we solve for the concentrations of the ions in solution. Once we know these concentrations, we use the formula weight to determine solubility in g/L.

Solve

Assume that initially no salt has dissolved, and then allow x mol/L of CaF_2 to dissociate completely when equilibrium is achieved:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	$CaF_2(s)$	$Ca^{2+}(aq)$	$2\,F^-(aq)$
Initial concentration (M)	—	0	0
Change (M)	—	$+x$	$+2x$
Equilibrium concentration (M)	—	x	$2x$

The stoichiometry of the equilibrium dictates that $2x$ mol/L of F^- are produced for each x mol/L of CaF_2 that dissolve. We now use the expression for K_{sp} and substitute the equilibrium concentrations to solve for the value of x:

$$K_{sp} = [Ca^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

(Remember that $\sqrt[3]{y} = y^{1/3}$.) Thus, the molar solubility of CaF_2 is 2.1×10^{-4} mol/L.

$$x = \frac{\sqrt[3]{3.9 \times 10^{-11}}}{4} = 2.1 \times 10^{-4}$$

The mass of CaF_2 that dissolves in water to form 1 L of solution is:

$$\left(\frac{2.1 \times 10^{-4}\ \text{mol CaF}_2}{1\ \text{L soln}}\right)\left(\frac{78.1\ \text{g CaF}_2}{1\ \text{mol CaF}_2}\right) = 1.6 \times 10^{-2}\ \text{g CaF}_2/\text{L solution}$$

Check We expect a small number for the solubility of a slightly soluble salt. If we reverse the calculation, we should be able to recalculate the solubility product: $K_{sp} = (2.1 \times 10^{-4})(4.2 \times 10^{-4})^2 = 3.7 \times 10^{-11}$, close to the value given in the problem statement, 3.9×10^{-11}.

Comment Because F^- is the anion of a weak acid, you might expect hydrolysis of the ion to affect the solubility of CaF_2. The basicity of F^- is so small ($K_b = 1.5 \times 10^{-11}$), however, that the hydrolysis occurs to only a slight extent and does not significantly influence the solubility. The reported solubility is 0.017 g/L at 25 °C, in good agreement with our calculation.

Practice Exercise

Of the five salts listed here, which has the highest concentration of its cation in water? Assume that all salt solutions are saturated and that the ions do not undergo any additional reactions in water.

(**a**) lead(II) chromate, $K_{sp} = 2.8 \times 10^{-13}$
(**b**) cobalt(II) hydroxide, $K_{sp} = 1.3 \times 10^{-15}$
(**c**) cobalt(II) sulfide, $K_{sp} = 5 \times 10^{-22}$
(**d**) chromium(III) hydroxide, $K_{sp} = 1.6 \times 10^{-30}$
(**e**) silver sulfide, $K_{sp} = 6 \times 10^{-51}$

A CLOSER LOOK Limitations of Solubility Products

Ion concentrations calculated from K_{sp} values sometimes deviate appreciably from those found experimentally. In part, these deviations are due to electrostatic interactions between ions in solution, which can lead to ion pairs. ("The van't Hoff Factor") These interactions increase in magnitude both as the concentrations of the ions increase and as their charges increase. The solubility calculated from K_{sp} tends to be low unless corrected to account for these interactions.

As an example of the effect of these interactions, consider $CaCO_3$ (calcite), whose solubility product, 4.5×10^{-9}, gives a calculated solubility of 6.7×10^{-5} mol/L; correcting for ionic interactions in the solution yields 7.3×10^{-5} mol/L. The reported solubility, however, is 1.4×10^{-4} mol/L, indicating that there must be additional factors involved.

Another common source of error in calculating ion concentrations from K_{sp} is ignoring other equilibria that occur simultaneously in the solution. It is possible, for example, that acid–base equilibria take place simultaneously with solubility equilibria. In particular, both basic anions and cations with high charge-to-size ratios undergo hydrolysis reactions that can measurably increase the solubilities of their salts. For example, $CaCO_3$ contains the basic carbonate ion ($K_b = 1.8 \times 10^{-4}$), which reacts with water:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

If we consider the effect of ion–ion interactions as well as simultaneous solubility and K_b equilibria, we calculate a solubility of 1.4×10^{-4} mol/L, in agreement with the measured value for calcite.

Finally, we generally assume that ionic compounds dissociate completely when they dissolve, but this assumption is not always valid. When MgF_2 dissolves, for example, it yields not only Mg^{2+} and F^- ions but also MgF^+ ions.

Self-Assessment Exercise

17.25 Without doing a calculation, predict which of the following compounds has the greatest molar solubility in water.

(a) $BaCO_3$ $K_{sp} = 5.1 \times 10^{-9}$

(b) $BaSO_4$ $K_{sp} = 1.1 \times 10^{-10}$

(c) $PbSO_4$ $K_{sp} = 6.3 \times 10^{-7}$

Exercises

17.26 The solubility of two slightly soluble salts of M^{2+}, MA and MZ_2, is the same, 4×10^{-4} mol/L. (**a**) Which has the larger numerical value for the solubility product constant? (**b**) In a saturated solution of each salt in water, which has the higher concentration of M^{2+}? (**c**) If you added an equal volume of a solution saturated in MA to one saturated in MZ_2, what would be the equilibrium concentration of the cation, M^{2+}?

17.27 (**a**) True or false: "solubility" and "solubility-product constant" are the same number for a given compound. (**b**) Write the expression for the solubility-product constant for each of the following ionic compounds: $MnCO_3$, $Hg(OH)_2$, and $Cu_3(PO_4)_2$.

17.28 (**a**) The molar solubility of $PbBr_2$ at 25 °C is 1.0×10^{-2} mol/L. Calculate K_{sp}. (**b**) If 0.0490 g of $AgIO_3$ dissolves per liter of solution, calculate the solubility-product constant. (**c**) Using the appropriate K_{sp} value from Appendix D, calculate the pH of a saturated solution of $Ca(OH)_2$.

17.29 A 1.00 L solution saturated at 25 °C with lead(II) iodide contains 0.54 g of PbI_2. Calculate the solubility-product constant for this salt at 25 °C.

Answers to Self-Assessment Exercises

17.25 (c)

17.5 Factors That Affect Solubility



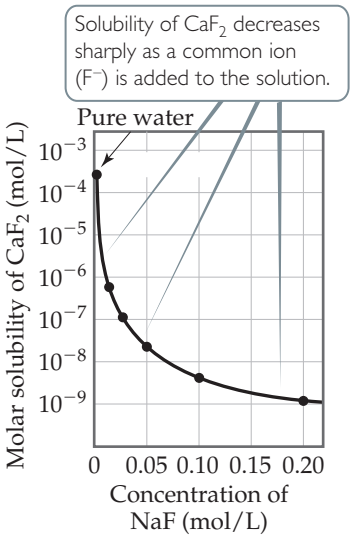
Coral reefs are a striking example of aqueous chemistry at work in nature. Coral reefs are built by tiny animals called stony corals, which secrete a hard calcium carbonate exoskeleton. Over time, the stony corals build up large networks of calcium carbonate upon which a reef is built. The size of such structures can be immense, as illustrated by the Great Barrier Reef.

Stony corals make their exoskeletons from dissolved Ca^{2+} and CO_3^{2-} ions. This process is aided by the fact that the CO_2 concentration is supersaturated in most parts of the ocean. However, well documented increases in the amount of CO_2 in the atmosphere threaten to upset the aqueous chemistry that stony corals depend on. As atmospheric CO_2 levels increase, the amount of CO_2 dissolved in the ocean also increases. This lowers the pH of the ocean and leads to a decrease in the CO_3^{2-} concentration. As a result, it becomes more difficult for stony corals and other important ocean creatures to maintain their exoskeletons. We will take a closer look at the consequences of ocean acidification later in Chapter 18.

By the end of this section, you should be able to

- Calculate the solubility of a substance in the presence of a common ion or at different pH values.

Solubility is affected by temperature and by the presence of other solutes. The presence of an acid, for example, can have a major influence on the solubility of a substance. In Section 17.4, we considered the dissolving of ionic compounds in pure water. In this section, we examine three factors that affect the solubility of ionic compounds: (1) presence of common ions, (2) solution pH, and (3) presence of complexing agents. We will also examine the phenomenon of *amphoterism*, which is related to the effects of both pH and complexing agents.



▲ **Figure 17.17 Common-ion effect.** Notice that the CaF_2 solubility is on a logarithmic scale.

The Common-Ion Effect

The presence of either $Ca^{2+}(aq)$ or $F^-(aq)$ in a solution reduces the solubility of CaF_2, shifting the equilibrium concentrations to the left:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Addition of Ca^{2+} or F^- shifts equilibrium concentrations, reducing solubility

This reduction in solubility is another manifestation of the common-ion effect we looked at in Section 17.1. In general, *the solubility of a slightly soluble salt is decreased by the presence of a second solute that furnishes a common ion*, as Figure 17.17 shows for CaF_2.

Sample Exercise 17.13

Calculating the Effect of a Common Ion on Solubility

Calculate the molar solubility of CaF_2 at 25 °C in a solution that is (**a**) 0.010 *M* in $Ca(NO_3)_2$ and (**b**) 0.010 *M* in NaF.

SOLUTION

Analyze We are asked to determine the solubility of CaF_2 in the presence of two strong electrolytes, each containing an ion common to CaF_2. In (**a**) the common ion is Ca^{2+}, and NO_3^- is a spectator ion. In (**b**) the common ion is F^-, and Na^+ is a spectator ion.

Plan Because the slightly soluble compound is CaF_2, we need to use K_{sp} for this compound, which Appendix D gives as 3.9×10^{-11}. *The value of K_{sp} is unchanged by the presence of additional solutes*. Because of the common-ion effect, however, the solubility of the salt decreases in the presence of common ions. We use our standard equilibrium techniques of starting with the equation for CaF_2 dissolution, setting up a table of initial and equilibrium concentrations, and using the K_{sp} expression to determine the concentration of the ion that comes only from CaF_2.

Solve

(**a**) The initial concentration of Ca^{2+} is 0.010 *M* because of the dissolved $Ca(NO_3)_2$:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

Initial Concentration (*M*)	—	0.010	0
Change (*M*)	—	$+x$	$+2x$
Equilibrium Concentration (*M*)	—	$(0.010 + x)$	$2x$

Substituting into the solubility-product expression gives:

$$K_{sp} = 3.9 \times 10^{-11} = [Ca^{2+}][F^-]^2 = (0.010 + x)(2x)^2$$

If we assume that x is small compared to 0.010, we have:

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x^2 = \frac{3.9 \times 10^{-11}}{4(0.010)} = 9.8 \times 10^{-10}$$

$$x = \sqrt{9.8 \times 10^{-10}} = 3.1 \times 10^{-5}\,M$$

This very small value for x validates the simplifying assumption we made. Our calculation indicates that 3.1×10^{-5} mol of solid CaF_2 dissolves per liter of 0.010 *M* $Ca(NO_3)_2$ solution.

(**b**) The common ion is F^-, and at equilibrium we have:

$$[Ca^{2+}] = x \quad \text{and} \quad [F^-] = 0.010 + 2x$$

Assuming that $2x$ is much smaller than 0.010 *M* (that is, $0.010 + 2x \simeq 0.010$), we have:

$$3.9 \times 10^{-11} = (x)(0.010 + 2x)^2 \simeq x(0.010)^2$$

Thus, 3.9×10^{-7} mol of solid CaF_2 should dissolve per liter of 0.010 *M* NaF solution.

$$x = \frac{3.9 \times 10^{-11}}{(0.010)^2} = 3.9 \times 10^{-7}\,M$$

Comment The molar solubility of CaF_2 in water is $2.1 \times 10^{-4}\,M$ (Sample Exercise 17.12). By comparison, our calculations here give a CaF_2 solubility of $3.1 \times 10^{-5}\,M$ in the presence of 0.010 *M* Ca^{2+} and $3.9 \times 10^{-7}\,M$ in the presence of 0.010 *M* F^- ion. Thus, the addition of either Ca^{2+} or F^- to a solution of CaF_2 decreases the solubility. However, the effect of F^- on the solubility is more pronounced than that of Ca^{2+} because $[F^-]$ appears to the second power in the K_{sp} expression for CaF_2, whereas $[Ca^{2+}]$ appears to the first power.

Practice Exercise

Consider a saturated solution of the salt MA_3, in which M is a metal cation with a 3+ charge and A is an anion with a 1− charge, in water at 298 K. Which of the following will affect the K_{sp} of MA_3 in water?
(**a**) The addition of more M^{3+} to the solution. (**b**) The addition of more A^- to the solution. (**c**) Diluting the solution. (**d**) Raising the temperature of the solution. (**e**) More than one of the above factors.

Solubility and pH

The solubility of almost any ionic compound is affected if the solution is made sufficiently acidic or basic. The effects are noticeable, however, only when one (or both) ions in the compound is at least moderately acidic or basic. The metal hydroxides, such as $Mg(OH)_2$, are examples of compounds containing a strongly basic ion, the hydroxide ion. Let's look at $Mg(OH)_2$, for which the solubility equilibrium is

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq) \quad K_{sp} = 1.8 \times 10^{-11} \qquad [17.17]$$

A saturated solution of $Mg(OH)_2$ has a calculated pH of 10.52, and its Mg^{2+} concentration is $1.7 \times 10^{-4}\,M$. Now suppose that solid $Mg(OH)_2$ is equilibrated with a solution buffered at pH 9.0. The pOH, therefore, is 5.0, so $[OH^-] = 1.0 \times 10^{-5}$. Inserting this value for $[OH^-]$ into the solubility-product expression, we have

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$$

$$[Mg^{2+}](1.0 \times 10^{-5})^2 = 1.8 \times 10^{-11}$$

$$[Mg^{2+}] = \frac{1.8 \times 10^{-11}}{(1.0 \times 10^{-5})^2} = 0.18\,M$$

Thus, the $Mg(OH)_2$ dissolves until $[Mg^{2+}] = 0.18\,M$. It is apparent that $Mg(OH)_2$ is much more soluble in this solution.

If $[OH^-]$ were reduced further by making the solution even more acidic, the Mg^{2+} concentration would have to increase to maintain the equilibrium condition. Thus, a sample of $Mg(OH)_2(s)$ dissolves completely if sufficient acid is added, as we saw in Figure 4.7 (page 190).

As we have seen, the solubility of $Mg(OH)_2$ greatly increases as the acidity of the solution increases. Based on this observation we can make the following generalization:

In general, the solubility of a compound containing a basic anion (that is, the anion of a weak acid) increases as the solution becomes more acidic.

The solubility of PbF_2 increases as the solution becomes more acidic, too, because F^- is a base (it is the conjugate base of the weak acid HF). As a result, the solubility equilibrium of PbF_2 is shifted to the right as the concentration of F^- is reduced by protonation to form HF. Thus, the solution process can be understood in terms of two consecutive reactions:

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,F^-(aq) \qquad [17.18]$$

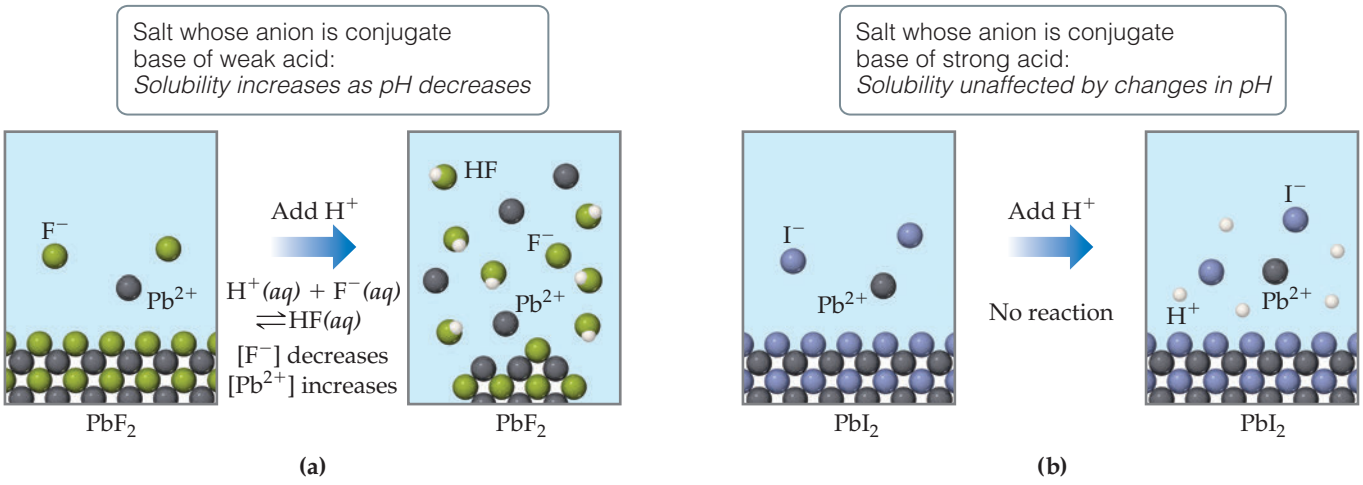
$$F^-(aq) + H^+(aq) \rightleftharpoons HF(aq) \qquad [17.19]$$

The equation for the overall process is

$$PbF_2(s) + 2\,H^+(aq) \rightleftharpoons Pb^{2+}(aq) + 2\,HF(aq) \qquad [17.20]$$

The processes responsible for the increase in solubility of PbF_2 in acidic solution are illustrated in **Figure 17.18**(**a**).

Other salts that contain basic anions, such as CO_3^{2-}, PO_4^{3-}, CN^-, or S^{2-}, behave similarly. These examples illustrate a general rule: *The solubility of slightly soluble salts containing basic anions increases as* $[H^+]$ *increases (as pH is lowered).* The more basic the anion, the more the solubility is influenced by pH. The solubility of salts with anions of negligible basicity (the anions of strong acids), such as Cl^-, Br^-, I^-, and NO_3^-, is unaffected by pH changes, as shown in Figure 17.18(**b**).



▲ **Figure 17.18 Response of two ionic compounds to addition of a strong acid.** (**a**) The solubility of PbF_2 increases upon addition of acid. (**b**) The solubility of PbI_2 is not affected by the addition of acid. The water molecules and the anion of the strong acid have been omitted for clarity.

Sample Exercise 17.14

Predicting the Effect of Acid on Solubility

Which of these substances are more soluble in acidic solution than in basic solution:
(**a**) $Ni(OH)_2(s)$, (**b**) $CaCO_3(s)$, (**c**) $BaF_2(s)$, (**d**) $AgCl(s)$?

SOLUTION

Analyze The problem lists four sparingly soluble salts, and we are asked to determine which are more soluble at low pH than at high pH.

Plan We will identify ionic compounds that dissociate to produce a basic anion, as these are especially soluble in acid solution.

Solve

(**a**) $Ni(OH)_2(s)$ is more soluble in acidic solution because of the basicity of OH^-; the H^+ reacts with the OH^- ion, forming water:

$$\begin{aligned} Ni(OH)_2(s) &\rightleftharpoons Ni^{2+}(aq) + 2\,OH^-(aq) \\ 2\,OH^-(aq) + 2\,H^+(aq) &\longrightarrow 2\,H_2O(l) \\ \text{Overall: } Ni(OH)_2(s) + 2\,H^+(aq) &\rightleftharpoons Ni^{2+}(aq) + 2\,H_2O(l) \end{aligned}$$

(**b**) Similarly, $CaCO_3(s)$ dissolves in acid solutions because CO_3^{2-} is a basic anion:

The reaction between CO_3^{2-} and H^+ occurs in steps, with HCO_3^- forming first and H_2CO_3 forming in appreciable amounts only when $[H^+]$ is sufficiently high.

$$\begin{aligned} CaCO_3(s) &\rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \\ CO_3^{2-}(aq) + 2\,H^+(aq) &\rightleftharpoons H_2CO_3(aq) \\ H_2CO_3(aq) &\rightleftharpoons CO_2(g) + H_2O(l) \\ \text{Overall: } CaCO_3(s) + 2\,H^+(aq) &\rightleftharpoons Ca^{2+}(aq) + CO_2(g) + H_2O(l) \end{aligned}$$

(**c**) The solubility of BaF_2 is enhanced by lowering the pH because F^- is a basic anion:

$$\begin{aligned} BaF_2(s) &\rightleftharpoons Ba^{2+}(aq) + 2\,F^-(aq) \\ 2\,F^-(aq) + 2\,H^+(aq) &\rightleftharpoons 2\,HF(aq) \\ \text{Overall: } BaF_2(s) + 2\,H^+(aq) &\rightleftharpoons Ba^{2+}(aq) + 2\,HF(aq) \end{aligned}$$

(**d**) The solubility of AgCl is unaffected by changes in pH because Cl^- is the anion of a strong acid and therefore has negligible basicity.

Practice Exercise

Which of the following actions will increase the solubility of AgBr in water?

(**a**) increasing the pH (**b**) decreasing the pH (**c**) adding NaBr (**d**) adding $NaNO_3$ (**e**) none of the above

CHEMISTRY AND LIFE Tooth Decay and Fluoridation

Tooth enamel consists mainly of the mineral hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, the hardest substance in the body. Tooth cavities form when acids dissolve tooth enamel:

$$Ca_{10}(PO_4)_6(OH)_2(s) + 8\,H^+(aq) \longrightarrow 10\,Ca^{2+}(aq) + 6\,HPO_4^{2-}(aq) + 2\,H_2O(l)$$

The Ca^{2+} and HPO_4^{2-} ions diffuse out of the enamel and are washed away by saliva. The acids that attack the hydroxyapatite are formed by the action of bacteria on sugars and other carbohydrates present in the plaque adhering to the teeth.

Fluoride ion, which is added to municipal water systems and toothpastes, can react with hydroxyapatite to form fluoroapatite, $Ca_{10}(PO_4)_6F_2$. This mineral, in which F^- has replaced OH^-, is much more resistant to attack by acids because the fluoride ion is a much weaker Brønsted–Lowry base than the hydroxide ion.

The usual concentration of F^- in municipal water systems is 1 mg/L (1 ppm). The compound added may be NaF or Na_2SiF_6. The silicon-fluorine anion reacts with water to release fluoride ions:

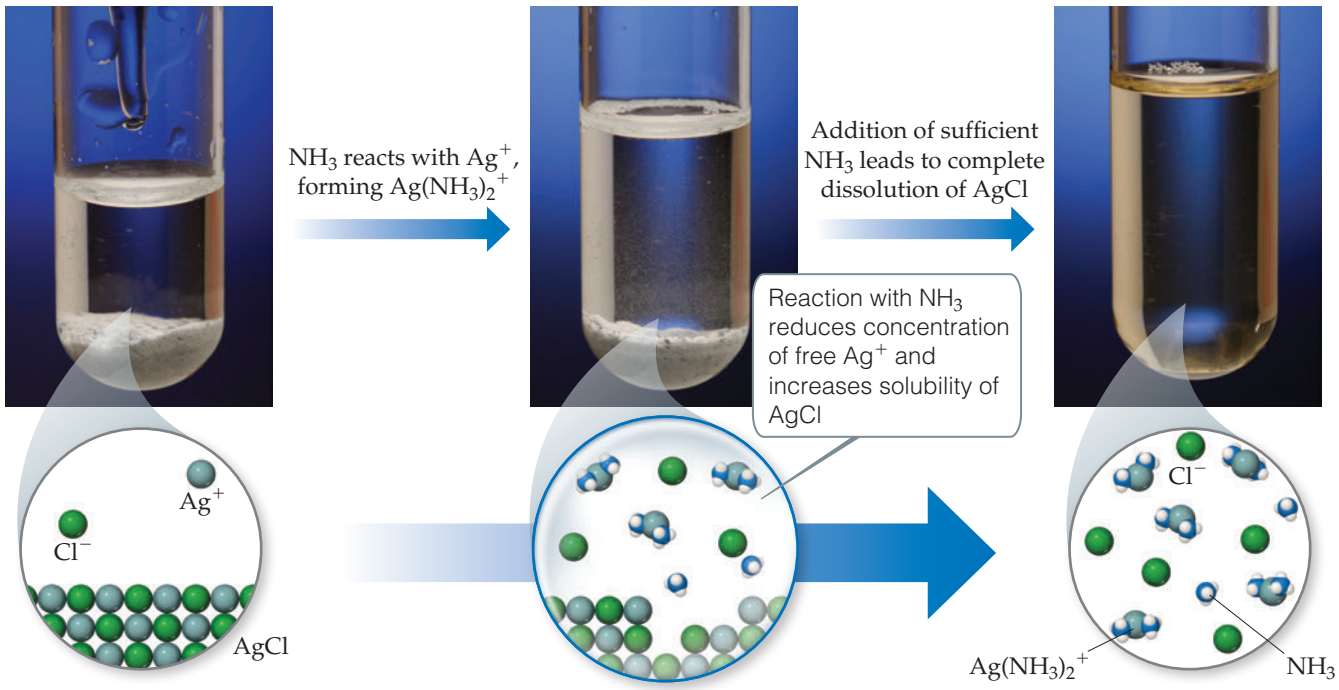
$$SiF_6^{2-}(aq) + 2\,H_2O(l) \longrightarrow 6\,F^-(aq) + 4\,H^+(aq) + SiO_2(s)$$

Many toothpastes now sold in the United States contain fluoride compounds, usually at the level of 0.1% fluoride by mass. The most common compounds in toothpastes are sodium fluoride (NaF), sodium monofluorophosphate (Na_2PO_3F), and stannous fluoride (SnF_2).

Related Exercises: 17.110, 17.128

Formation of Complex Ions

A characteristic property of metal ions is their ability to act as Lewis acids toward water molecules, which act as Lewis bases. Lewis bases other than water can also interact with metal ions, particularly transition-metal ions. Such interactions can dramatically affect the solubility of a metal salt. For example, AgCl ($K_{sp} = 1.8 \times 10^{-10}$) dissolves in the



$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

▲ **Figure 17.19** **Concentrated $NH_3(aq)$ dissolves $AgCl(s)$, which otherwise has very low solubility in water.**

presence of aqueous ammonia because Ag^+ interacts with the Lewis base NH_3, as shown in Figure 17.19. This process can be viewed as the sum of two reactions:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad [17.21]$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad [17.22]$$

$$\text{Overall: } AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \qquad [17.23]$$

The presence of NH_3 drives the reaction, the dissolution of AgCl, to the right as $Ag^+(aq)$ is consumed to form $Ag(NH_3)_2^+$, which is a very soluble species.

For a Lewis base such as NH_3 to increase the solubility of a metal salt, the base must be able to interact more strongly with the metal ion than water does. In other words, the NH_3 must displace solvating H_2O molecules in order to form $[Ag(NH_3)_2]^+$:

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad [17.24]$$

An assembly of a metal ion and the Lewis bases bonded to it, such as $Ag(NH_3)_2^+$, is called a **complex ion**. Complex ions are very soluble in water. The stability of a complex ion in aqueous solution can be judged by the size of the equilibrium constant for its formation from the hydrated metal ion. For example, the equilibrium constant for Equation 17.24 is

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.7 \times 10^7 \qquad [17.25]$$

Note that the equilibrium constant for this kind of reaction is called a **formation constant**, K_f. The formation constants for several complex ions are listed in Table 17.1.

The general rule is that the solubility of metal salts increases in the presence of suitable Lewis bases, such as NH_3, CN^-, or OH^-, provided the metal forms a complex with the base. The ability of metal ions to form complexes is an extremely important aspect of their chemistry.

TABLE 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C

Complex Ion	K_f	Chemical Equation
$Ag(NH_3)_2^+$	1.7×10^7	$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
$Ag(CN)_2^-$	1×10^{21}	$Ag^+(aq) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	$Ag^+(aq) + 2\,S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq)$
$Al(OH)_4^-$	1.1×10^{33}	$Al^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$
$CdBr_4^{2-}$	5×10^3	$Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4^{2-}(aq)$
$Cr(OH)_4^-$	8×10^{29}	$Cr^{3+}(aq) + 4\,OH^-(aq) \rightleftharpoons Cr(OH)_4^-(aq)$
$Co(SCN)_4^{2-}$	1×10^3	$Co^{2+}(aq) + 4\,SCN^-(aq) \rightleftharpoons Co(SCN)_4^{2-}(aq)$
$Cu(NH_3)_4^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$
$Cu(CN)_4^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4\,CN^-(aq) \rightleftharpoons Cu(CN)_4^{2+}(aq)$
$Ni(NH_3)_6^{2+}$	1.2×10^9	$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq)$
$Fe(CN)_6^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{4-}(aq)$
$Fe(CN)_6^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6\,CN^-(aq) \rightleftharpoons Fe(CN)_6^{3-}(aq)$
$Zn(OH)_4^{2-}$	4.6×10^{17}	$Zn^{2+}(aq) + 4\,OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$

Sample Exercise 17.15

Evaluating an Equilibrium Involving a Complex Ion

Calculate the concentration of Ag^+ present in solution at equilibrium when concentrated ammonia is added to a 0.010 *M* solution of $AgNO_3$ to give an equilibrium concentration of $[NH_3] = 0.20\ M$. Neglect the small volume change that occurs when NH_3 is added.

SOLUTION

Analyze Addition of $NH_3(aq)$ to $Ag^+(aq)$ forms $Ag(NH_3)_2^+(aq)$, as shown in Equation 17.22. We are asked to determine what concentration of $Ag^+(aq)$ remains uncombined when the NH_3 concentration is brought to 0.20 *M* in a solution originally 0.010 *M* in $AgNO_3$.

Plan We assume that the $AgNO_3$ is completely dissociated, giving 0.010 *M* Ag^+. Because K_f for the formation of $Ag(NH_3)_2^+$ is quite large, we assume that essentially all the Ag^+ is converted to $Ag(NH_3)_2^+$ and approach the problem as though we are concerned with the dissociation of $Ag(NH_3)_2^+$ rather than its formation. To facilitate this approach, we need to reverse Equation 17.22 and make the corresponding change to the equilibrium constant:

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2\,NH_3(aq)$$

$$\frac{1}{K_f} = \frac{1}{1.7 \times 10^7} = 5.9 \times 10^{-8}$$

Solve If $[Ag^+]$ is 0.010 *M* initially, $[Ag(NH_3)_2^+]$ will be 0.010 *M* following addition of the NH_3. We construct a table to solve this equilibrium problem. Note that the NH_3 concentration given in the problem is an equilibrium concentration rather than an initial concentration.

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2\,NH_3(aq)$$

Initial (*M*)	0.010	0	—
Change (*M*)	$-x$	$+x$	—
Equilibrium (*M*)	$(0.010 - x)$	x	0.20

Because $[Ag^+]$ is very small, we can assume x is small compared to 0.010. Substituting these values into the equilibrium expression for the dissociation of $Ag(NH_3)_2^+$, we obtain

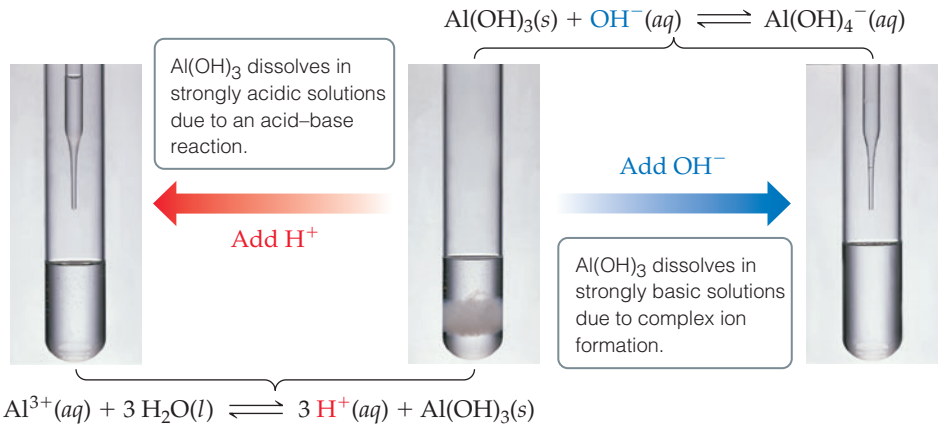
$$\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

$$x = 1.5 \times 10^{-8}\ M = [Ag^+]$$

Formation of the $Ag(NH_3)_2^+$ complex drastically reduces the concentration of free Ag^+ ion in solution.

Practice Exercise

You have an aqueous solution of chromium(III) nitrate that you titrate with an aqueous solution of sodium hydroxide. After a certain amount of titrant has been added, you observe a precipitate forming. You add more sodium hydroxide solution and the precipitate dissolves, leaving a solution again. What has happened? (**a**) The precipitate was sodium hydroxide, which redissolved in the larger volume. (**b**) The precipitate was chromium hydroxide, which dissolved once more solution was added, forming $Cr^{3+}(aq)$. (**c**) The precipitate was chromium hydroxide, which then reacted with more hydroxide to produce a soluble complex ion, $Cr(OH)_4^-(aq)$. (**d**) The precipitate was sodium nitrate, which reacted with more nitrate to produce the soluble complex ion $Na(NO_3)_3^{2-}(aq)$.



▲ **Figure 17.20 Amphoterism.** Some metal oxides and hydroxides, such as $Al(OH)_3$, are amphoteric, which means they dissolve in both strongly acidic and strongly basic solutions.

Amphoterism

Some metal oxides and hydroxides that are relatively insoluble in water dissolve in strongly acidic and strongly basic solutions. These substances, called **amphoteric oxides** and **amphoteric hydroxides**,* are soluble in strong acids and bases because they themselves are capable of behaving as either an acid or base. Examples of amphoteric substances include the oxides and hydroxides of Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.

Like other metal oxides and hydroxides, amphoteric species dissolve in acidic solutions because their anions, O^{2-} or OH^-, react with acids. What makes amphoteric oxides and hydroxides special, though, is that they also dissolve in strongly basic solutions. This behavior results from the formation of complex anions containing several (typically four) hydroxides bound to the metal ion (**Figure 17.20**):

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq) \qquad [17.26]$$

The extent to which an insoluble metal hydroxide reacts with either acid or base varies with the particular metal ion involved. Many metal hydroxides—such as $Ca(OH)_2$, $Fe(OH)_2$, and $Fe(OH)_3$—are capable of dissolving in acidic solution but do not react with excess base. These hydroxides are not amphoteric.

The purification of aluminum ore in the manufacture of aluminum metal provides an interesting application of amphoterism. As we have seen, $Al(OH)_3$ is amphoteric, whereas $Fe(OH)_3$ is not. Aluminum occurs in large quantities as the ore *bauxite*, which is essentially hydrated Al_2O_3 contaminated with Fe_2O_3. When bauxite is added to a strongly basic solution, the Al_2O_3 dissolves because the aluminum forms complex ions, such as $Al(OH)_4^-$. The Fe_2O_3 impurity, however, is not amphoteric and remains as a solid. The solution is filtered, getting rid of the iron impurity. Aluminum hydroxide is then precipitated by addition of acid. The purified hydroxide receives further treatment and eventually yields aluminum metal.

*Notice that the term *amphoteric* is applied to the behavior of insoluble oxides and hydroxides that dissolve in acidic or basic solutions. The similar term *amphiprotic* (Section 16.1) relates more generally to any molecule or ion that can either gain or lose a proton.

A CLOSER LOOK Lead Contamination in Drinking Water

Access to clean drinking water is something most people in the industrialized world take for granted. Unfortunately, there are rare instances in which tap water is not safe to drink, as illustrated by the discovery in 2015 of elevated levels of lead in the municipal water supply of Flint, a city in Michigan State, USA.

Lead is detrimental to many organs in the human body, but the brain and central nervous system are particularly sensitive to its presence. In the brain, Pb^{2+} ions interfere with cell communication and growth by mimicking Ca^{2+} ions. One of the most serious side effects of lead poisoning occurs in young children, where it leads to cognitive impairment. Although lead compounds were once used in a variety of applications—as a gasoline additive, in pigments, shotgun pellets, glass, and water pipes—our daily exposure to lead dropped dramatically once governmental agencies started regulating its use in the 1970s. According to the National Health and Nutrition Examination Survey, the mean concentration of lead in the blood for an average U.S. resident dropped from 150 ppb in 1976 to 16 ppb by 2002, nearly an order-of-magnitude decrease.

The regulatory limit set by the U.S. Environmental Protection Agency (EPA) for lead in drinking water is 15 parts per billion (ppb). According to EPA regulations, utilities serving more than 50,000 people must monitor the level of lead in their water and take corrective action if more than 10% of the homes sampled exceed the 15 ppb limit. Tests performed on samples collected in September 2015 by researchers from Virginia Tech found that in 10% of the 252 Flint homes tested the lead concentration exceeded 25 ppb, and in several homes the concentration exceeded 100 ppb. At the same time, a local pediatrician analyzed the results of infant blood tests and found that the percentage of children with elevated concentrations of lead in their bloodstream (>50 ppb) had doubled from 2.4% in the 2013 to 4.9% in 2015.

The troubles began in April 2014 when the city began using the nearby Flint River as the natural source of its municipal water. Prior to that, Flint obtained water from Detroit, where water taken from Lake Huron was treated before piping it to Flint. The source of the lead was not the Flint River itself, but corrosion from lead pipes that are present in the underground water distribution network. Why did the change in water supply dramatically increase the leaching of lead from the old pipes? Many factors were at play, but basically they all came down to solubility considerations.

When water is properly treated, a passivation layer of insoluble lead salts builds up on the inner surface of the lead pipes (Figure 17.21). This layer prevents corrosion that would otherwise allow lead to be oxidized and dissolve into the water as Pb^{2+} ions. The water treatment facility in Detroit was adding phosphate ions, PO_4^{3-}, to their water to inhibit corrosion, whereas the people managing water treatment in Flint elected not to do so. The presence of PO_4^{3-} ions promotes the formation of highly insoluble phosphate salts on the inner surface of the pipes that helps prevent corrosion.

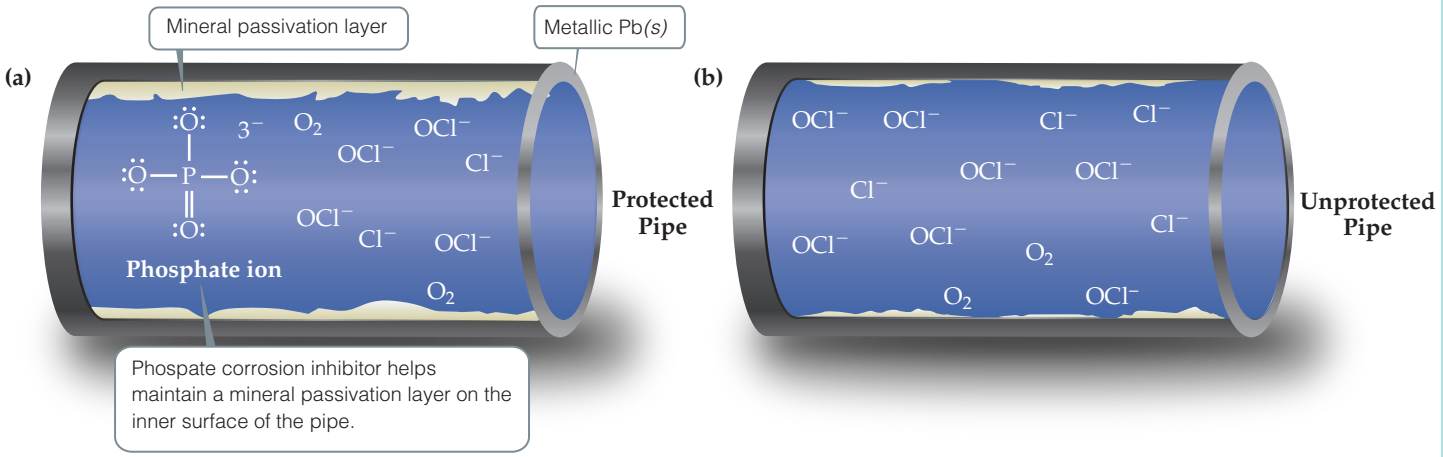
Another factor that appears to have contributed to the problem is a drop in the pH of the water, from 8.0 in December 2014 to 7.3 in August 2015. Because the insoluble lead salts that form the passivating layer, like $Pb_3(PO_4)_2$, $PbHSO_4$, and $PbCO_3$, contain anions that can act as weak bases, anything that makes the water more acidic increases their solubility.

Another contributing factor was the presence of high levels of chloride ions. The treated water from Detroit had chloride levels of about 11 ppm, whereas the treated Flint water had chloride levels of 85 ppm in August 2015. While $PbCl_2$ is fairly insoluble ($K_{sp} = 1.7 \times 10^{-5}$), high concentrations of chloride ions can lead to the formation of soluble complex ions such as $PbCl_3^-$ and $PbCl_4^{2-}$. The increased chloride levels were due in part to the addition of $FeCl_3$, which was used to help coagulate and filter out unwanted organic matter that was leading to problems with *E. coli* contamination. Chloride ions are also produced when unwanted organic matter is oxidized by hypochlorite ions, which are added to kill bacteria. Runoff containing chloride salts used to treat icy roads in the winter may have also contributed.

In the face of mounting evidence that the lead in Flint's drinking water was at unsafe levels, in October of 2015 the city switched back to water piped in from Detroit. Over a period of many months, the circulation of properly treated water should restore the passivating layers inside the pipes. However, cleanup costs are expected to be in excess of $120 million and possibly much more, a large sum compared to the estimated $50,000 per year that it would have cost to treat the water with phosphates. More importantly, the damage done to people who drank the contaminated water, especially children, cannot be undone.

Although the use of lead in plumbing has been banned in the United States since 1986, it is estimated that millions of kilometers of buried lead pipe are still in use in America's cities. Vigilance by water treatment facilities and environmental protection agencies is needed to avoid a repeat of the tragedy in Flint.

Related Exercises: 17.107, 17.111



▲ **Figure 17.21 Protected and unprotected lead pipes.** (**a**) A lead pipe that has a protective passivation layer, and (**b**) a lead pipe where the lack of a phosphate corrosion inhibitor causes the passivation layer to dissolve and fall off, exposing the lead to oxidizing agents such as O_2 and OCl^-.

Self-Assessment Exercises

17.30 Which of the following actions will increase the solubility of $Mg(OH)_2$ at 25 °C?

(a) Adding dilute HCl(*aq*)

(b) Adding dilute $MgCl_2(aq)$

(c) Adding dilute NaOH(*aq*)

17.31 What is the molar solubility of AgCl in in 0.10 *M* HCl at 25 °C given $K_{sp} = 1.80 \times 10^{-10}$ at this temperature.

(a) $1.80 \times 10^{-10}\ M$

(b) $1.80 \times 10^{-9}\ M$

(c) $1.34 \times 10^{-5}\ M$

Exercises

17.32 Calculate the solubility of LaF_3 in grams per liter in (**a**) pure water, (**b**) 0.010 *M* KF solution, (**c**) 0.050 *M* $LaCl_3$ solution.

17.33 Consider a beaker containing a saturated solution of PbI_2 in equilibrium with undissolved $PbI_2(s)$. Now solid KI is added to this solution. (**a**) Will the amount of solid PbI_2 at the bottom of the beaker increase, decrease, or remain the same? (**b**) Will the concentration of Pb^{2+} ions in solution increase or decrease? (**c**) Will the concentration of I^- ions in solution increase or decrease?

17.34 Calculate the molar solubility of $Ni(OH)_2$ when buffered at pH (**a**) 8.0, (**b**) 10.0, (**c**) 12.0.

17.35 Which of the following salts will be substantially more soluble in an HNO_3 solution than in pure water: (**a**) $BaSO_4$, (**b**) CuS, (**c**) $Cd(OH)_2$, (**d**) PbF_2, (**e**) $Cu(NO_3)_2$?

17.36 From the value of K_f listed in Table 17.1, calculate the concentration of NH_3 required to just dissolve 0.020 mol of NiC_2O_4 ($K_{sp} = 4 \times 10^{-10}$) in 1.00 L of solution? (*Hint:* You can neglect the hydrolysis of $C_2O_4^{2-}$ because the solution will be quite basic.)

17.37 Using the value of K_{sp} for Ag_2S, K_{a1} and K_{a2} for H_2S, and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$, calculate the equilibrium constant for the following reaction:

$$Ag_2S(s) + 4\,Cl^-(aq) + 2\,H^+(aq) \rightleftharpoons 2\,AgCl_2^-(aq) + H_2S(aq)$$

Answers to Self-Assessment Exercises

17.30 (a) **17.31** (b)

17.6 Precipitation and Separation of Ions



One of the first steps in many commercial water treatment plants is to add either aluminum sulfate or iron(III) chloride. This results in the precipitation of hydroxide salts of Al^{3+} or Fe^{3+} and flocculation of other ions present in the water. The water is then filtered and disinfected and in some countries a source of fluoride ion added as part of public health policy.

In this section, we examine the precipitation and separation of ions, by the end of which, you should be able to

- Understand how to separate cations based on their solubility.

Equilibrium can be achieved starting with the substances on either side of a chemical equation. For example, the equilibrium that exists between $BaSO_4(s)$, $Ba^{2+}(aq)$, and $SO_4^{2-}(aq)$ (Equation 17.15), can be achieved by starting either with $BaSO_4(s)$ or with solutions containing Ba^{2+} and SO_4^{2-}. If we mix, say, a $BaCl_2$ aqueous solution with a Na_2SO_4 aqueous solution, $BaSO_4$ might precipitate out. How can we predict whether a precipitate will form under various conditions?

Recall that we used the reaction quotient Q in Section 15.4 to determine the direction in which a reaction must proceed to reach equilibrium. The form of Q is the same as the equilibrium expression for a reaction, but instead of only equilibrium concentrations, you can use whatever concentrations are being considered. The direction in which a reaction proceeds to reach equilibrium depends on the relationship between Q and K for the reaction. If $Q < K$, the product concentrations are too low and reactant concentrations are too high relative to the equilibrium concentrations, and so the reaction will proceed to the right (toward products) to achieve equilibrium. If $Q > K$, product concentrations are too high and reactant concentrations are too low, and so the reaction will proceed to the left to achieve equilibrium. If $Q = K$, the reaction is at equilibrium.

For solubility-product equilibria, the relationship between Q and K_{sp} is exactly like that for other equilibria. For K_{sp} reactions, products are always the soluble ions, and the reactant is always the solid.

Therefore, for solubility equilibria,

- If $Q = K_{sp}$, the system is at equilibrium, which means the solution is saturated; this is the highest concentration the solution can have without precipitating.
- If $Q < K_{sp}$, the reaction will proceed to the right, toward the soluble ions; no precipitate will form.
- If $Q > K_{sp}$, the reaction will proceed to the left, toward the solid; precipitate will form.

For the case of the barium sulfate solution, then we would calculate $Q = [Ba^{2+}][SO_4^{2-}]$, and compare this quantity to the K_{sp} for barium sulfate.

Sample Exercise 17.16

Predicting Whether a Precipitate Forms

Does a precipitate form when 0.10 L of $8.0 \times 10^{-3}\ M\ Pb(NO_3)_2$ is added to 0.40 L of $5.0 \times 10^{-3}\ M\ Na_2SO_4$?

SOLUTION

Analyze The problem asks us to determine whether a precipitate forms when two salt solutions are combined.

Plan We should determine the concentrations of all ions just after the solutions are mixed and compare the value of Q with K_{sp} for any potentially insoluble product. The possible metathesis products are $PbSO_4$ and $NaNO_3$. Like all sodium salts $NaNO_3$ is soluble, but $PbSO_4$ has a K_{sp} of 6.3×10^{-7} (Appendix D) and will precipitate if the Pb^{2+} and SO_4^{2-} concentrations are high enough for Q to exceed K_{sp}.

Solve

When the two solutions are mixed, the volume is 0.10 L + 0.40 L = 0.50 L. The number of moles of Pb^{2+} in 0.10 L of $8.0 \times 10^{-3}\ M\ Pb(NO_3)_2$ is:

$$(0.10\ \cancel{L})\left(\frac{8.0 \times 10^{-3}\ \text{mol}}{\cancel{L}}\right) = 8.0 \times 10^{-4}\ \text{mol}$$

The concentration of Pb^{2+} in the 0.50 L mixture is therefore:

$$[Pb^{2+}] = \frac{8.0 \times 10^{-4}\ \text{mol}}{0.50\ \text{L}} = 1.6 \times 10^{-3}\ M$$

Continued

The number of moles of SO_4^{2-} in 0.40 L of $5.0 \times 10^{-3}\,M\,Na_2SO_4$ is:

$$(0.40\,\cancel{L})\left(\frac{5.0 \times 10^{-3}\,\text{mol}}{\cancel{L}}\right) = 2.0 \times 10^{-3}\,\text{mol}$$

Therefore:

$$[SO_4^{2-}] = \frac{2.0 \times 10^{-3}\,\text{mol}}{0.50\,\text{L}} = 4.0 \times 10^{-3}\,M$$

and:

$$Q = [Pb^{2+}][SO_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$$

Because $Q > K_{sp}$, $PbSO_4$ precipitates.

Practice Exercise

An insoluble salt MA has a K_{sp} of 1.0×10^{-16}. Two solutions, MNO_3 and NaA are mixed, to yield a final solution that is $1.0 \times 10^{-8}\,M$ in $M^+(aq)$ and $1.00 \times 10^{-7}\,M$ in $A^-(aq)$. Will a precipitate form?
(**a**) Yes (**b**) No

Selective Precipitation of Ions

Ions can be separated from each other based on the solubilities of their salts. Consider a solution containing both Ag^+ and Cu^{2+}. If HCl is added to the solution, AgCl ($K_{sp} = 1.8 \times 10^{-10}$) precipitates, while Cu^{2+} remains in solution because $CuCl_2$ is soluble. Separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or more (but not all) of the ions is called *selective precipitation*.

Sulfide ion is often used to separate metal ions because the solubilities of sulfide salts span a wide range and depend greatly on solution pH. For example, Cu^{2+} and Zn^{2+} can be separated by bubbling H_2S gas through an acidified solution containing these two cations. Because CuS ($K_{sp} = 6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp} = 2 \times 10^{-25}$), CuS precipitates from an acidified solution (pH $\approx$ 1) while ZnS does not (**Figure 17.22**):

$$Cu^{2+}(aq) + H_2S(aq) \rightleftharpoons CuS(s) + 2\,H^+(aq) \qquad [17.27]$$

The CuS can be separated from the Zn^{2+} solution by filtration. The separated CuS can then be dissolved by raising the concentration of H^+ even further, shifting the equilibrium concentrations of the compounds in Equation 17.27 to the left.

Qualitative Analysis for Metallic Elements

We turn our attention to how solubility equilibria and complex-ion formation can be used to detect the presence of particular metal ions in solution. Before the development of modern analytical instrumentation, it was necessary to analyze mixtures of

Sample Exercise 17.17

Selective Precipitation

A solution contains $1.0 \times 10^{-2}\,M\,Ag^+(aq)$ and $2.0 \times 10^{-2}\,M\,Pb^{2+}(aq)$. When $Cl^-(aq)$ is added, both AgCl ($K_{sp} = 1.8 \times 10^{-10}$) and $PbCl_2$ ($K_{sp} = 1.7 \times 10^{-5}$) can precipitate. What concentration of $Cl^-(aq)$ is necessary to begin the precipitation of each salt? Which salt precipitates first?

SOLUTION

Analyze We are asked to determine the concentration of $Cl^-(aq)$ necessary to begin the precipitation from a solution containing $Ag^+(aq)$ and $Pb^{2+}(aq)$ ions, and to predict which metal chloride will begin to precipitate first.

Plan We are given K_{sp} values for the two precipitates. Using these and the metal ion concentrations, we can calculate what $Cl^-(aq)$ concentration is necessary to precipitate each salt. The salt requiring the lower $Cl^-(aq)$ ion concentration precipitates first.

Solve For AgCl we have $K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$.

Because $[Ag^+] = 1.0 \times 10^{-2}\,M$, the greatest concentration of $Cl^-(aq)$ that can be present without causing precipitation of AgCl can be calculated from the K_{sp} expression:

$$K_{sp} = (1.0 \times 10^{-2})[Cl^-] = 1.8 \times 10^{-10}$$

$$[Cl^-] = \frac{1.8 \times 10^{-10}}{1.0 \times 10^{-2}} = 1.8 \times 10^{-8}\,M$$

Any $Cl^-(aq)$ in excess of this very small concentration will cause AgCl to precipitate from solution. Proceeding similarly for $PbCl_2$, we have

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = 1.7 \times 10^{-5}$$

$$(2.0 \times 10^{-2})[Cl^-]^2 = 1.7 \times 10^{-5}$$

$$[Cl^-]^2 = \frac{1.7 \times 10^{-5}}{2.0 \times 10^{-2}} = 8.5 \times 10^{-4}$$

$$[Cl^-] = \sqrt{8.5 \times 10^{-4}} = 2.9 \times 10^{-2}\,M$$

Thus, a concentration of $Cl^-(aq)$ in excess of $2.9 \times 10^{-2}\,M$ causes $PbCl_2$ to precipitate.

Comparing the $Cl^-(aq)$ concentration required to precipitate each salt, we see that as $Cl^-(aq)$ is added, AgCl precipitates first because it requires a much smaller concentration of Cl^-.

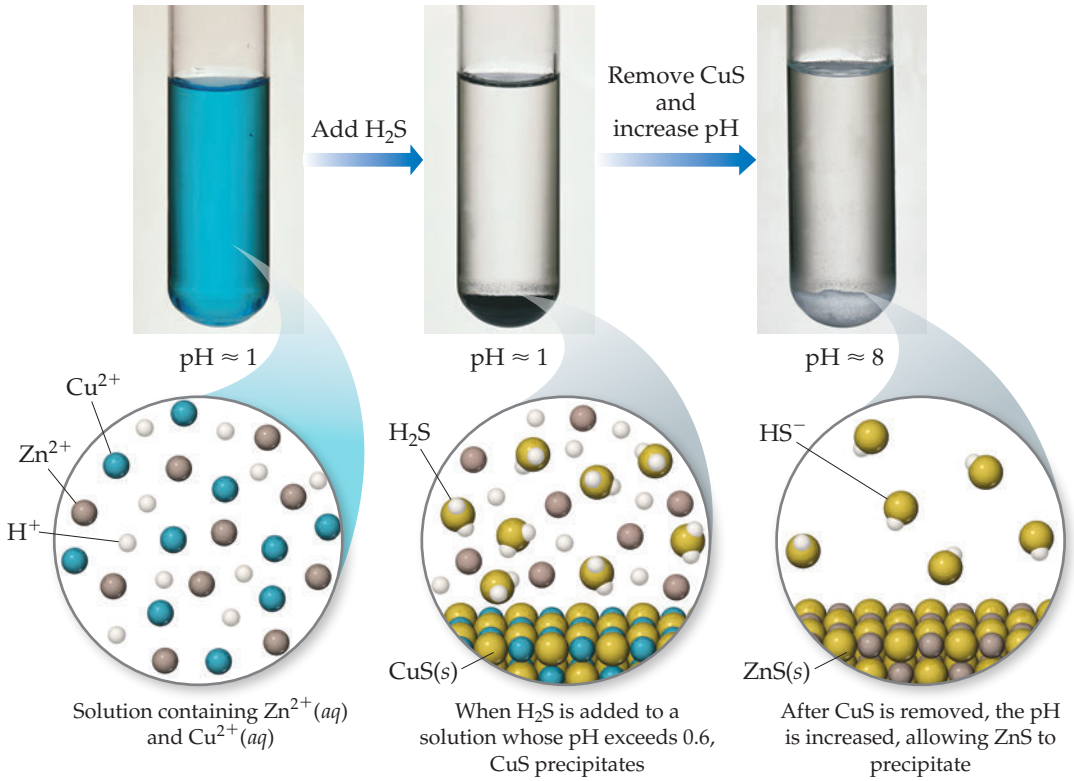
Thus, $Ag^+(aq)$ can be separated from $Pb^{2+}(aq)$ by slowly adding $Cl^-(aq)$ so that the chloride ion concentration remains between $1.8 \times 10^{-8}\,M$ and $2.9 \times 10^{-2}\,M$.

Comment Precipitation of AgCl will keep the $Cl^-(aq)$ concentration low until the number of moles of $Cl^-(aq)$ added exceeds the number of moles of $Ag^+(aq)$ in the solution. Once past this point, $[Cl^-]$ rises sharply and $PbCl_2$ will soon begin to precipitate.

Practice Exercise

Under what conditions does an ionic compound precipitate from a solution of the constituent ions?
(**a**) always (**b**) when $Q = K_{sp}$ (**c**) when Q exceeds K_{sp} (**d**) when Q is less than K_{sp} (**e**) never, if it is very soluble

Go Figure Why is the sulfide reagent HS^- in the third test tube and not H_2S?



▲ **Figure 17.22 Selective precipitation.** In this example, Cu^{2+} ions are separated from Zn^{2+} ions.

metals in a sample by what were called *wet chemical methods*. For example, an ore sample that might contain several metallic elements was dissolved in a concentrated acid solution that was then tested in a systematic way for the presence of various metal ions.

Qualitative analysis determines only the presence or absence of a particular metal ion relative to some threshold, whereas **quantitative analysis** determines how much of a given substance is present. Even though wet methods of qualitative analysis have become less important in the chemical industry, they are frequently used in general chemistry laboratory programs to illustrate equilibria, to teach the properties of common metal ions in solution, and to develop laboratory skills. Typically, such analyses proceed in three stages: (1) The ions are separated into broad groups on the basis of solubility properties. (2) The ions in

each group are separated by selectively dissolving members in the group. (3) The ions are identified by means of specific tests.

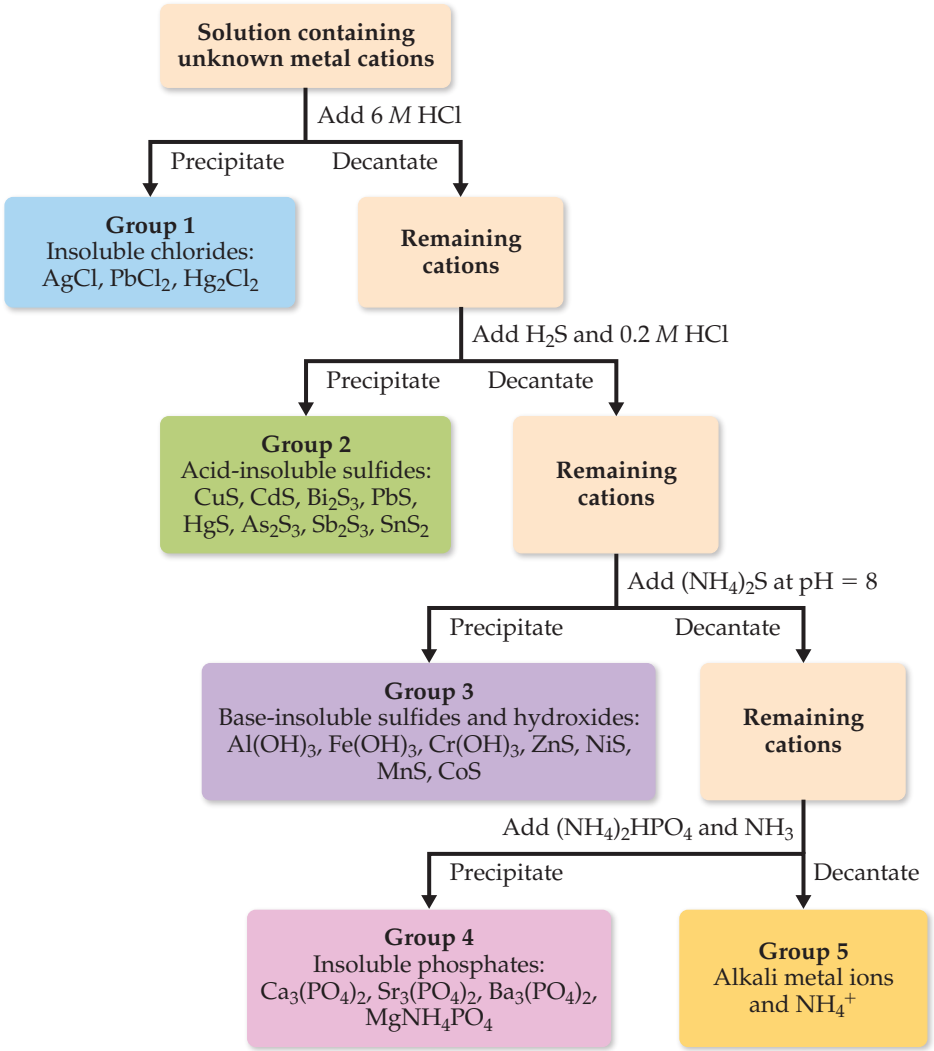
A scheme in general use divides the common cations into five groups (**Figure 17.23**). The order in which reagents are added is important in this scheme. The most selective separations—those that involve the smallest number of ions—are carried out first. The reactions used must proceed so far toward completion that any concentration of cations remaining in the solution is too small to interfere with subsequent tests.

Let's look at each of these five groups of cations, briefly examining the logic used in this qualitative analysis scheme.

Group 1. *Insoluble chlorides:* Of the common metal ions, only $Ag^+(aq)$, $Hg_2^{2+}(aq)$, and $Pb^{2+}(aq)$ form insoluble chlorides. When HCl is added to a mixture of cations, therefore, only AgCl, Hg_2Cl_2, and $PbCl_2$ precipitate, leaving the other cations in solution. The absence of a precipitate indicates that the starting solution contains no $Ag^+(aq)$, $Hg_2^{2+}(aq)$, or $Pb^{2+}(aq)$.

Group 2. *Acid-insoluble sulfides:* After any insoluble chlorides have been removed, the remaining solution, now acidic from HCl treatment, is treated with H_2S. Since

Go Figure If a solution contained a mixture of $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ ions, would this separation scheme work? After which step would the first precipitate be observed?



▲ **Figure 17.23 Qualitative analysis.** A flowchart showing a common scheme for identifying cations.

H_2S is a weak acid compared to HCl, its role here is to act as a source for small amounts of sulfide. Only the most insoluble metal sulfides—CuS, Bi_2S_3, CdS, PbS, HgS, As_2S_3, Sb_2S_3, and SnS_2—precipitate. (Note the very small values of K_{sp} for some of these sulfides in Appendix D.) Those metal ions whose sulfides are somewhat more soluble—for example, ZnS or NiS—remain in solution.

Group 3. *Base-insoluble sulfides and hydroxides:* After the solution is filtered to remove any acid-insoluble sulfides, it is made slightly basic, and $(NH_4)_2S$ is added. In basic solutions the concentration of $S^{2-}(aq)$ is higher than in acidic solutions. Under these conditions, the ion products for many of the more soluble sulfides exceed their K_{sp} values and thus precipitation occurs. The metal ions precipitated at this stage are $Al^{3+}(aq)$, $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, $Zn^{2+}(aq)$, $Ni^{2+}(aq)$, $Co^{2+}(aq)$, and $Mn^{2+}(aq)$. (The $Al^{3+}(aq)$, $Fe^{3+}(aq)$, and $Cr^{3+}(aq)$ ions do not form insoluble sulfides; instead they precipitate as insoluble hydroxides, as Figure 17.23 shows.)

Group 4. *Insoluble phosphates:* At this point, the solution contains only metal ions from Groups 1 and 2 of the periodic table. Adding $(NH_4)_2HPO_4$ to a basic solution precipitates the Group 2 elements $Mg^{2+}(aq)$, $Ca^{2+}(aq)$, $Sr^{2+}(aq)$, and $Ba^{2+}(aq)$ because these metals form insoluble phosphates.

Group 5. *The alkali metal ions and $NH_4^+(aq)$*: The ions that remain after removing the insoluble phosphates are tested for individually. A flame test can be used to determine the presence of $K^+(aq)$, for example, because the flame turns a characteristic violet color if $K^+(aq)$ is present (Figure 7.22).

Self-Assessment Exercise

17.38 In the analysis of metal ions by the precipitation of insoluble sulfides, why is it important to perform the test at pH 2 before pH 8?

(a) Performing the test first at pH 8 will precipitate all metal sulfides that are insoluble up to this pH including those only precipitated at pH 2.

(b) It is more convenient to increase pH from 2 to 8 rather than decrease pH from 8 to 2.

(c) Cations from Group 2 of Figure 17.23 can react with those of Group 3 of Figure 17.23 and need to be removed as soon as possible.

Exercises

17.39 (**a**) Will $Co(OH)_2$ precipitate from solution if the pH of a 0.020 *M* solution of $Co(NO_3)_2$ is adjusted to 8.5? (**b**) Will $AgIO_3$ precipitate when 20 mL of 0.010 *M* $AgIO_3$ is mixed with 10 mL of 0.015 *M* $NaIO_3$? (K_{sp} of $AgIO_3$ is 3.1×10^{-8}.)

17.40 Suppose that a 10 mL sample of a solution is to be tested for I^- ion by addition of 1 drop (0.2 mL) of 0.10 *M* $Pb(NO_3)_2$. What is the minimum number of grams of I^- that must be present for $PbI_2(s)$ to form?

17.41 A solution of Na_2SO_4 is added dropwise to a solution that is 0.010 *M* in $Ba^{2+}(aq)$ and 0.010 *M* in $Sr^{2+}(aq)$. (**a**) What concentration of SO_4^{2-} is necessary to begin precipitation? (Neglect volume changes. $BaSO_4$: $K_{sp} = 1.1 \times 10^{-10}$; $SrSO_4$: $K_{sp} = 3.2 \times 10^{-7}$.) (**b**) Which cation precipitates first? (**c**) What is the concentration of $SO_4^{2-}(aq)$ when the second cation begins to precipitate?

17.42 A 1.0 *M* Na_2SO_4 solution is slowly added to 10.0 mL of a solution that is 0.20 *M* in Ca^{2+} and 0.30 *M* in Ag^+. (**a**) Which compound will precipitate first: $CaSO_4$($K_{sp} = 2.4 \times 10^{-5}$) or Ag_2SO_4 ($K_{sp} = 1.5 \times 10^{-5}$)? (**b**) How much Na_2SO_4 solution must be added to initiate the precipitation?

17.43 An unknown solid is entirely soluble in water. On addition of dilute HCl, a precipitate forms. After the precipitate is filtered off, the pH is adjusted to about 1 and H_2S is bubbled in; a precipitate again forms. After filtering off this precipitate, the pH is adjusted to 8 and H_2S is again added; no precipitate forms. No precipitate forms upon addition of $(NH_4)_2HPO_4$. The remaining solution shows a yellow color in a flame test (see Figure 7.22). Based on these observations, which of the following compounds might be present, which are definitely present, and which are definitely absent: CdS, $Pb(NO_3)_2$, HgO, $ZnSO_4$, $Cd(NO_3)_2$, and Na_2SO_4?

17.44 Suggest how the cations in each of the following solution mixtures can be separated: (**a**) Na^+ and Cd^{2+}, (**b**) Cu^{2+} and Mg^{2+}, (**c**) Pb^{2+} and Al^{3+}, (**d**) Ag^+ and Hg^{2+}.

17.45 (**a**) Precipitation of the Group 4 cations of Figure 17.23 requires a basic medium. Why is this so? (**b**) What is the most significant difference between the sulfides precipitated in Group 2 and those precipitated in Group 3? (**c**) Suggest a procedure that would serve to redissolve the Group 3 cations following their precipitation.

Answers to Self-Assessment Exercises

17.38 (a)

Sample Integrative Exercise

Putting Concepts Together

A sample of 1.25 L of HCl gas at 21 °C and 96.3 kPa is bubbled through 0.500 L of 0.150 *M* NH_3 solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.500 L.

SOLUTION

The number of moles of HCl gas is calculated from the ideal gas law:

$$n = \frac{PV}{RT} = \frac{(96.3\ \text{kPa})(1.25\ \cancel{\text{L}})}{(8.314\ \text{L-kPa/mol-}\cancel{\text{K}})(294\ \cancel{\text{K}})} = 0.0492\ \text{mol HCl}$$

The number of moles of NH_3 in the solution is given by the product of the volume of the solution and its concentration:

$$\text{Moles } NH_3 = (0.500\ \cancel{\text{L}})(0.150\ \text{mol } NH_3/\cancel{\text{L}}) = 0.0750\ \text{mol } NH_3$$

The acid HCl and base NH_3 react, transferring a proton from HCl to NH_3, producing NH_4^+ and Cl^- ions:

$$HCl(g) + NH_3(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

To determine the pH of the solution, we first calculate the amount of each reactant and each product present at the completion of the reaction. Because you can assume this neutralization reaction proceeds as far toward the product side as possible, this is a limiting reactant problem.

	$HCl(g)$	$+\ NH_3(aq)$	$\longrightarrow\ NH_4^+(aq)$	$+\ Cl^-(aq)$
Before reaction (mol)	0.0492	0.0750	0	0
Change (limiting reactant) (mol)	−0.0492	−0.0492	+0.0492	+0.0492
After reaction (mol)	0	0.0258	0.0492	0.0492

Thus, the reaction produces a solution containing a mixture of NH_3, NH_4^+, and Cl^-. The NH_3 is a weak base ($K_b = 1.8 \times 10^{-5}$), NH_4^+ is its conjugate acid, and Cl^- is neither acidic nor basic. Consequently, the pH depends on $[NH_3]$ and $[NH_4^+]$:

$$[NH_3] = \frac{0.0258\ \text{mol } NH_3}{0.500\ \text{L solution}} = 0.0516\ M$$

$$[NH_4^+] = \frac{0.0492\ \text{mol } NH_4^+}{0.500\ \text{L solution}} = 0.0984\ M$$

We can calculate the pH using either K_b for NH_3 or K_a for NH_4^+. Using the K_b expression, we have:

	$NH_3(aq)$	$+\ H_2O(l) \rightleftharpoons$	$NH_4^+(aq)$	$+\ OH^-(aq)$
Initial (*M*)	0.0516	—	0.0984	0
Change (*M*)	$-x$	—	$+x$	$+x$
Equilibrium (*M*)	$(0.0516 - x)$	—	$(0.0984 + x)$	x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.0984 + x)(x)}{(0.0516 - x)} \cong \frac{(0.0984)x}{0.0516} = 1.8 \times 10^{-5}$$

$$x = [OH^-] = \frac{(0.0516)(1.8 \times 10^{-5})}{0.0984} = 9.4 \times 10^{-6}\ M$$

Hence, $\text{pOH} = -\log(9.4 \times 10^{-6}) = 5.03$
and $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.03 = 8.97$.

Chapter Summary and Key Terms

THE COMMON ION EFFECT (SECTION 17.1) In this chapter, we have considered several types of important equilibria that occur in aqueous solution. Our primary emphasis has been on acid–base equilibria in solutions containing two or more solutes and on solubility equilibria. The dissociation of a weak acid or weak base is repressed by the presence of a strong electrolyte that provides an ion common to the equilibrium (the **common-ion effect**).

BUFFERS (SECTION 17.2) A particularly important type of acid–base mixture is that of a weak conjugate acid–base pair that functions as a **buffered solution (buffer)**. Addition of small amounts of a strong acid or a strong base to a buffered solution causes only small changes in pH because the buffer reacts with the added acid or base. (Strong acid–strong base, strong acid–weak base, and weak acid–strong base reactions proceed essentially

to completion.) Buffered solutions are usually prepared from a weak acid and a salt of that acid or from a weak base and a salt of that base. Two important characteristics of a buffered solution are its **buffer capacity** and its pH range. The optimal pH of a buffer is equal to pK_a (or pK_b) of the acid (or base) used to prepare the buffer. The relationship between pH, pK_a, and the concentrations of an acid and its conjugate base can be expressed by the **Henderson–Hasselbalch equation**. It is important to realize that the Henderson–Hasselbalch equation is an approximation, and more detailed calculations may need to be performed to obtain equilibrium concentrations.

ACID–BASE TITRATIONS (SECTION 17.3) The plot of the pH of an acid (or base) as a function of the volume of added base (or acid) is called a **pH titration curve**. The titration curve of a strong acid–strong base titration exhibits a large change in pH in the immediate vicinity of the equivalence point; at the equivalence point for such a titration pH = 7. For strong acid–weak base or weak acid–strong base titrations, the pH change in the vicinity of the equivalence point is not as large as for a strong acid–strong base titration, nor will the pH equal 7 at the equivalence point in these cases. Instead, what determines the pH at the equivalence point is the conjugate base or acid salt solution that results from the neutralization reaction. For this reason, it is important to choose an indicator whose color change is near the pH at the equivalence point for titrations involving either weak acids or weak bases. It is possible to calculate the pH at any point of the titration curve by first considering the effects of the acid–base reaction on solution concentrations and then examining equilibria involving the remaining solute species.

SOLUBILITY EQUILIBRIA (SECTION 17.4) The equilibrium between a solid compound and its ions in solution provides an example of heterogeneous equilibrium. The **solubility-product constant** (or simply the **solubility product**), K_{sp}, is an equilibrium constant that expresses quantitatively the extent to which the compound dissolves. The K_{sp} can be used to calculate the solubility of an ionic compound, and the solubility can be used to calculate K_{sp}.

FACTORS THAT AFFECT SOLUBILITY (SECTION 17.5) Several experimental factors, including temperature, affect the solubilities of ionic compounds in water. The solubility of a slightly soluble ionic compound is decreased by the presence of a second solute that furnishes a common ion (the common-ion effect). The solubility of compounds containing basic anions increases as the solution is made more acidic (as pH decreases). Salts with anions of negligible basicity (the anions of strong acids) are unaffected by pH changes.

The solubility of metal salts is also affected by the presence of certain Lewis bases that react with metal ions to form stable **complex ions**. Complex-ion formation in aqueous solution involves the displacement by Lewis bases (such as NH_3 and CN^-) of water molecules attached to the metal ion. The extent to which such complex formation occurs is expressed quantitatively by the **formation constant** for the complex ion. **Amphoteric oxides** and **hydroxides** are those that are only slightly soluble in water but dissolve on addition of either acid or base.

PRECIPITATION AND SEPARATION OF IONS (SECTION 17.6) Comparison of the reaction quotient, Q, with the value of K_{sp} can be used to judge whether a precipitate will form when solutions are mixed or whether a slightly soluble salt will dissolve under various conditions. Precipitates form when $Q > K_{sp}$. If two salts have sufficiently different solubilities, selective precipitation can be used to precipitate one ion while leaving the other in solution, effectively separating the two ions.

Metallic elements vary a great deal in the solubilities of their salts, in their acid–base behavior, and in their tendencies to form complex ions. These differences can be used to separate and detect the presence of metal ions in mixtures. **Qualitative analysis** determines the presence or absence of species in a sample, whereas **quantitative analysis** determines how much of each species is present. The qualitative analysis of metal ions in solution can be carried out by separating the ions into groups on the basis of precipitation reactions and then analyzing each group for individual metal ions.

Learning Outcomes After studying this chapter, you should be able to:

- Describe the common-ion effect. (Section 17.1) *Related Exercises: 17.2, 17.58*
- Explain how a buffer functions and calculate the pH of a buffered solution. (Section 17.2) *Related Exercises: 17.8, 17.61*
- Calculate the pH of a buffer after the addition of small amounts of a strong acid or a strong base. (Section 17.2) *Related Exercises: 17.12, 17.65*
- Calculate the appropriate quantities of compounds to make a buffer at a given pH. (Section 17.2) *Related Exercises: 17.14, 17.67*
- Calculate the pH at any point for an acid–base titration curve. (Section 17.3) *Related Exercises: 17.23, 17.74*
- Estimate the pK_a for monoprotic or polyprotic acids from their titration curves. (Section 17.3) *Related Exercises: 17.17, 17.68*
- Given either K_{sp}, molar solubility, or mass solubility for a substance, calculate the other two quantities. (Section 17.4) *Related Exercises: 17.26, 17.28, 17.76, 17.78*
- Qualitatively predict, and quantitatively calculate, the molar solubility of a substance in the presence of a common ion or at different pH values. (Section 17.5) *Related Exercises: 17.29, 17.35, 17.37, 17.79, 17.83, 17.85*
- Qualitatively predict whether a precipitate will form when solutions are mixed, and quantitatively calculate the ion concentrations required to initiate precipitation. (Section *17.6)* *Related Exercises: 17.39, 17.41, 17.86, 17.88*
- Explain the effect of complex-ion formation on solubility. (Section 17.6) *Related Exercises: 17.36, 17.84*
- Predict how to separate and identify cations based on their solubility characteristics. (Section 17.6) *Related Exercises: 17.44, 17.91*

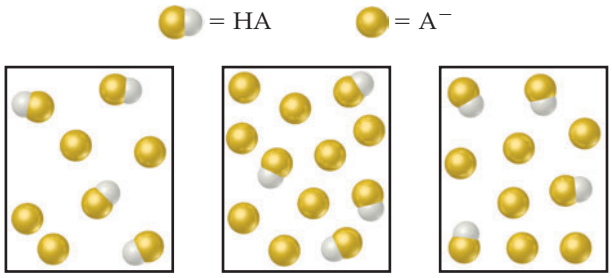
Key Equations

- $\text{pH} = pK_a + \log\dfrac{[\text{base}]}{[\text{acid}]}$ [17.9] The Henderson–Hasselbalch equation, used to estimate the pH of a buffer from the concentrations of a conjugate acid–base pair

Exercises

Visualizing Concepts

17.46 The following boxes represent aqueous solutions containing a weak acid, HA, and its conjugate base, A^-. Water molecules, hydronium ions, and cations are not shown. Which solution has the highest pH? Explain. [Section 17.1]

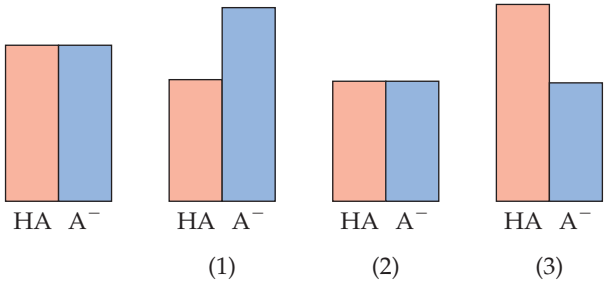


17.47 The beaker on the right contains 0.1 *M* acetic acid solution with methyl orange as an indicator. The beaker on the left contains a mixture of 0.1 *M* acetic acid and 0.1 *M* sodium acetate with methyl orange. (**a**) Using Figures 16.8 and 16.9, which solution has a higher pH? (**b**) Which solution is better able to maintain its pH when small amounts of NaOH are added? Explain. [Sections 17.1 and 17.2]

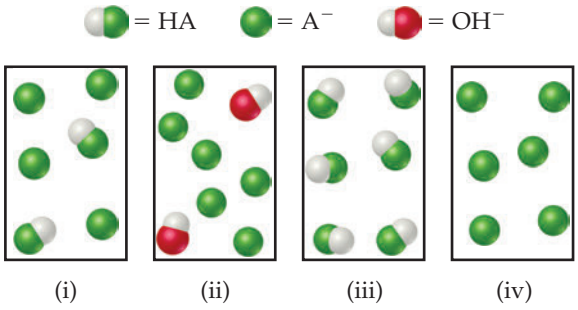


17.48 A buffer contains a weak acid, HA, and its conjugate base. The weak acid has a pK_a of 4.5, and the buffer has a pH of 4.7. Without doing a calculation, state which of these possibilities are correct at pH 4.7. (**a**) [HA] > [A^-], (**b**) [HA] = [A^-], or (**c**) [HA] < [A^-].

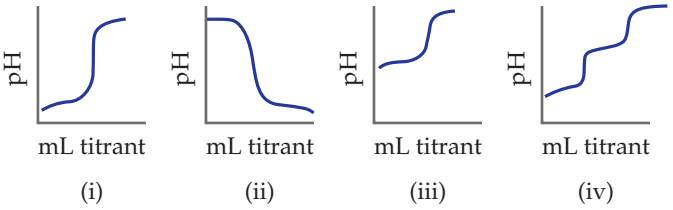
17.49 The following diagram represents a buffer composed of equal concentrations of a weak acid, HA, and its conjugate base, A^-. The heights of the columns are proportional to the concentrations of the components of the buffer. (**a**) Which of the three drawings, (1), (2), or (3), represents the buffer after the addition of a strong acid? (**b**) Which of the three represents the buffer after the addition of a strong base? (**c**) Which of the three represents a situation that cannot arise from the addition of either an acid or a base? [Section 17.2]



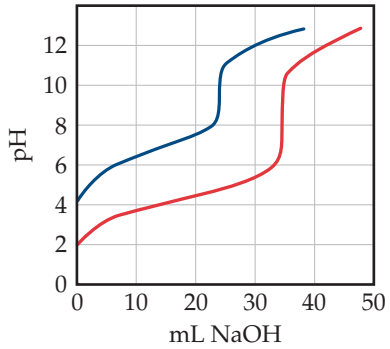
17.50 The following figure represents solutions at various stages of the titration of a weak acid, HA, with NaOH. (The Na^+ ions and water molecules have been omitted for clarity.) To which of the following regions of the titration curve does each drawing correspond: (**a**) before addition of NaOH, (**b**) after addition of NaOH but before the equivalence point, (**c**) at the equivalence point, (**d**) after the equivalence point? [Section 17.3]



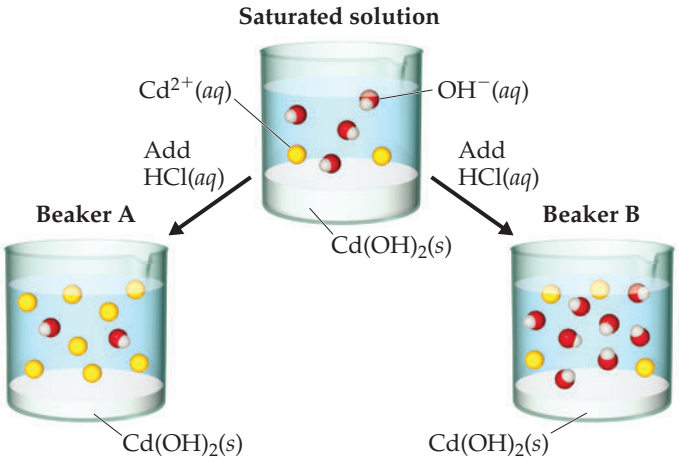
17.51 Match the following descriptions of titration curves with the diagrams: (**a**) strong acid added to strong base, (**b**) strong base added to weak acid, (**c**) strong base added to strong acid, (**d**) strong base added to polyprotic acid. [Section 17.3]



17.52 Equal volumes of two acids are titrated with 0.10 *M* NaOH resulting in the two titration curves shown in the following figure. (**a**) Which curve corresponds to the more concentrated acid solution? (**b**) Which corresponds to the acid with the larger K_a? [Section 17.3]

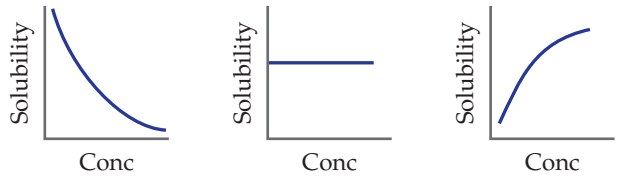


17.53 A saturated solution of $Cd(OH)_2$ is shown in the middle beaker. If hydrochloric acid solution is added, the solubility of $Cd(OH)_2$ will increase, causing additional solid to

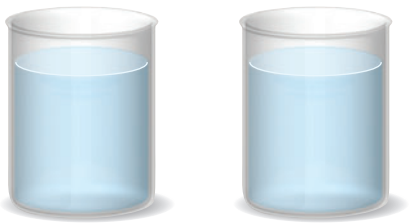


dissolve. Which of the two choices, Beaker A or Beaker B, accurately represents the solution after equilibrium is reestablished? (The water molecules and Cl^- ions are omitted for clarity.) [Sections 17.4 and 17.5]

17.54 The following graphs represent the behavior of $BaCO_3$ under different circumstances. In each case, the vertical axis indicates the solubility of the $BaCO_3$ and the horizontal axis represents the concentration of some other reagent. (**a**) Which graph represents what happens to the solubility of $BaCO_3$ as HNO_3 is added? (**b**) Which graph represents what happens to the $BaCO_3$ solubility as Na_2CO_3 is added? (**c**) Which represents what happens to the $BaCO_3$ solubility as $NaNO_3$ is added? [Section 17.5]



17.55 $Ca(OH)_2$ has a K_{sp} of 6.5×10^{-6}. (**a**) If 0.370 g of $Ca(OH)_2$ is added to 500 mL of water and the mixture is allowed to come to equilibrium, will the solution be saturated? (**b**) If 50 mL of the solution from part (a) is added to each of the beakers shown here, in which beakers, if any, will a precipitate form? In those cases where a precipitate forms, what is its identity? [Section 17.6]



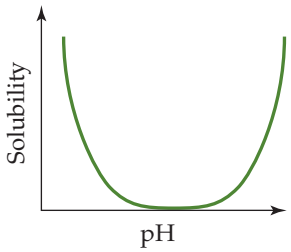
(**i**) 50 mL 1.0 *M* HCl(*aq*)

(**ii**) 50 mL 1.0 *M* NaCl(*aq*)

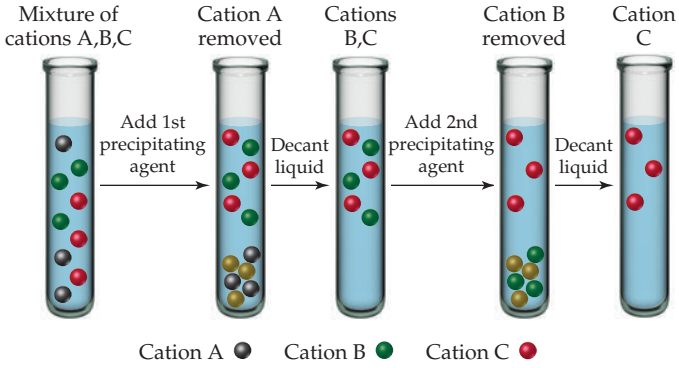
(**iii**) 50 mL 1.0 *M* $CaCl_2(aq)$

(**iv**) 50 mL 0.10 *M* $CaCl_2(aq)$

17.56 This graph shows the solubility of a salt as a function of pH. Which of the following choices explain the shape of this graph? (**a**) None; this behavior is not possible. (**b**) A soluble salt reacts with acid to form a precipitate, and additional acid reacts with this product to dissolve it. (**c**) A soluble salt forms an insoluble hydroxide, then additional base reacts with this product to dissolve it. (**d**) The solubility of the salt increases with pH, then decreases because of the heat generated from the neutralization reactions. [Section 17.5]



17.57 Three cations, Ni^{2+}, Cu^{2+}, and Ag^+, are separated using two different precipitating agents. Based on Figure 17.23, what two precipitating agents could be used? Using these agents, indicate which of the cations is A, which is B, and which is C. [Section 17.6]



The Common-Ion Effect (Section 17.1)

17.58 Which of these statements about the common-ion effect is most correct? (**a**) The solubility of a salt MA is decreased in a solution that already contains either M^+ or A^-. (**b**) Common ions alter the equilibrium constant for the reaction of an ionic solid with water. (**c**) The common-ion effect does not apply to unusual ions like SO_3^{2-}. (**d**) The solubility of a salt MA is affected equally by the addition of either A^- or a noncommon ion.

17.59 Use information from Appendix D to calculate the pH of (**a**) a solution that is 0.070 *M* in potassium propanoate (C_2H_5COOK or $KC_3H_5O_2$) and 0.085 *M* in propanonic acid (C_2H_5COOH or $HC_3H_5O_2$); (**b**) a solution that is 0.085 *M* in trimethylamine, $(CH_3)_3N$, and 0.10 *M* in trimethylammonium chloride, $(CH_3)_3NCl$; (**c**) a solution that is made by mixing 25.0 mL of 0.20 *M* acetic acid and 25.0 mL of 0.25 *M* sodium acetate.

17.60 (**a**) Calculate the percent ionization of 0.0085 *M* butanoic acid ($K_a = 1.5 \times 10^{-5}$). (**b**) Calculate the percent ionization of 0.0085 *M* butanoic acid in a solution containing 0.075 *M* sodium butanoate.

Buffers (Section 17.2)

17.61 Which of the following solutions is a buffer? (**a**) 0.20 *M* formic acid (HCOOH), (**b**) 0.20 *M* formic acid (HCOOH) and 0.20 *M* sodium formate (HCOONa), (**c**) 0.20 *M* nitric acid (HNO_3) and 0.20 *M* sodium nitrate ($NaNO_3$), (**d**) both b and c, (**e**) all of a, b, and c.

17.62 (**a**) Calculate the pH of a buffer that is 0.150 *M* in lactic acid and 0.120 *M* in sodium lactate. (**b**) Calculate the pH of a buffer formed by mixing 75 mL of 0.150 *M* lactic acid with 25 mL of 0.120 *M* sodium lactate.

17.63 A buffer is prepared by adding 15.0 g of sodium acetate (CH_3COONa) to 500 mL of a 0.100 *M* acetic acid (CH_3COOH) solution. (**a**) Determine the pH of the buffer. (**b**) Write the complete ionic equation for the reaction that occurs when a few drops of nitric acid are added to the buffer. (**c**) Write the complete ionic equation for the reaction that occurs when a few drops of potassium hydroxide solution are added to the buffer.

17.64 You are asked to prepare a pH = 2.50 buffer solution starting from 1.50 L of a 0.75 *M* solution of hydrofluoric acid (HF) and any amount you need of sodium fluoride (NaF). (**a**) What is the pH of the hydrofluoric acid solution prior to adding sodium fluoride? (**b**) How many grams of sodium fluoride should be added to prepare the buffer solution? Neglect the small volume change that occurs when the sodium fluoride is added.

17.65 A buffer contains 0.20 mol of acetic acid and 0.25 mol of sodium acetate in 2.50 L. (**a**) What is the pH of this buffer? (**b**) What is the pH of the buffer after the addition of 0.05 mol of NaOH? (**c**) What is the pH of the buffer after the addition of 0.05 mol of HCl?

17.66 (**a**) What is the ratio of HCO_3^- to H_2CO_3 in blood of pH 7.4? (**b**) What is the ratio of HCO_3^- to H_2CO_3 in an exhausted marathon runner whose blood pH is 7.1?

17.67 You have to prepare a pH = 2.50 buffer, and you have the following 0.20 *M* solutions available: HCOOH, CH_3COOH, H_3PO_4, KCH_3COO, KHCOO, and KH_2PO_4. Which solutions would you use? How many liters of each solution would you use to make approximately 2 L of the buffer?

Acid–Base Titrations (Section 17.3)

17.68 Compare the titration of a strong, monoprotic acid with a strong base to the titration of a weak, monoprotic acid with a strong base. Assume the strong and weak acid solutions initially have the same concentrations. Indicate whether the following statements are true or false. (**a**) More base is required to reach the equivalence point for the strong acid than the weak acid. (**b**) The pH at the beginning of the titration is lower for the weak acid than the strong acid. (**c**) The pH at the equivalence point is 7 no matter which acid is titrated.

17.69 The samples of nitric and acetic acids shown here are both titrated with a 0.100 *M* solution of NaOH(*aq*).



25.0 mL of 1.0 *M* $HNO_3(aq)$



25.0 mL of 1.0 *M* $CH_3COOH(aq)$

Determine whether each of the following statements concerning these titrations is true or false.

(**a**) A larger volume of NaOH(*aq*) is needed to reach the equivalence point in the titration of HNO_3.

(**b**) The pH at the equivalence point in the HNO_3 titration will be lower than the pH at the equivalence point in the CH_3COOH titration.

(**c**) Phenolphthalein would be a suitable indicator for both titrations.

17.70 Predict whether the equivalence point of each of the following titrations is below, above, or at pH 7: (**a**) $NaHCO_3$ titrated with NaOH, (**b**) NH_3 titrated with HCl, (**c**) KOH titrated with HBr.

17.71 As shown in Figure 16.7, the indicator thymol blue has two color changes. Which color change will generally be more suitable for the titration of a weak acid with a strong base?

17.72 How many milliliters of 0.0750 *M* KOH are required to titrate each of the following solutions to the equivalence point: (**a**) 30.0 mL of 0.0900 *M* HCOOH, (**b**) 45.0 mL of 0.0750 *M* HNO_3, (**c**) 50.0 mL of a solution that contains 3.00 g of HBr per liter?

17.73 A 10.0 mL sample of 0.250 *M* HNO_3 solution is titrated with 0.100 *M* KOH solution. Calculate the pH of the solution after the following volumes of base have been added: (**a**) 20.0 mL, (**b**) 24.9 mL, (**c**) 25.0 mL, (**d**) 25.1 mL, (**e**) 30.0 mL.

17.74 A 10.0 mL sample of 0.250 *M* acetic acid (CH_3COOH) is titrated with 0.100 *M* KOH solution. Calculate the pH after the following volumes of base have been added: (**a**) 0 mL, (**b**) 12.5 mL, (**c**) 24.5 mL, (**d**) 25.0 mL, (**e**) 25.5 mL, (**f**) 30.0 mL.

17.75 Calculate the pH at the equivalence point for titrating 0.200 *M* solutions of each of the following bases with 0.200 *M* HBr: (**a**) sodium hydroxide (NaOH), (**b**) hydroxylamine (NH_2OH), (**c**) aniline ($C_6H_5NH_2$).

Solubility Equilibria and Factors Affecting Solubility (Sections 17.4 and 17.5)

17.76 For each statement, indicate whether it is true or false.

(**a**) The solubility of a slightly soluble salt can be expressed in units of moles per liter.

(**b**) The solubility product of a slightly soluble salt is simply the square of the solubility.

(**c**) The solubility of a slightly soluble salt is independent of the presence of a common ion.

(**d**) The solubility product of a slightly soluble salt is independent of the presence of a common ion.

17.77 Write the expression for the solubility-product constant for each of the following ionic compounds: $BaCrO_4$, CuS, $PbCl_2$ and LaF_3.

17.78 (**a**) If the molar solubility of CaF_2 at 35 °C is 1.24×10^{-3} mol/L, what is K_{sp} at this temperature? (**b**) It is found that 1.1×10^{-2} g SrF_2 dissolves per 100 mL of aqueous solution at 25 °C. Calculate the solubility product for SrF_2. (**c**) The K_{sp} of $Ba(IO_3)_2$ at 25 °C is 6.0×10^{-10}. What is the molar solubility of $Ba(IO_3)_2$?

17.79 A 1.50 L solution saturated at 25 °C with cobalt carbonate ($CoCO_3$) contains 2.71 mg of $CoCO_3$. Calculate the solubility-product constant for this salt at 25 °C.

17.80 Using Appendix D, calculate the molar solubility of AgI in (**a**) pure water, (**b**) 0.15 *M* KI solution, (**c**) 5.0×10^{-2} *M* $AgNO_3$ solution.

17.81 Consider a beaker containing a saturated solution of CaF_2 in equilibrium with undissolved $CaF_2(s)$. Solid $CaCl_2$ is then added to the solution. (**a**) Will the amount of solid CaF_2 at the bottom of the beaker increase, decrease, or

remain the same? (**b**) Will the concentration of Ca^{2+} ions in solution increase or decrease? (**c**) Will the concentration of F^- ions in solution increase or decrease?

17.82 Calculate the solubility of $Mn(OH)_2$ in grams per liter when buffered at pH (**a**) 7.0, (**b**) 9.5, (**c**) 11.8.

17.83 For each of the following slightly soluble salts, write the net ionic equation, if any, for reaction with a strong acid: (**a**) MnS, (**b**) PbF_2, (**c**) $AuCl_3$, (**d**) $Hg_2C_2O_4$, (**e**) CuBr.

17.84 From the value of K_f listed in Table 17.1, calculate the concentration of $Cu^{2+}(aq)$ and $Cu(NH_3)_4^{2+}$ that are present at equilibrium after dissolving 5.00 g $CuCl_2$ in 1.00 L of 0.10 *M* $NH_3(aq)$.

17.85 Use values of K_{sp} for AgI and K_f for $Ag(CN)_2^-$ to (**a**) calculate the molar solubility of AgI in pure water, (**b**) calculate the equilibrium constant for the reaction $AgI(s) + 2\,CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq) + I^-(aq)$, (**c**) determine the molar solubility of AgI in a 0.100 *M* NaCN solution.

Precipitation and Separation of Ions (Section 17.6)

17.86 (**a**) Will $Ca(OH)_2$ precipitate from solution if the pH of a 0.050 *M* solution of $CaCl_2$ is adjusted to 8.0? (**b**) Will Ag_2SO_4 precipitate when 100 mL of 0.050 *M* $AgNO_3$ is mixed with 10 mL of 5.0×10^{-2} *M* Na_2SO_4 solution?

17.87 Calculate the minimum pH needed to precipitate $Mn(OH)_2$ so completely that the concentration of $Mn^{2+}(aq)$ is less than 1 μg per liter [1 part per billion (ppb)].

17.88 A solution contains 1.0×10^{-4} $Ca^{2+}(aq)$ and 1.0×10^{-4} $La^{3+}(aq)$. If NaF is added, will CaF_2 ($K_{sp} = 3.9 \times 10^{-11}$) or LaF_3 ($K_{sp} = 2 \times 10^{-19}$) precipitate first? Specify the concentration of $F^-(aq)$ needed to begin precipitation.

17.89 A solution contains three anions with the following concentrations: 0.20 *M* CrO_4^{2-}, 0.10 *M* CO_3^{2-}, and 0.010 *M* Cl^-. If a dilute $AgNO_3$ solution is slowly added to the solution, what is the first compound to precipitate: Ag_2CrO_4 ($K_{sp} = 1.2 \times 10^{-12}$), Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$), or AgCl ($K_{sp} = 1.8 \times 10^{-10}$)?

17.90 A solution containing several metal ions is treated with dilute HCl; no precipitate forms. The pH is adjusted to about 1, and H_2S is bubbled through. Again, no precipitate forms. The pH of the solution is then adjusted to about 8. Again, H_2S is bubbled through. This time a precipitate forms. The filtrate from this solution is treated with $(NH_4)_2HPO_4$. No precipitate forms. Which of these metal cations are either possibly present or definitely absent: Al^{3+}, Na^+, Ag^+, Mg^{2+}?

17.91 In the course of various qualitative analysis procedures, the following mixtures are encountered: (**a**) Zn^{2+} and Cd^{2+}, (**b**) $Cr(OH)_3$ and $Fe(OH)_3$, (**c**) Mg^{2+} and K^+, (**d**) Ag^+ and Mn^{2+}. Suggest how each mixture might be separated.

17.92 A student who is in a great hurry to finish his laboratory work decides that his qualitative analysis unknown contains a metal ion from Group 4 of Figure 17.23. He therefore tests his sample directly with $(NH_4)_2HPO_4$, skipping earlier tests for the metal ions in Groups 1, 2, and 3. He observes a precipitate and concludes that a metal ion from Group 4 is indeed present. Why is this possibly an erroneous conclusion?

Additional Exercises

17.93 Derive an equation similar to the Henderson–Hasselbalch equation relating the pOH of a buffer to the pK_b of its base component.

17.94 Rainwater is acidic because $CO_2(g)$ dissolves in the water, creating carbonic acid, H_2CO_3. If the rainwater is too acidic, it will react with limestone and seashells (which are principally made of calcium carbonate, $CaCO_3$). Calculate the concentrations of carbonic acid, bicarbonate ion (HCO_3^-) and carbonate ion (CO_3^{2-}) that are in a raindrop that has a pH of 5.60, assuming that the sum of all three species in the raindrop is 1.0×10^{-5} *M*.

17.95 Furoic acid ($HC_5H_3O_3$) has a K_a value of 6.76×10^{-4} at 25 °C. Calculate the pH at 25 °C of (**a**) a solution formed by adding 30.0 g of furoic acid and 25.0 g of sodium furoate ($NaC_5H_3O_3$) to enough water to form 0.300 L of solution, (**b**) a solution formed by mixing 20.0 mL of 0.200 *M* $HC_5H_3O_3$ and 30.0 mL of 0.250 *M* $NaC_5H_3O_3$ and diluting the total volume to 125 mL, (**c**) a solution prepared by adding 25.0 mL of 1.00 *M* NaOH solution to 100.0 mL of 0.100 *M* $HC_5H_3O_3$.

17.96 The acid–base indicator bromcresol green is a weak acid. The yellow acid and blue base forms of the indicator are present in equal concentrations in a solution when the pH is 4.68. What is the pK_a for bromcresol green?

17.97 Equal quantities of 0.010 *M* solutions of an acid HA and a base B are mixed. The pH of the resulting solution is 9.2. (**a**) Write the chemical equation and equilibrium expression for the reaction between HA and B. (**b**) If K_a for HA is 8.0×10^{-5}, what is the value of the equilibrium constant for the reaction between HA and B? (**c**) What is the value of K_b for B?

17.98 Two buffers are prepared by adding an equal number of moles of methanoic acid (HCOOH) and sodium methanoate (HCOONa) to enough water to make 1.00 L of solution. Buffer A is prepared using 1.00 mol each of methanoic acid and sodium methanoate. Buffer B is prepared by using 0.010 mol of each. (**a**) Calculate the pH of each buffer. (**b**) Which buffer will have the greater buffer capacity? (**c**) Calculate the change in pH for each buffer upon the addition of 1.0 mL of 1.00 *M* HCl. (**d**) Calculate the change in pH for each buffer upon the addition of 10 mL of 1.00 *M* HCl.

17.99 A biochemist needs 750 mL of an acetic acid–sodium acetate buffer with pH 4.50. Solid sodium acetate (CH_3COONa) and glacial acetic acid (CH_3COOH) are available. Glacial acetic acid is 99% CH_3COOH by mass and has a density of 1.05 g/mL. If the buffer is to be 0.15 *M* in CH_3COOH, how many grams of CH_3COONa and how many milliliters of glacial acetic acid must be used?

17.100 A sample of 0.2140 g of an unknown monoprotic acid was dissolved in 25.0 mL of water and titrated with 0.0950 *M* NaOH. The acid required 30.0 mL of base to reach the equivalence point. (**a**) What is the molar mass of the acid? (**b**) After 15.0 mL of base had been added in the titration, the pH was found to be 6.50. What is the K_a for the unknown acid?

17.101 A sample of 500 mg of an unknown monoprotic acid was dissolved in 50.0 mL of water and titrated with 0.200 *M* KOH. The acid required 20.60 mL of base to reach the equivalence point. (**a**) What is the molar mass of the acid? (**b**) After 10.30 mL of base had been added in the titration, the pH was found to be 4.20. What is the pK_a for the unknown acid?

17.102 Mathematically prove that the pH at the halfway point of a titration of a weak acid with a strong base (where the volume of added base is half of that needed to reach the equivalence point) is equal to pK_a for the acid.

17.103 A weak monoprotic acid is titrated with 0.100 *M* NaOH. It requires 25.0 mL of the NaOH solution to reach the equivalence point. After 12.5 mL of base is added, the pH of the solution is 4.16. Estimate the pK_a of the weak acid.

17.104 What is the pH of a solution made by mixing 0.40 mol NaOH, 0.25 mol Na_2HPO_4, and 0.30 mol H_3PO_4 with water and diluting to 2.00 L?

17.105 Suppose you want to do a physiological experiment that calls for a pH 6.50 buffer. You find that the organism with which you are working is not sensitive to the weak acid H_2A ($K_{a1} = 2 \times 10^{-2}$; $K_{a2} = 5.0 \times 10^{-7}$) or its sodium salts. You have available a 1.0 *M* solution of this acid and a 1.0 *M* solution of NaOH. How much of the NaOH solution should be added to 1.0 L of the acid to give a buffer at pH 6.50? (Ignore any volume change.)

17.106 How many microliters of 1.000 *M* NaOH solution must be added to 25.00 mL of a 0.1000 *M* solution of lactic acid [$CH_3CH(OH)COOH$ or $HC_3H_5O_3$] to produce a buffer with pH = 3.75?

17.107 Lead(II) carbonate, $PbCO_3$, is one of the components of the passivating layer that forms inside lead pipes. (**a**) If the K_{sp} for $PbCO_3$ is 7.4×10^{-14} what is the molarity of Pb^{2+} in a saturated solution of lead(II) carbonate? (**b**) What is the concentration in ppb of Pb^{2+} ions in a saturated solution? (**c**) Will the solubility of $PbCO_3$ increase or decrease as the pH is lowered? (**d**) The EPA threshold for acceptable levels of lead ions in water is 15 ppb. Does a saturated solution of lead(II) carbonate produce a solution that exceeds the EPA limit?

17.108 For each pair of compounds, use K_{sp} values to determine which has the greater molar solubility: (**a**) CdS or CuS, (**b**) $PbCO_3$ or $BaCrO_4$, (**c**) $Ni(OH)_2$ or $NiCO_3$, (**d**) AgI or Ag_2SO_4.

17.109 The solubility of $CaCO_3$ is pH dependent. (**a**) Calculate the molar solubility of $CaCO_3$ ($K_{sp} = 4.5 \times 10^{-9}$) neglecting the acid–base character of the carbonate ion. (**b**) Use the K_b expression for the CO_3^{2-} ion to determine the equilibrium constant for the reaction

$$CaCO_3(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq) + OH^-(aq)$$

(**c**) If we assume that the only sources of Ca^{2+}, HCO_3^-, and OH^- ions are from the dissolution of $CaCO_3$, what is the molar solubility of $CaCO_3$ using the equilibrium expression from part (b)? (**d**) What is the molar solubility of $CaCO_3$ at the pH of the ocean (8.3)? (**e**) If the pH is buffered at 7.5, what is the molar solubility of $CaCO_3$?

17.110 Tooth enamel is composed of hydroxyapatite, whose simplest formula is $Ca_5(PO_4)_3OH$, and whose corresponding $K_{sp} = 6.8 \times 10^{-27}$. As discussed in the Chemistry and Life box on page 845, fluoride in fluorinated water or in toothpaste reacts with hydroxyapatite to form fluoroapatite, $Ca_5(PO_4)_3F$, whose $K_{sp} = 1.0 \times 10^{-60}$. (**a**) Write the expression for the solubility-constant for hydroxyapatite and for fluoroapatite. (**b**) Calculate the molar solubility of each of these compounds.

17.111 Salts containing the phosphate ion are added to municipal water supplies to prevent the corrosion of lead pipes. (**a**) Based on the pK_a values for phosphoric acid ($pK_{a1} = 7.5 \times 10^{-3}$, $pK_{a2} = 6.2 \times 10^{-8}$, $pK_{a3} = 4.2 \times 10^{-13}$) what is the K_b value for the PO_4^{3-} ion? (**b**) What is the pH of a 1×10^{-3} *M* solution of Na_3PO_4 (you can ignore the formation of $H_2PO_4^-$ and H_3PO_4)?

17.112 Calculate the solubility of $Fe(OH)_2$ in 0.50 *M* NH_4Cl.

17.113 The solubility-product constant for barium permanganate, $Ba(MnO_4)_2$, is 2.5×10^{-10}. Assume that solid $Ba(MnO_4)_2$ is in equilibrium with a solution of $KMnO_4$. What concentration of $KMnO_4$ is required to establish a concentration of 2.0×10^{-8} *M* for the Ba^{2+} ion in solution?

17.114 Calculate the ratio of $[Ca^{2+}]$ to $[Fe^{2+}]$ in a lake in which the water is in equilibrium with deposits of both $CaCO_3$ and $FeCO_3$. Assume that the water is slightly basic and that the hydrolysis of the carbonate ion can therefore be ignored.

17.115 The solubility product constants of $PbSO_4$ and $SrSO_4$ are 6.3×10^{-7} and 3.2×10^{-7}, respectively. What are the values of $[SO_4^{2-}]$, $[Pb^{2+}]$, and $[Sr^{2+}]$ in a solution at equilibrium with both substances?

17.116 A buffer of what pH is needed to give a Mg^{2+} concentration of 3.0×10^{-2} *M* in equilibrium with solid magnesium oxalate?

17.117 The value of K_{sp} for $Mg_3(AsO_4)_2$ is 2.1×10^{-20}. The AsO_4^{3-} ion is derived from the weak acid H_3AsO_4 ($pK_{a1} = 2.22$; $pK_{a2} = 6.98$; $pK_{a3} = 11.50$). (**a**) Calculate the molar solubility of $Mg_3(AsO_4)_2$ in water. (**b**) Calculate the pH of a saturated solution of $Mg_3(AsO_4)_2$ in water.

17.118 The solubility product for $Zn(OH)_2$ is 3.0×10^{-16}. The formation constant for the hydroxo complex, $Zn(OH)_4^{2-}$, is 4.6×10^{17}. What concentration of OH^- is required to dissolve 0.015 mol of $Zn(OH)_2$ in a liter of solution?

17.119 The value of K_{sp} for $Cd(OH)_2$ is 2.5×10^{-14}. (**a**) What is the molar solubility of $Cd(OH)_2$? (**b**) The solubility of $Cd(OH)_2$ can be increased through formation of the complex ion $CdBr_4^{2-}$ ($K_f = 5 \times 10^3$). If solid $Cd(OH)_2$ is added to a NaBr solution, what is the initial concentration of NaBr needed to increase the molar solubility of $Cd(OH)_2$ to 1.0×10^{-3} mol/L

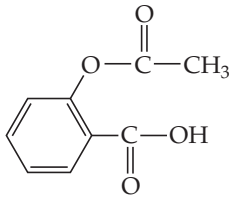
Integrative Exercises

17.120 (**a**) Write the net ionic equation for the reaction that occurs when a solution of nitric acid (HNO_3) is mixed with a solution of potassium propionate ($KC_2H_5CO_2$). (**b**) Calculate the equilibrium constant for this reaction. (**c**) Calculate the equilibrium concentrations of K^+, H^+, NO_3^-, $C_2H_5COO^-$ and C_2H_5COOH when 100.0 mL of 0.30 *M* HNO_3 is mixed with 100.0 mL of 0.30 *M* $KC_2H_5CO_2$.

17.121 (**a**) A 0.1044 g sample of an unknown monoprotic acid requires 22.10 mL of 0.0500 *M* NaOH to reach the end point. What is the molar mass of the unknown? (**b**) As the acid is titrated, the pH of the solution after the addition of 11.05 mL of the base is 4.89. What is the K_a for the acid? (**c**) Using Appendix D, suggest the identity of the acid.

17.122 A sample of 7.5 L of NH_3 gas at 22 °C and 98 kPa is bubbled into a 0.50 L solution of 0.40 *M* HCl. Assuming that all the NH_3 dissolves and that the volume of the solution remains 0.50 L, calculate the pH of the resulting solution.

17.123 Aspirin has the structural formula



At body temperature (37 °C), K_a for aspirin equals 3×10^{-5}. If two aspirin tablets, each having a mass of 325 mg, are dissolved in a full stomach whose volume is 1 L and whose pH is 2, what percent of the aspirin is in the form of neutral molecules?

17.124 What is the pH at 25 °C of water saturated with CO_2 at a partial pressure of 111.5 kPa? The Henry's law constant for CO_2 at 25 °C is 3.1×10^{-4} mol/L kPa.

17.125 Excess $Ca(OH)_2$ is shaken with water to produce a saturated solution. The solution is filtered, and a 50.00 mL sample titrated with HCl requires 11.23 mL of 0.0983 *M* HCl to reach the end point. Calculate K_{sp} for $Ca(OH)_2$. Compare your result with that in Appendix D. Suggest a reason for any differences you find between your value and the one in Appendix D.

17.126 The osmotic pressure of a saturated solution of lead(II) sulfate ($PbSO_4$) at 25 °C is 3.93 kPa. What is the solubility product of this salt at 25 °C?

17.127 A concentration of 10–100 parts per billion (by mass) of Ag^+ is an effective disinfectant in swimming pools. However, if the concentration exceeds this range, the Ag^+ can cause adverse health effects. One way to maintain an appropriate concentration of Ag^+ is to add a slightly soluble salt to the pool. Using K_{sp} values from Appendix D, calculate the equilibrium concentration of Ag^+ in parts per billion that would exist in equilibrium with (**a**) AgCl, (**b**) AgBr, (**c**) AgI.

17.128 Fluoridation of drinking water is employed in many places to aid in the prevention of tooth decay. Typically. the F^- ion concentration is adjusted to about 1 ppm. Some water supplies are also "hard"; that is, they contain certain cations such as Ca^{2+} that interfere with the action of soap. Consider a case where the concentration of Ca^{2+} is 8 ppm. Could a precipitate of CaF_2 form under these conditions? (Make any necessary approximations.)

17.129 Baking soda (sodium bicarbonate, $NaHCO_3$) reacts with acids in foods to form carbonic acid (H_2CO_3), which in turn decomposes to water and carbon dioxide gas. In a cake batter, the $CO_2(g)$ forms bubbles and causes the cake to rise. (**a**) A rule of thumb in baking is that 1/2 teaspoon of baking soda is neutralized by one cup of sour milk. The acid component in sour milk is lactic acid, $CH_3CH(OH)COOH$. Write the chemical equation for this neutralization reaction. (**b**) The density of baking soda is 2.16 g/cm^3. Calculate the concentration of lactic acid in one cup of sour milk (assuming the rule of thumb applies), in units of mol/L. (One cup = 236.6 mL = 48 teaspoons). (**c**) If 1/2 teaspoon of baking soda is indeed completely neutralized by the lactic acid in sour milk, calculate the volume of carbon dioxide gas that would be produced at a pressure of 101.3 kPa, in an oven set to 177 °C.

17.130 In nonaqueous solvents, it is possible to react HF to create H_2F^+. Which of these statements follows from this observation? (**a**) HF can act like a strong acid in nonaqueous solvents, (**b**) HF can act like a base in nonaqueous solvents, (**c**) HF is thermodynamically unstable, (**d**) There is an acid in the nonaqueous medium that is a stronger acid than HF.

Design an Experiment

You are cleaning up an old chemistry lab and find a glass bottle labeled "6.00 *M* NaOH." The bottle looks like it holds about 5 mL of solution. However, it is possible that sodium hydroxide, over a long period of time, has reacted with glass (SiO_2). It is also possible that the bottle was not well sealed, and some water evaporated.

Design an experiment to determine the concentration of the NaOH, using a very small amount from the bottle (less than 1 mL). Consider that you have unlimited water available, a stock solution of 2.00 *M* HCl, and any pH indicators you need. Also consider that your equipment only allows you to measure volumes to the nearest mL.

WHAT'S AHEAD

18.1 ▶ Earth's Atmosphere

18.2 ▶ Human Activities and Earth's Atmosphere

18.3 ▶ Earth's Water

18.4 ▶ Human Activities and Water Quality

18.5 ▶ Green Chemistry

18

CHEMISTRY OF THE ENVIRONMENT

18.1 | Earth's Atmosphere



The richness of life on Earth, represented in the section-opening photograph, is made possible by our planet's supportive atmosphere, the energy received from the Sun, and an abundance of water. These are the signature environmental features believed to be necessary for life.

As technology has advanced and human population has increased, humans have put new and greater stresses on the environment. Paradoxically, the very technology that enables population growth also provides the tools to help understand and manage the environment in a beneficial way. Chemistry is often at the heart of environmental issues. The economic growth of both developed and developing nations depends critically on chemical processes that range from treatment of water supplies to the extraction of fossil fuels. Some of these processes produce products or by products that are harmful to the environment.

We are now in a position to apply the principles we have learned in preceding chapters to an understanding of how our environment operates and how human activities affect it. To understand and protect the environment in which we live, we must understand how human-made and natural chemical compounds interact on land and in the sea and sky. Our daily actions as consumers turn on the same choices made by leading experts and governmental leaders: each decision should reflect the costs versus the benefits of our choices. Unfortunately, the environmental impacts of our decisions are often subtle and not immediately evident.

By the end of this section, you should be able to

- Describe the regions of Earth's atmosphere.
- Calculate concentrations of gases in parts per million (ppm).
- Describe the processes of photodissociation and photoionization.

Because most of us have never been very far from Earth's surface, we often take for granted the many ways in which the atmosphere determines the environment in which we live. In this section we examine some of the important characteristics of our planet's atmosphere.

The temperature of the atmosphere varies with altitude (**Figure 18.1**), and the atmosphere is divided into four regions based on this temperature profile. Just above the surface, in the **troposphere**, the temperature normally decreases with increasing altitude, reaching a minimum of about 215 K at about 10 km. Nearly all of us live our entire lives in the troposphere. Howling winds and soft breezes, rain, and sunny skies—all that we normally think of as "weather"—occur in this region. Commercial jet aircraft typically fly about 10 km above Earth, an altitude that defines the upper limit of the troposphere, which we call the *tropopause*.

Above the tropopause, air temperature increases with altitude, reaching a maximum of about 275 K at about 50 km. The region from 10 km to 50 km is the **stratosphere**, and above it are the *mesosphere* and *thermosphere*. Notice in Figure 18.1 that the temperature extremes that form the boundaries between adjacent regions are denoted by the suffix *-pause*. The boundaries are important because gases mix across them relatively slowly. For example, pollutant gases generated in the troposphere pass through the tropopause and find their way into the stratosphere only very slowly.

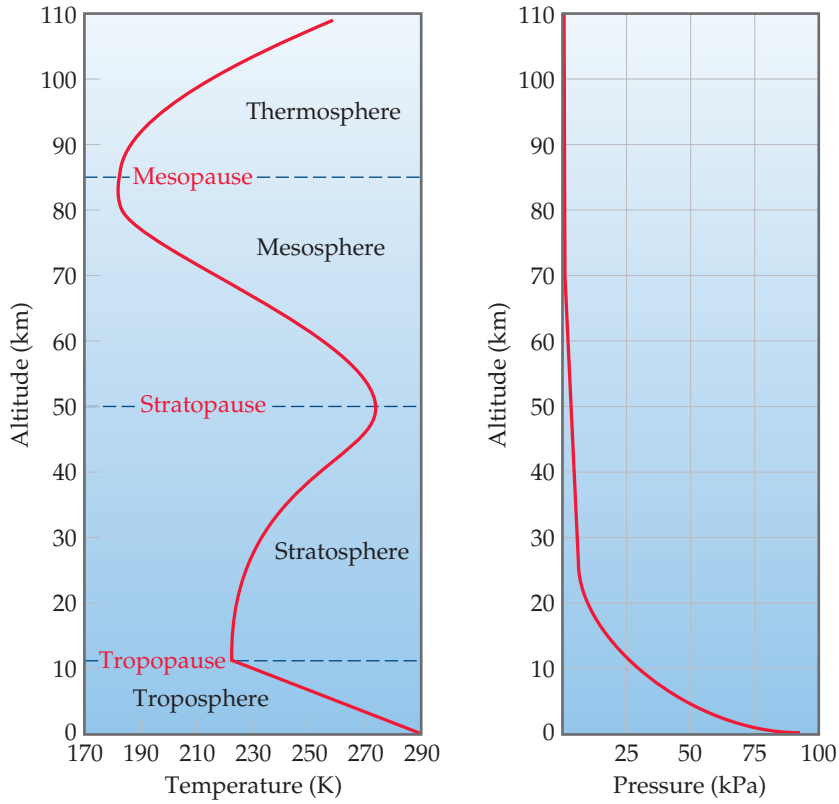
Atmospheric pressure decreases with increasing elevation (Figure 18.1), declining much more rapidly at lower elevations than at higher ones because of the atmosphere's compressibility. Thus, the pressure decreases from an average value of 101.3 kPa at sea level to 3.1×10^{-4} kPa at 100 km, to only 1.3×10^{-7} kPa at 200 km.

The troposphere and stratosphere together account for 99.9% of the mass of the atmosphere, 75% of which is the mass in the troposphere. Nevertheless, the thin upper atmosphere plays many important roles in determining the conditions of life at the surface.

Composition of the Atmosphere

Earth's atmosphere is constantly bombarded by radiation and energetic particles from the Sun. This barrage of energy has profound chemical and physical effects, especially in the upper regions of the atmosphere, above about 80 km (**Figure 18.2**). In addition, because of Earth's gravitational field, heavier atoms and molecules tend to sink in the atmosphere, leaving lighter atoms and molecules at the top of the atmosphere. (This is

Go Figure At what altitude is the atmospheric temperature lowest?



▲ **Figure 18.1** **Temperature and pressure in the atmosphere vary as a function of altitude above sea level.**



▲ **Figure 18.2** **The aurora borealis (northern lights).**

why, as just noted, 75% of the atmosphere's mass is in the troposphere.) Because of all these factors, the composition of the atmosphere is not uniform.

Table 18.1 shows the composition of dry air near sea level. Note that although traces of many substances are present, N_2 and O_2 make up about 99% of sea-level air. The noble gases and CO_2 make up most of the remainder.

When applied to substances in aqueous solution, the concentration unit *parts per million* (ppm) refers to grams of substance per million grams of solution. When dealing

TABLE 18.1 The Major Components of Dry Air near Sea Level

Component*	Content (mole fraction)	Molar Mass (g/mol)
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000400	44.0099
Neon	0.00001818	20.183
Helium	0.00000524	4.003
Methane	0.000002	16.043
Krypton	0.00000114	83.80
Hydrogen	0.0000005	2.0159
Nitrous oxide	0.0000005	44.0128
Xenon	0.000000087	131.30

*Ozone, sulfur dioxide, nitrogen dioxide, ammonia, and carbon monoxide are present as trace gases in variable amounts.

TABLE 18.2 Sources and Typical Concentrations of Some Minor Atmospheric Constituents

Constituent	Sources	Typical Concentration
Carbon dioxide, CO_2	Decomposition of organic matter, release from oceans, fossil fuel combustion	400 ppm throughout troposphere
Carbon monoxide, CO	Decomposition of organic matter, industrial processes, fossil fuel combustion	0.05 ppm in unpolluted air; 1–50 ppm in urban areas
Methane, CH_4	Decomposition of organic matter, natural-gas seepage, livestock emissions	1.82 ppm throughout troposphere
Nitric oxide, NO	Atmospheric electrical discharges, internal combustion engines, combustion of organic matter	0.01 ppm in unpolluted air; 0.2 ppm in smog
Ozone, O_3	Atmospheric electrical discharges, diffusion from the stratosphere, photochemical smog	0–0.01 ppm in unpolluted air; 0.5 ppm in photochemical smog
Sulfur dioxide, SO_2	Volcanic gases, forest fires, bacterial action, fossil fuel combustion, industrial processes	0–0.01 ppm in unpolluted air; 0.1–2 ppm in polluted urban areas

with gases, however, 1 ppm means one part by *volume* in 1 million volumes of the whole. Because volume is proportional to number of moles of gas via the ideal gas equation ($PV = nRT$), volume fraction and mole fraction are the same. Thus, 1 ppm of a trace constituent of the atmosphere amounts to 1 mol of that constituent in 1 million moles of air; that is, the concentration in parts per million is equal to the mole fraction times 10^6. For example, Table 18.1 lists the mole fraction of CO_2 in the atmosphere as 0.000400, which means its concentration in parts per million is $0.000400 \times 10^6 = 400$ ppm.

Other minor constituents of the troposphere, in addition to CO_2, are listed in Table 18.2.

Before we consider the chemical processes that occur in the atmosphere, let's review some of the properties of the two major components, N_2 and O_2. Recall that the N_2 molecule possesses a triple bond between the nitrogen atoms. This very strong bond (bond energy 941 kJ/mol) is largely responsible for the very low reactivity of N_2. The bond energy in O_2 is only 495 kJ/mol, making O_2 much more reactive than N_2. For example, oxygen reacts with many substances to form oxides.

Sample Exercise 18.1

Calculating Concentration from Partial Pressure

What is the concentration, in parts per million, of water vapor in a sample of air if the partial pressure of the water is 0.11 kPa and the total pressure of the air is 98.0 kPa?

SOLUTION

Analyze We are given the partial pressure of water vapor and the total pressure of an air sample and asked to determine the water vapor concentration.

Plan Recall that the partial pressure of a component in a mixture of gases is given by the product of its mole fraction and the total pressure of the mixture:

$$P_{H_2O} = X_{H_2O} P_t$$

Solve Solving for the mole fraction of water vapor in the mixture, X_{H_2O}, gives

$$X_{H_2O} = \frac{P_{H_2O}}{P_t} = \frac{0.11\ \text{kPa}}{98.0\ \text{kPa}} = 0.0011$$

The concentration in ppm is the mole fraction times 10^6:

$$0.0011 \times 10^6 = 1100\ \text{ppm}$$

Practice Exercise

The concentration of CO in a sample of air is 4.3 ppm. What is the partial pressure of the CO if the total air pressure is 92.7 kPa?

Photochemical Reactions in the Atmosphere

Although the atmosphere beyond the stratosphere contains only a small fraction of the atmospheric mass, it forms the outer defense against the hail of radiation and high-energy particles that continuously bombard Earth. As the bombarding radiation passes through the upper atmosphere, it causes two kinds of chemical changes: *photodissociation* and *photoionization*. These processes protect us from high-energy radiation by absorbing most of the radiation before it reaches the troposphere. If it were not for these photochemical processes, plant and animal life as we know it could not exist on Earth.

The Sun emits radiant energy over a wide range of wavelengths (**Figure 18.3**). To understand the connection between the wavelength of radiation and its effect on atoms and molecules, recall that electromagnetic radiation can be pictured as a stream of photons. The energy of each photon is given by $E = h\nu$, where h is Planck constant and ν is the radiation frequency. For a chemical change to occur when radiation strikes atoms or molecules, two conditions must be met. First, the incoming photons must have sufficient energy to break a chemical bond or remove an electron from the atom or molecule. Second, the atoms or molecules being bombarded must absorb these photons. When these requirements are met, the energy of the photons is used to do the work associated with some chemical change.

Photodissociation The rupture of a chemical bond resulting from absorption of a photon by a molecule is called **photodissociation**. No ions are formed when the bond between two atoms is cleaved by photodissociation. Instead, half the bonding electrons stay with one atom and half stay with the other atom. The result is two electrically neutral particles.

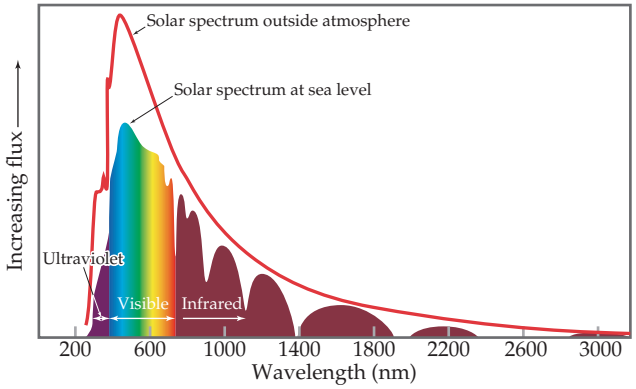
One of the most important processes occurring above an altitude of about 120 km is photodissociation of the oxygen molecule:

$$:\ddot{O}{=}\ddot{O}: + h\nu \longrightarrow :\dot{O} + \dot{O}: \qquad [18.1]$$

The minimum energy required to cause this change is determined by the bond energy (or *dissociation energy*) of O_2, 495 kJ/mol.

Fortunately for us, O_2 absorbs much of the high-energy, short-wavelength radiation from the solar spectrum before that radiation reaches the lower atmosphere. As it does, atomic oxygen, O, is formed. The dissociation of O_2 is very extensive at higher elevations. At 400 km, for example, only 1% of the oxygen is in the form of O_2; 99% is atomic oxygen. At 130 km, O_2 and atomic oxygen are just about equally abundant. Below 130 km, O_2 is more abundant than atomic oxygen because most of the solar energy has been absorbed in the upper atmosphere.

Go Figure Why doesn't the solar spectrum at sea level perfectly match the solar spectrum outside the atmosphere?



▲ Figure 18.3 The solar spectrum above Earth's atmosphere compared to that at sea level. The more structured curve at sea level is due to gases in the atmosphere absorbing specific wavelengths of light. "Flux," the unit on the vertical axis, is light energy per area per unit of time.

Sample Exercise 18.2

Calculating the Wavelength Required to Break a Bond

What is the maximum wavelength of light, in nanometers, that has enough energy per photon to dissociate the O_2 molecule?

SOLUTION

Analyze We are asked to determine the wavelength of a photon that has just enough energy to break the O═O double bond in O_2.

Plan We first need to calculate the energy required to break the O═O double bond in one molecule and then find the wavelength of a photon of this energy.

Solve

The dissociation energy of O_2 is 495 kJ/mol. Using this value and Avogadro's number, we can calculate the amount of energy needed to break the bond in a single O_2 molecule:

$$\left(495 \times 10^3 \frac{\text{J}}{\cancel{\text{mol}}}\right)\left(\frac{1\ \cancel{\text{mol}}}{6.022 \times 10^{23}\ \text{molecules}}\right) = 8.22 \times 10^{-19} \frac{\text{J}}{\text{molecule}}$$

We next use the Planck relationship, $E = h\nu$, to calculate the frequency ν of a photon that has this amount of energy:

$$\nu = \frac{E}{h} = \frac{8.22 \times 10^{-19}\ \cancel{\text{J}}}{6.626 \times 10^{-34}\ \cancel{\text{J}}\,\text{s}} = 1.24 \times 10^{15}\ \text{s}^{-1}$$

Finally, we use the relationship between frequency and wavelength to calculate the wavelength of the light:

$$\lambda = \frac{c}{\nu} = \left(\frac{3.00 \times 10^8\ \cancel{\text{m}}/\cancel{\text{s}}}{1.24 \times 10^{15}/\cancel{\text{s}}}\right)\left(\frac{10^9\ \text{nm}}{1\ \cancel{\text{m}}}\right) = 242\ \text{nm}$$

Comment Thus, light of wavelength 242 nm, which is in the ultraviolet region of the electromagnetic spectrum, has sufficient energy per photon to photodissociate an O_2 molecule. Because photon energy increases as wavelength *decreases*, any photon of wavelength *shorter* than 242 nm will have sufficient energy to dissociate O_2.

Practice Exercise

The bond dissociation energy of the Br—Br bond is 193 kJ/mol. What wavelength of light has just enough energy to cause Br—Br bond dissociation?

(**a**) 620 nm (**b**) 310 nm (**c**) 148 nm (**d**) 6200 nm (**e**) 563 nm

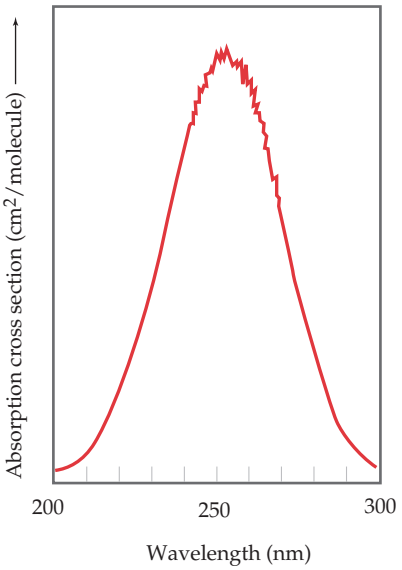
The dissociation energy of N_2 is very high, 941 kJ/mol. As you should have seen in working out Practice Exercise 2 of Sample Exercise 18.2, only photons having a wavelength shorter than 127 nm possess sufficient energy to dissociate N_2. Furthermore, N_2 does not readily absorb photons, even when they possess sufficient energy. As a result, very little atomic nitrogen is formed in the upper atmosphere by photodissociation of N_2.

Photoionization Other photochemical processes besides photodissociation occur in the upper atmosphere, although their discovery has taken many twists and turns. In 1901, Guglielmo Marconi received a radio signal in St. John's, Newfoundland, that had been transmitted from Land's End, England, 2900 km away. Because people at the time thought radio waves traveled in straight lines, they assumed that the curvature of Earth's surface would make radio communication over large distances impossible. Marconi's successful experiment suggested that Earth's atmosphere in some way substantially affects radio-wave propagation. His discovery led to intensive study of the upper atmosphere. In about 1924, the existence of electrons in the upper atmosphere was established by experimental studies.

The electrons in the upper atmosphere result mainly from **photoionization**, which occurs when a molecule in the upper atmosphere absorbs solar radiation and the absorbed energy causes an electron to be ejected from the molecule. The molecule then becomes a positively charged ion. For photoionization to occur, therefore, a molecule must absorb a photon, and the photon must have enough energy to remove an electron. Notice that this is a very different process from photodissociation.

Go Figure

In what region of the electromagnetic spectrum does ozone most strongly absorb light: (a) IR, (b) visible, or (c) UV?



▲ **Figure 18.4** **The absorption spectrum of ozone.**

TABLE 18.3 Photoionization Reactions for Four Components of the Atmosphere

Process	Ionization Energy (kJ/mol)	λ_{max} (nm)
$N_2 + h\nu \longrightarrow N_2^+ + e^-$	1495	80.1
$O_2 + h\nu \longrightarrow O_2^+ + e^-$	1205	99.3
$O + h\nu \longrightarrow O^+ + e^-$	1313	91.2
$NO + h\nu \longrightarrow NO^+ + e^-$	890	134.5

Four important photoionization processes occurring in the atmosphere above about 90 km are shown in **Table 18.3**. Photons of any wavelength shorter than the maximum lengths given in the table have enough energy to cause photoionization. A look back at Figure 18.3 shows you that virtually all of these high-energy photons are filtered out of the radiation reaching Earth because they are absorbed by the upper atmosphere.

Ozone in the Stratosphere

Although N_2, O_2, and atomic oxygen absorb photons having wavelengths shorter than 240 nm, ozone, O_3, is the key absorber of photons whose wavelengths range from 240 to 310 nm, in the ultraviolet region of the electromagnetic spectrum, as illustrated in **Figure 18.4**. Ozone in the upper atmosphere protects us from these harmful high-energy photons, which would otherwise penetrate to Earth's surface. Let's consider how ozone forms in the upper atmosphere and how it absorbs photons.

By the time radiation from the Sun reaches an altitude of 90 km above Earth's surface, most of the short-wavelength radiation capable of photoionization has been absorbed. Nevertheless, radiation capable of dissociating the O_2 molecule is sufficiently intense for photodissociation of O_2 (Equation 18.1) to remain important down to an altitude of 30 km. In the region between 30 and 90 km, the concentration of O_2 is much greater than the concentration of atomic oxygen. Consequently, the oxygen atoms formed by photodissociation of O_2 in this region frequently collide with O_2 molecules and form ozone:

$$:\ddot{O} + O_2 \longrightarrow O_3^* \qquad [18.2]$$

The asterisk on O_3 denotes that the product contains an excess of energy, because the reaction is exothermic. The 105 kJ/mol that is released must be transferred away from the O_3^* molecule quickly or else the molecule will fly apart into O_2 and atomic O—a decomposition that is the reverse of the reaction by which O_3^* is formed.

An energy-rich O_3^* molecule can release its excess energy by colliding with another atom or molecule and transferring some of the excess energy to it. Let's use M to represent the atom or molecule with which O_3^* collides. (Usually, M is N_2 or O_2 because these are the most abundant molecules in the atmosphere.) The formation of O_3^* and the transfer of excess energy to M are summarized by the equations

$$O(g) + O_2(g) \rightleftharpoons O_3^*(g) \qquad [18.3]$$

$$O_3^*(g) + M(g) \longrightarrow O_3(g) + M^*(g) \qquad [18.4]$$

$$O(g) + O_2(g) + M(g) \longrightarrow O_3(g) + M^*(g) \qquad [18.5]$$

The rate at which the reactions of Equations 18.3 and 18.4 proceed depends on two factors that vary in opposite directions with increasing altitude. First, the formation of O_3^* (Equation 18.3) depends on the presence of O atoms. At low altitudes, most of the radiation energetic enough to dissociate O_2 molecules into O atoms has been absorbed; thus, O atoms are not very plentiful at low altitudes. Second, Equations 18.3 and 18.4 both depend on molecular collisions. The concentration of molecules is greater at low altitudes, and so the rates of both reactions are greater at lower altitudes.

Because these two effects vary with altitude in opposite directions, the highest rate of O_3 formation occurs in a band at an altitude of about 50 km, near the stratopause (Figure 18.1). Overall, roughly 90% of Earth's ozone is found in the stratosphere.

The photodissociation of ozone reverses the reaction that forms it. We thus have a cycle of ozone formation and decomposition, summarized on the next page:

$$O_2(g) + h\nu \longrightarrow O(g) + O(g)$$
$$O(g) + O_2(g) + M(g) \longrightarrow O_3(g) + M^*(g) \quad \text{(heat released)}$$
$$O_3(g) + h\nu \longrightarrow O_2(g) + O(g)$$
$$O(g) + O(g) + M(g) \longrightarrow O_2(g) + M^*(g) \quad \text{(heat released)}$$

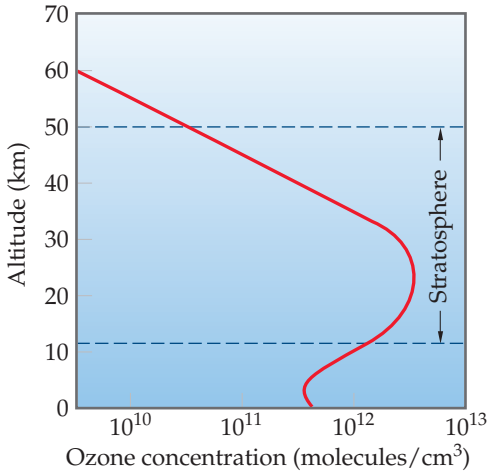
The first and third processes are photochemical; they use a solar photon to initiate a chemical reaction. The second and fourth are exothermic chemical reactions. The net result of the four reactions is a cycle in which solar radiant energy is converted into thermal energy. The ozone cycle in the stratosphere is responsible for the rise in temperature that reaches its maximum at the stratopause (Figure 18.1).

The reactions of the ozone cycle account for some, but not all, of the facts about the ozone layer. Many chemical reactions occur that involve substances other than oxygen. We must also consider the effects of turbulence and winds that mix up the stratosphere. A complicated picture results. The overall result of ozone formation and removal reactions, coupled with atmospheric turbulence and other factors, is to produce the upper-atmosphere ozone profile shown in **Figure 18.5**, with a maximum ozone concentration occurring at an altitude of about 25 km. This band of relatively high ozone concentration is referred to as the "ozone layer" or the "ozone shield."

Photons with wavelengths shorter than about 300 nm are energetic enough to break many kinds of single chemical bonds. Thus, the "ozone shield" is essential for our continued well-being. The ozone molecules that form this essential shield against high-energy radiation represent only a tiny fraction of the oxygen atoms present in the stratosphere, however, because these molecules are continually destroyed even as they are formed.

Go Figure

Estimate the ozone concentration in moles per liter for the peak value in this graph.



▲ **Figure 18.5** **Variation in ozone concentration in the atmosphere as a function of altitude.**

Self-Assessment Exercises

18.1 Would you expect the ratio of atmospheric helium to argon to be larger in the troposphere or the mesosphere?

(a) Troposphere

(b) Mesosphere

18.2 Which equation best represents the photoionization of ozone?

(a) $O_3 + h\nu \longrightarrow O_3^+ + e^-$

(b) $O_3 + e^- \longrightarrow O_3^- + h\nu$

(c) $O_3 + h\nu \longrightarrow O_2 + O$

18.3 Based on its Lewis structure, which molecule will have stronger oxygen-oxygen bonds, O_2 or O_3?

(a) Oxygen

(b) Ozone

Exercises

18.4 (**a**) How are the boundaries between the regions of the atmosphere determined? (**b**) Explain why the stratosphere, which is about 35 km thick, has a smaller total mass than the troposphere, which is about 12 km thick.

18.5 The Environmental Protection Agency (EPA) has established air quality standards. For ozone (O_3), the 8-hour average concentration permitted under the standards is 0.085 parts per million (ppm). (**a**) Calculate the partial pressure of ozone at 0.085 ppm if the atmospheric pressure is 100 kPa. (**b**) How many ozone molecules are in 1.0 L of air? Assume $T = 25$ °C.

18.6 (**a**) From the data in Table 18.1, what is the concentration of helium in the atmosphere in ppm? (**b**) What is the concentration of helium in the atmosphere in atoms per liter, assuming an atmospheric pressure of 101 kPa and a temperature of 298 K?

18.7 In CH_3I the C—I bond-dissociation energy is 241 kJ/mol. In C_6H_5I the C—I bond-dissociation energy is 280 kJ/mol. What is the range of wavelengths of photons that can cause C—I bond rupture in one molecule but not in the other?

18.8 Why is the photodissociation of N_2 in the atmosphere relatively unimportant compared with the photodissociation of O_2?

18.9 The ultraviolet spectrum can be divided into three regions based on wavelength: UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (100–280 nm). (**a**) Photons from which region have the highest energy and therefore are the most harmful to living tissue? (**b**) In the absence of ozone, which of these three regions, if any, are absorbed by the atmosphere? (**c**) When appropriate concentrations of ozone are present in the stratosphere, is all of the UV light absorbed before reaching the Earth's surface? If not, which region or regions are not filtered out?

Answers to Self-Assessment Exercises

18.1 (b) **18.2** (a) **18.3** (a)

18.2 Human Activities and Earth's Atmosphere



Both natural and *anthropogenic* (human-caused) events can modify Earth's atmosphere. One impressive natural event was the eruption of Mount Pinatubo in June 1991. The volcano ejected approximately 10 km^3 of material into the stratosphere, causing a 10% drop in the amount of sunlight reaching Earth's surface during the next 2 years. That drop in sunlight led to a temporary 0.5 °C drop in Earth's surface temperature. The volcanic particles that made it to the stratosphere remained there for approximately 3 years, *raising* the temperature of the stratosphere by several degrees due to

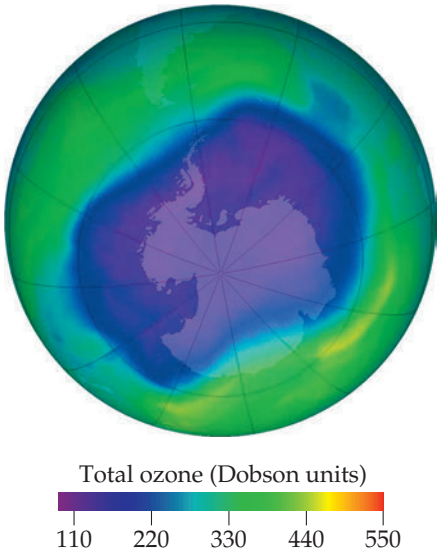
light absorption. Measurements of the stratospheric ozone concentration showed significantly increased ozone decomposition in this 3-year period.

By the end of this section, you should be able to

- Describe the origins and behavior of sulfur oxides and nitrogen oxides as air pollutants, including the generation of acid rain and photochemical smog.
- Describe how water and carbon dioxide cause an increase in atmospheric temperature near Earth's surface.

The Ozone Layer and Its Depletion

The ozone layer protects Earth's surface from the damaging ultraviolet (UV) radiation. Therefore, if the concentration of ozone in the stratosphere decreases substantially, more UV radiation will reach Earth's surface, causing unwanted photochemical reactions, including reactions correlated with skin cancer. Satellite monitoring of ozone, which began in 1978, has revealed a depletion of ozone in the stratosphere that is particularly severe over Antarctica, a phenomenon known as the *ozone hole* (**Figure 18.6**). The first scientific paper on this phenomenon appeared in 1985, and the National Aeronautics and Space Administration (NASA) maintains an "Ozone Hole Watch" website with daily updates and data from 1999 to the present.



▲ **Figure 18.6 Ozone present in the Southern Hemisphere, September 24, 2006.** The data were taken from an orbiting satellite. This day had the lowest stratospheric ozone concentration yet recorded. One "Dobson unit" corresponds to 2.69×10^{16} ozone molecules in a 1 cm^2 column of atmosphere.

In 1995, the Nobel Prize in Chemistry was awarded to F. Sherwood Rowland, Mario Molina, and Paul Crutzen for their studies of ozone depletion. In 1970, Crutzen showed that naturally occurring nitrogen oxides catalytically destroy ozone. Rowland and Molina recognized in 1974 that chlorine from **chlorofluorocarbons** (CFCs) may deplete the ozone layer. These substances, principally $CFCl_3$ and CF_2Cl_2, do not occur in nature and have been widely used as propellants in spray cans, as refrigerant and air-conditioner gases, and as foaming agents for plastics. They are virtually unreactive in the lower atmosphere. Furthermore, they are relatively insoluble in water and are therefore not removed from the atmosphere by rainfall or by dissolution in the oceans. Unfortunately, the lack of reactivity that makes them commercially useful also allows them to survive in the atmosphere and to diffuse into the stratosphere. It is estimated that several million tons of chlorofluorocarbons are now present in the atmosphere.

As CFCs diffuse into the stratosphere, they are exposed to high-energy radiation, which can cause photodissociation. Because C—Cl bonds are considerably weaker than C—F bonds, free chlorine atoms are formed readily in the presence of light with wavelengths in the range from 190 to 225 nm, as shown in this typical reaction:

$$CF_2Cl_2(g) + h\nu \longrightarrow CF_2Cl(g) + Cl(g) \qquad [18.6]$$

Calculations suggest that chlorine atom formation occurs at the greatest rate at an altitude of about 30 km, the altitude at which ozone is at its highest concentration.

Atomic chlorine reacts rapidly with ozone to form chlorine monoxide and molecular oxygen:

$$Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2(g) \qquad [18.7]$$

This reaction follows a second-order rate law with a very large rate constant:

$$\text{Rate} = k[Cl][O_3] \quad k = 7.2 \times 10^9\, M^{-1}\,s^{-1} \text{ at } 298\text{ K} \qquad [18.8]$$

Under certain conditions, the ClO generated in Equation 18.7 can react to regenerate free Cl atoms. One way that this can happen is by photodissociation of ClO:

$$ClO(g) + h\nu \longrightarrow Cl(g) + O(g) \qquad [18.9]$$

The Cl atoms generated in Equations 18.6 and 18.9 can react with more O_3, according to Equation 18.7. The result is a sequence of reactions that accomplishes the Cl-catalyzed decomposition of O_3 to O_2:

$$\begin{aligned} 2\,Cl(g) + 2\,O_3(g) &\longrightarrow 2\,ClO(g) + 2\,O_2(g) \\ 2\,ClO(g) + h\nu &\longrightarrow 2\,Cl(g) + 2\,O(g) \\ O(g) + O(g) &\longrightarrow O_2(g) \\ \hline 2\,Cl(g) + 2\,O_3(g) + 2\,ClO(g) + 2\,O(g) &\longrightarrow 2\,Cl(g) + 2\,ClO(g) + 3\,O_2(g) + 2\,O(g) \end{aligned}$$

The equation can be simplified by eliminating like species from each side to give

$$2\,O_3(g) \xrightarrow{Cl} 3\,O_2(g) \qquad [18.10]$$

Because the rate of Equation 18.7 increases linearly with [Cl], the rate at which ozone is destroyed increases as the quantity of Cl atoms increases. Thus, the higher the concentration of CFCs in the stratosphere, the faster the destruction of the ozone layer. Even though troposphere-to-stratosphere diffusion rates are slow, a substantial thinning of the ozone layer over the South Pole has been observed, particularly during September and October (Figure 18.6).

Because of the environmental problems associated with CFCs, steps have been taken to limit their manufacture and use. A major step was the signing in 1987 of the Montreal Protocol on Substances That Deplete the Ozone Layer, in which participating nations agreed to reduce CFC production. More stringent limits were set in 1992, when representatives of approximately 100 nations agreed to ban the production and use of CFCs by 1996, with some exceptions for "essential uses." Since then, the production of CFCs has indeed dropped precipitously. Images such as that shown in Figure 18.6 taken annually reveal that the depth and size of the ozone hole has begun to slowly decline. Nevertheless, because CFCs are unreactive and because they diffuse so slowly into the stratosphere, scientists estimate that it will take many decades for ozone concentrations in the stratosphere to return to pre-1980 levels. What substances have replaced CFCs? At this time, the main alternatives are hydrofluorocarbons (HFCs), compounds in which C—H bonds replace the C—Cl bonds of CFCs. One such compound in current use is CH_2FCF_3, known as HFC-134a. While the HFCs are a big improvement over the CFCs because they contain no C—Cl bonds, it turns out that they are potent greenhouse warming gases, with which we will deal shortly.

There are no naturally occurring CFCs, but some natural sources contribute chlorine and bromine to the atmosphere, and, just like halogens from CFCs, these naturally occurring Cl and Br atoms can participate in ozone-depleting reactions. The principal natural sources are bromomethane and chloromethane, which are emitted from the oceans. It is estimated that these molecules contribute less than a third of the total Cl and Br in the atmosphere; the remaining two-thirds is a result of human activities.

Volcanoes are a source of HCl, but generally the HCl they release reacts with water in the troposphere and does not make it to the upper atmosphere.

Sulfur Compounds and Acid Rain

Sulfur-containing compounds are present to some extent in the natural, unpolluted atmosphere. They originate in the bacterial decay of organic matter, in volcanic gases, and from other sources listed in Table 18.2. The amount of these compounds released into the atmosphere worldwide from natural sources is about 24×10^{12} g per year, less than the amount from human activities, about 80×10^{12} g per year (principally related to combustion of fuels).

Sulfur compounds, chiefly sulfur dioxide, SO_2, are among the most unpleasant and harmful of the common pollutant gases. **Table 18.4** shows the concentrations of several pollutant gases in a *typical* urban environment (where by *typical* we mean one that is not particularly affected by smog). According to these data, the level of sulfur dioxide is 0.08 ppm or higher about half the time. This concentration is considerably lower than that of other pollutants, notably carbon monoxide. Nevertheless, SO_2 is regarded as the most serious health hazard among the pollutants shown, especially for people with respiratory difficulties.

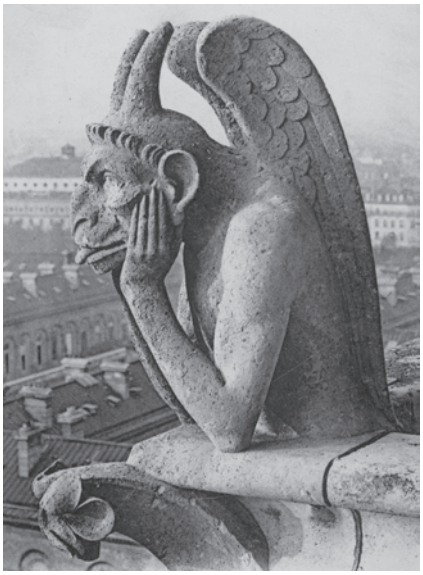
TABLE 18.4 Median Concentrations of Atmospheric Pollutants in a Typical Urban Atmosphere

Pollutant	Concentration (ppm)
Carbon monoxide	10
Hydrocarbons	3
Sulfur dioxide	0.08
Nitrogen oxides	0.05
Total oxidants (ozone and others)	0.02

Combustion of coal and oil accounts for about two thirds of the anthropogenic SO_2 released annually worldwide. The majority of this amount is from coal-burning electrical power plants, which generate about 50% of our electricity. The extent to which SO_2 emissions are a problem when coal is burned depends on the amount of sulfur in the coal. Because of concern about SO_2 pollution, low-sulfur coal is in greater demand and is thus more expensive.

Sulfur dioxide is harmful to both human health and property; furthermore, atmospheric SO_2 can be oxidized to SO_3 by several pathways (such as reaction with O_2 or O_3). When SO_3 dissolves in water, it produces sulfuric acid:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$





◀ **Figure 18.7 Damage from acid rain.** The right photograph, recently taken, shows how the statue has lost detail in its carvings.

Many of the environmental effects ascribed to SO_2 are actually due to H_2SO_4.

The presence of SO_2 in the atmosphere and the sulfuric acid it produces result in the phenomenon of **acid rain**. (Nitrogen oxides, which form nitric acid, are also major contributors to acid rain.) Uncontaminated rainwater generally has a pH value of about 5.6. The primary source of this natural acidity is CO_2, which reacts with water to form carbonic acid, H_2CO_3. Acid rain typically has a pH value of about 4. This shift toward greater acidity has affected many lakes in northern Europe, the northern United States, and Canada, reducing fish populations and affecting other parts of the ecological network in the lakes and surrounding forests.

The pH of most natural waters containing living organisms is between 6.5 and 8.5. At pH levels below 4.0, all vertebrates, most invertebrates, and many microorganisms are destroyed. The lakes most susceptible to damage are those with low concentrations of basic ions, such as HCO_3^-, that would act as a buffer to minimize changes in pH.

Because acids react with metals and with carbonates, acid rain is corrosive both to metals and to stone building materials. Marble and limestone, for example, whose major constituent is $CaCO_3$, are readily attacked by acid rain (**Figure 18.7**). Billions of dollars each year are lost because of corrosion due to SO_2 pollution.

Although difficult and expensive, several methods to reduce the quantity of SO_2 released into the environment have been developed. Powdered limestone ($CaCO_3$), for example, can be injected into the furnace of a power plant, where it decomposes into lime (CaO) and carbon dioxide:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The CaO then reacts with SO_2 to form calcium sulfite:

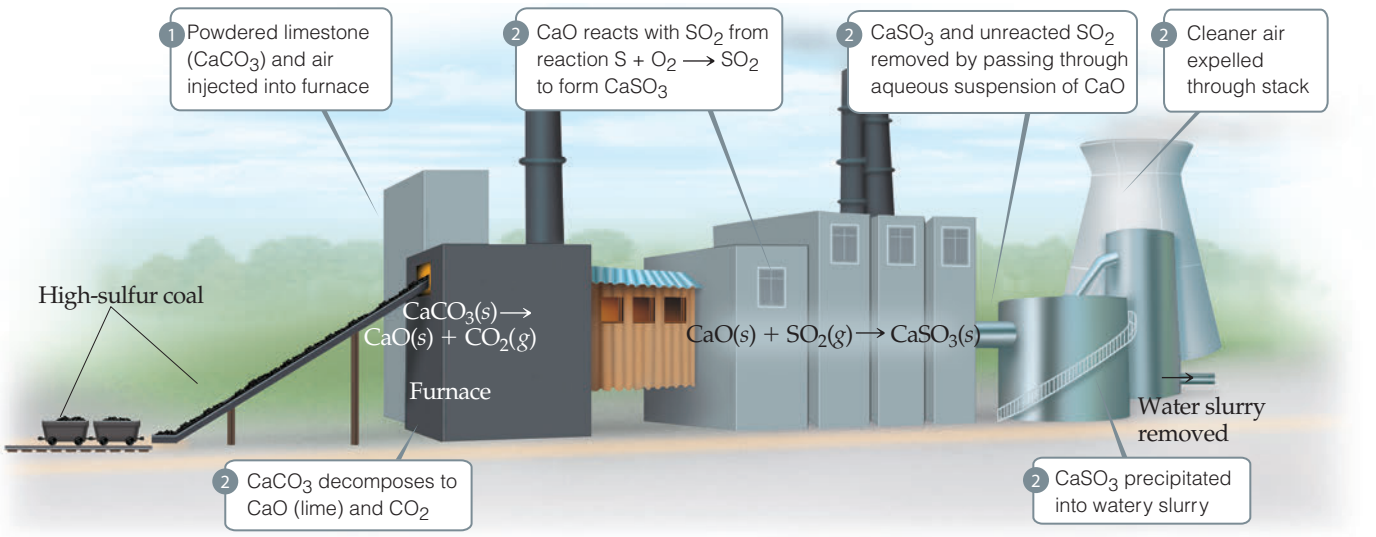
$$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

The solid particles of $CaSO_3$, as well as much of the unreacted SO_2, can be removed from the furnace gas by passing it through an aqueous suspension of CaO (**Figure 18.8**). Not all the SO_2 is removed, however, and given the enormous quantities of coal and oil burned worldwide, pollution by SO_2 will probably remain a problem for some time.

Nitrogen Oxides and Photochemical Smog

Nitrogen oxides are primary components of smog, a phenomenon with which city dwellers are all too familiar. The term *smog* refers to the pollution condition that occurs in certain urban environments when weather conditions produce a relatively stagnant air mass. Smog is more accurately described as **photochemical smog** because photochemical processes play a major role in its formation (**Figure 18.9**).

Go Figure What is the major solid product resulting from removal of SO_2 from furnace gas?



▲ **Figure 18.8** **One method for removing SO_2 from combusted fuel.**



▲ **Figure 18.9** **Photochemical smog is produced largely by the action of sunlight on vehicle exhaust gases, as illustrated in this photo of Beijing, China.**

Nitric oxide, NO, forms in small quantities in the cylinders of internal combustion engines in the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \quad \Delta H = 180.8\ kJ \qquad [18.11]$$

As noted in the Chemistry Put to Work box in Section 15.5, the equilibrium constant for this reaction increases from about 10^{-15} at 300 K to about 0.05 at 2400 K (approximate temperature in the cylinder of an engine during combustion). Thus, the reaction is more favorable at higher temperatures.

In air, nitric oxide is rapidly oxidized to nitrogen dioxide:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = -113.1\ kJ \qquad [18.12]$$

The equilibrium constant for this reaction decreases from about 10^{12} at 300 K to about 10^{-5} at 2400 K.

The photodissociation of NO_2 initiates the reactions associated with photochemical smog. Dissociation of NO_2 requires 304 kJ/mol, which corresponds to a photon wavelength of 393 nm. In sunlight, therefore, NO_2 dissociates to NO and O:

$$NO_2(g) + h\nu \longrightarrow NO(g) + O(g) \qquad [18.13]$$

The atomic oxygen formed undergoes several reactions, one of which gives ozone, as described earlier:

$$O(g) + O_2(g) + M(g) \longrightarrow O_3(g) + M^*(g) \qquad [18.14]$$

Although it is essential to screen out harmful UV radiation in the upper atmosphere, ozone is an undesirable pollutant in the troposphere. It is extremely reactive and toxic, and breathing air that contains appreciable amounts of ozone can be especially dangerous for asthma sufferers, exercisers, and the elderly. We therefore have two ozone problems: excessive amounts in many urban environments, where it is harmful, and depletion in the stratosphere, where its presence is vital.

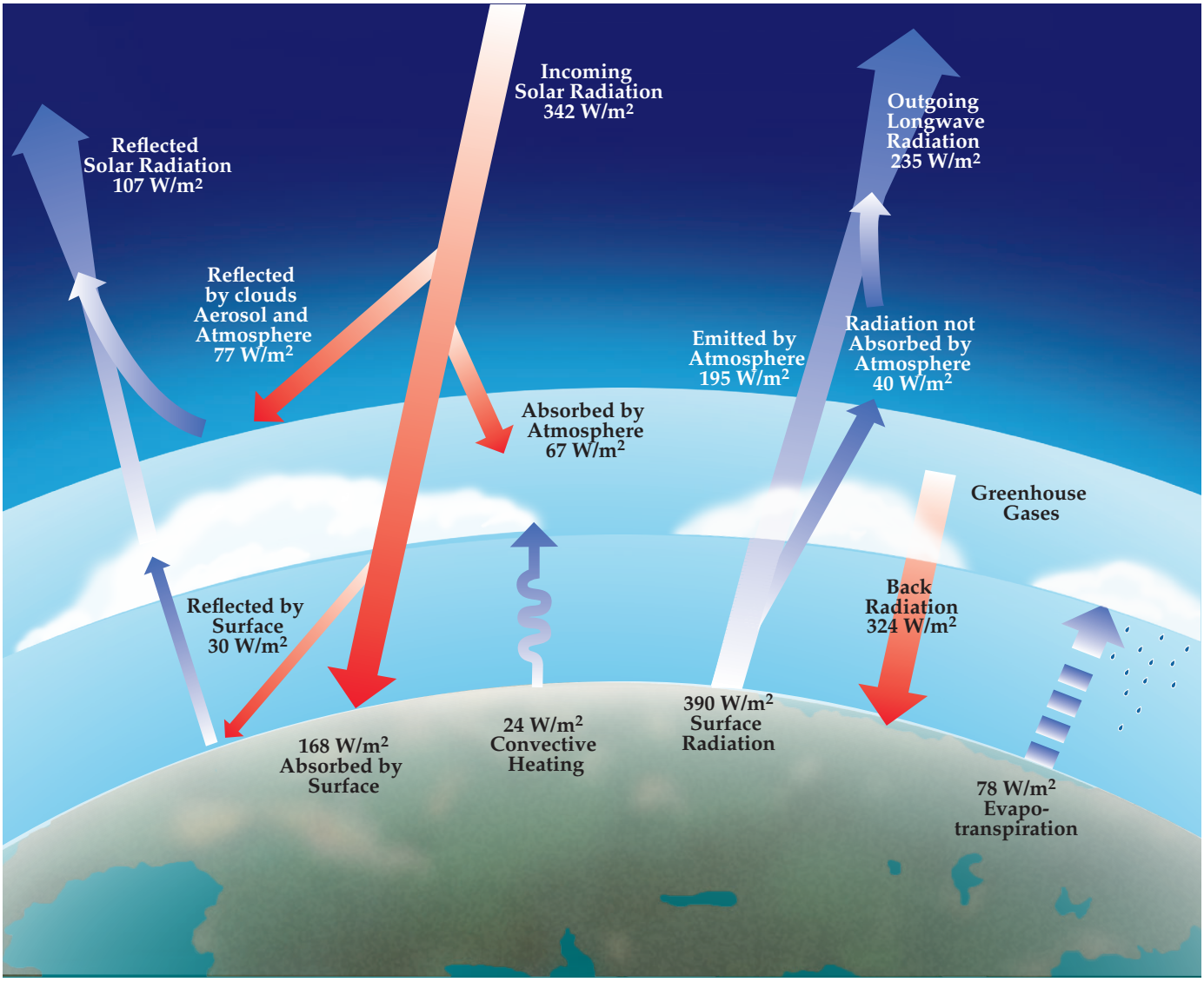
In addition to nitrogen oxides and carbon monoxide, a car engine also emits unburned *hydrocarbons* as pollutants. These organic compounds are the principal components of petrol and of many compounds we use as fuel (propane, C_3H_8, and butane, C_4H_{10}; for example), but are major ingredients of smog. Hydrocarbons are also emitted naturally from living organisms (see A Closer Look box later in this section).

Reduction or elimination of smog requires that the ingredients essential to its formation be removed from car exhaust. Catalytic converters reduce the levels of NO_x and hydrocarbons, two of the major ingredients of smog. (See the Chemistry Put to Work: Catalytic Converters in Section 14.7.)

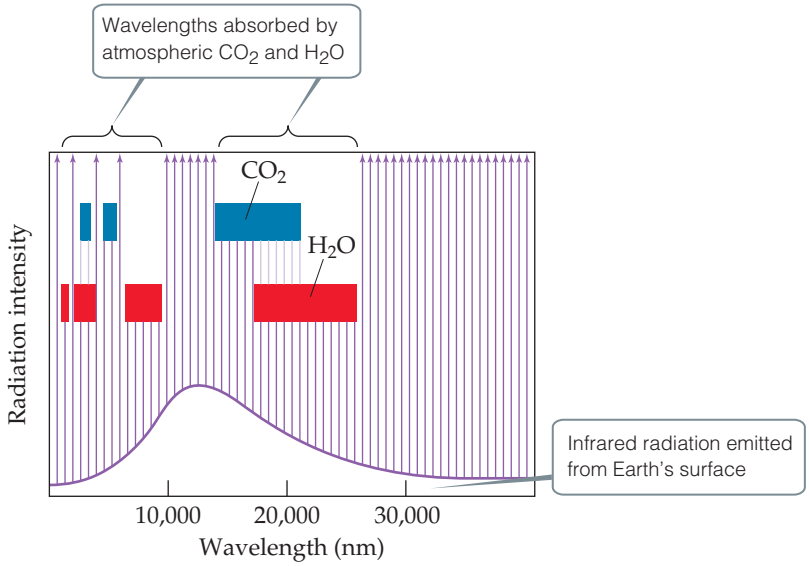
Greenhouse Gases: Water Vapor, Carbon Dioxide, and Climate

In addition to screening out harmful short-wavelength radiation, the atmosphere is essential in maintaining a reasonably uniform and moderate temperature on Earth's surface. Earth is in overall thermal balance with its surroundings. This means that the planet radiates energy into space at a rate equal to the rate at which it absorbs energy from the Sun. **Figure 18.10** shows the flow of energy into and out of Earth, and **Figure 18.11** shows the fraction of infrared radiation leaving the surface that is absorbed

Go Figure What is the total amount of energy absorbed by the surface? What fraction of that energy is emitted upward as infrared radiation?



▲ **Figure 18.10 Earth's thermal balance.** The amount of radiation reaching the surface of the planet is equal to the amount radiated back into space.



▲ **Figure 18.11** **Portions of the infrared radiation emitted by Earth's surface that are absorbed by atmospheric CO_2 and H_2O.**

by atmospheric water vapor and carbon dioxide. In absorbing this radiation, these two atmospheric gases help maintain a livable uniform temperature at the surface by holding in, as it were, the infrared radiation, which we feel as heat.

The influence of H_2O, CO_2, and certain other atmospheric gases on Earth's temperature is called the *greenhouse effect* because in trapping infrared radiation these gases act much like the glass of a greenhouse. The gases themselves are called **greenhouse gases**.

Water vapor makes the largest contribution to the greenhouse effect. The partial pressure of water vapor in the atmosphere varies greatly from place to place and time to time but is generally highest near Earth's surface and drops off with increasing elevation. Because water vapor absorbs infrared radiation so strongly, it plays the major role in maintaining the atmospheric temperature at night, when the surface is emitting radiation into space and not receiving energy from the Sun. In very dry desert climates, where the water-vapor concentration is low, it may be extremely hot during the day but very cold at night. In the absence of a layer of water vapor to absorb and then radiate part of the infrared radiation back to Earth, the surface loses this radiation into space and cools off very rapidly.

Carbon dioxide plays a secondary but very important role in maintaining the surface temperature. The worldwide combustion of fossil fuels, principally coal and oil, on a prodigious scale in the modern era has sharply increased carbon dioxide levels in the atmosphere. To get a sense of the amount of CO_2 produced—for example, by the combustion of hydrocarbons and other carbon-containing substances, which are the components of fossil fuels—consider the combustion of butane, C_4H_{10}. Combustion of 1.00 g of C_4H_{10} produces 3.03 g of CO_2. Combustion of fossil fuels releases about 2.2×10^{16} g of CO_2 into the atmosphere annually, with the largest quantity coming from transportation vehicles.

Sample Exercise 18.3

Estimating the Quantity of CO_2 Released from Combustion of Gasoline

What mass of carbon dioxide is produced when 5.0 liters of petrol is combusted? The approximate density and composition of petrol are 0.70 g/mL and C_8H_{18}, respectively.

SOLUTION

Analyze We are asked to calculate the mass of CO_2 produced when 5.0 liters of octane (C_8H_{18}) reacts with oxygen to form carbon dioxide and water.

Plan We first must determine the mass in grams of C_8H_{18} in 5.0 liters of gasoline. We then write a balanced chemical equation for the combustion of C_8H_{18} and use it to determine the theoretical yield of CO_2.

Solve

First, convert the volume from liters to mL.

$$(5.0 \text{ liters})\left(\frac{1000 \text{ mL}}{1 \cancel{L}}\right) = 5.0 \times 10^3 \text{ mL}$$

Next, use the density of octane to calculate its mass in grams.

$$(5.0 \times 10^3 \cancel{\text{mL}})\left(\frac{0.70 \text{ g}}{\cancel{\text{mL}}}\right) = 3.5 \times 10^3 \text{ g}$$

To calculate the theoretical yield of carbon dioxide, we must write a balanced chemical equation for the combustion of C_8H_{18} (octane):

$$2\,C_8H_{18}(l) + 25\,O_2(g) \rightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

Using the balanced equation and the mass of C_8H_{18}, we can calculate the theoretical yield of CO_2.

$$(3.5 \times 10^3 \cancel{\text{g } C_8H_{18}})\left(\frac{1 \cancel{\text{mol } C_8H_{18}}}{114.2 \cancel{\text{g } C_8H_{18}}}\right)\left(\frac{16 \cancel{\text{mol } CO_2}}{2 \cancel{\text{mol } C_8H_{18}}}\right)\left(\frac{44 \text{ g } CO_2}{1 \cancel{\text{mol } CO_2}}\right)$$
$$= 1.1 \times 10^4 \text{ g } CO_2$$

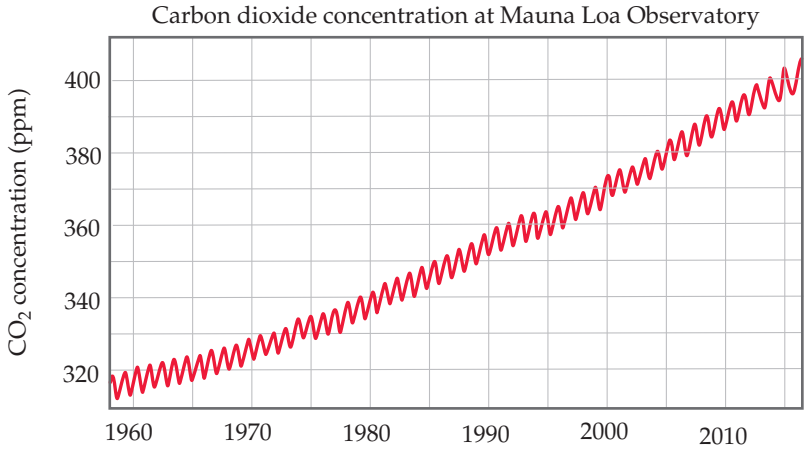
So we see that for every five liters of octane burned 11 kg of CO_2 are produced.

Practice Exercise

A typical propane, C_3H_8, tank for an outdoor grill contains 5 kg of propane. What mass of CO_2 is produced by combusting the propane in such a tank?

Much CO_2 is absorbed into oceans or used by plants. Nevertheless, we are now generating CO_2 much faster than it is being absorbed or used. Analysis of air trapped in ice cores taken from Antarctica and Greenland makes it possible to determine the atmospheric levels of CO_2 during the past 160,000 years. These measurements reveal that the level of CO_2 remained fairly constant from the last Ice Age, some 10,000 years ago, until roughly the beginning of the Industrial Revolution, about 300 years ago. Since that time, the concentration of CO_2 has increased by about 30% to a current high of about 400 ppm (**Figure 18.12**). Climate scientists believe that the CO_2 level has not been this high since 3 to 5 million years ago.

Go Figure What is the source of the steady increase in slope of this curve over time?



▲ **Figure 18.12 Rising CO_2 levels.** The sawtooth shape of the graph is due to regular seasonal variations in CO_2 concentration for each year.

The consensus among climate scientists is that the increase in atmospheric CO_2 is perturbing Earth's climate and is very likely playing a role in the observed increase in the average global air temperature of 0.3–0.6 °C over the past century. Scientists often use the term *climate change* instead of *global warming* to refer to this effect because as the Earth's temperature increases, winds and ocean currents are affected in ways that cool some areas and warm others.

On the basis of present and expected future rates of fossil-fuel use, the atmospheric CO_2 level is expected to double from its present level sometime between 2050 and 2100. Computer models predict that this increase will result in an average global temperature increase of 1 °C to 3 °C. Because so many factors go into determining climate, we cannot predict with certainty what changes will occur because of this warming. Clearly, however, atmospheric concentrations of CO_2 and other heat-trapping gases are rising as a result of human activity. The effects of these changes on the climate are already being felt, and if left unchecked they have the potential to substantially alter the climate of the planet.

The climate change threat posed by atmospheric CO_2 has sparked considerable research into ways of capturing the gas at its largest combustion sources and storing it under ground or under the seafloor. There is also much interest in developing new ways to use CO_2 as a chemical feedstock. However, the approximately 115 million tons of CO_2 used annually by the global chemical industry is but a small fraction of the approximately 24 billion tons of annual CO_2 emissions. The use of CO_2 as a raw material will probably never be great enough to significantly reduce its atmospheric concentration.

A CLOSER LOOK Other Greenhouse Gases

Although CO_2 receives most of the attention, other gases contribute to the greenhouse effect, including methane, CH_4, hydrofluorocarbons (HFCs), and chlorofluorocarbons (CFCs).

HFCs have replaced CFCs in a host of applications, including refrigerants and air-conditioner gases. Although they do not contribute to the depletion of the ozone layer, HFCs are nevertheless potent greenhouse gases. For example, one of the by-product molecules from production of HFCs that are used in commerce is HCF_3, which is estimated to have a global warming potential, gram for gram, more than 14,000 times that of CO_2. The total concentration of HFCs in the atmosphere has been increasing about 10% per year. Thus, these substances are becoming increasingly important contributors to the greenhouse effect. Methane already makes a significant contribution to the greenhouse effect. Studies of atmospheric gas trapped long ago in the Greenland and Antarctic ice sheets show that the atmospheric methane concentration has increased from preindustrial values of 0.3 to 0.7 ppm to the present value of about 1.8 ppm. The major sources of methane are associated with agriculture and fossil-fuel use.

Methane is formed in biological processes that occur in low-oxygen environments. Anaerobic bacteria, which flourish in swamps and landfills, near the roots of rice plants, and in the digestive systems of cows and other ruminant animals, produce methane (**Figure 18.13**). It also leaks into the atmosphere during natural-gas extraction and transport. It is estimated that about two-thirds of present-day methane emissions, which are increasing by about 1% per year, are related to human activities.

Methane has a half-life in the atmosphere of about 10 years, whereas CO_2 is much longer-lived. This might seem a good thing, but there are indirect effects to consider. Methane is oxidized in the stratosphere, producing water vapor, a powerful greenhouse gas that is otherwise virtually absent from the stratosphere. In the troposphere, methane is attacked by reactive species such as OH radicals or nitrogen oxides, eventually producing other greenhouse gases, such as O_3. It has been estimated that on a per-molecule level, the global warming potential of CH_4 is about 21 times that of CO_2. Given this large contribution, important reductions of the greenhouse effect could be achieved by reducing methane emissions or capturing the emissions for use as a fuel.



▲ **Figure 18.13 Methane production.** Ruminant animals, such as cows and sheep, produce methane in their digestive systems.

Related Exercises: 18.72, 18.74

Self-Assessment Exercises

18.10 What photochemical reaction involving nitrogen oxides initiates the formation of photochemical smog?

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $NO_2(g) + h\nu \longrightarrow NO(g) + O(g)$

18.11 What part of the electromagnetic spectrum is absorbed by water vapor in the atmosphere?

(a) Ultraviolet radiation

(b) Visible radiation

(c) Infrared radiation

Exercises

18.12 Which of the following reactions in the stratosphere cause an increase in temperature there?

(a) $O(g) + O_2(g) \longrightarrow O_3^*(g)$

(b) $O_3^*(g) + M(g) \longrightarrow O_3(g) + M^*(g)$

(c) $O_2(g) + h\nu \longrightarrow 2\,O(g)$

(d) $O(g) + N_2(g) \longrightarrow NO(g) + N(g)$

(e) All of these

18.13 (**a**) What is the difference between chlorofluorocarbons and hydrofluorocarbons? (**b**) Why are hydrofluorocarbons potentially less harmful to the ozone layer than CFCs?

18.14 (**a**) When chlorine atoms react with atmospheric ozone, what are the products of the reaction? (**b**) Based on average bond enthalpies, would you expect a photon capable of dissociating a C—Cl bond to have sufficient energy to dissociate a C—Br bond? (**c**) Would you expect the substance $CFBr_3$ to accelerate depletion of the ozone layer?

18.15 Why is rainwater naturally acidic, even in the absence of polluting gases such as SO_2?

18.16 Copper exposed to air and water may be oxidized. The green oxidized product is referred to as "patina". (**a**) Write a balanced chemical equation to show the reaction of copper to copper (II) ions with oxygen and protons from acid rain. (**b**) Would you expect some kind of "patina" on a silver surface? Explain.

18.17 An important reaction in the formation of photochemical smog is the photodissociation of NO_2:

$$NO_2 + h\nu \longrightarrow NO(g) + O(g)$$

The maximum wavelength of light that can cause this reaction is 420 nm. (**a**) In what part of the electromagnetic spectrum is light with this wavelength found? (**b**) What is the maximum strength of a bond, in kJ/mol, that can be broken by absorption of a photon of 420-nm light? (**c**) Write out the photodissociation reaction showing Lewis-dot structures.

18.18 The atmosphere of Mars is 96% CO_2, with a pressure of approximately 0.6 kPa at the surface. Based on measurements taken over a period of several years by the Rover Environmental Monitoring Station (REMS), the average daytime temperature at the REMS location on Mars is –5.7 °C, while the average nighttime temperature is –79 °C. This daily variation in temperature is much larger than what we experience on Earth. What factor plays the largest role in this wide temperature variation, the composition or the density of the atmosphere?

Answers to Self-Assessment Exercises

18.10 (c) **18.11** (c)

18.3 Earth's Water



Earth is called The Blue Planet because of the abundance of water on its surface.

Indeed, water covers 72% of Earth's surface and is essential to life. Our bodies are about 65% water by mass. Because of extensive hydrogen bonding, water has unusually high melting and boiling points and a high heat capacity. Water's highly polar character is responsible for its exceptional ability to dissolve a wide range of ionic and polar-covalent substances. Many reactions occur in water, including reactions in which H_2O itself is a reactant. Recall, for example, that H_2O can participate in acid–base reactions as either a proton donor or a proton acceptor. All these properties play a role in our environment.

By the end of this section you should be able to

- Appreciate the complexity of the global water cycle

The Global Water Cycle

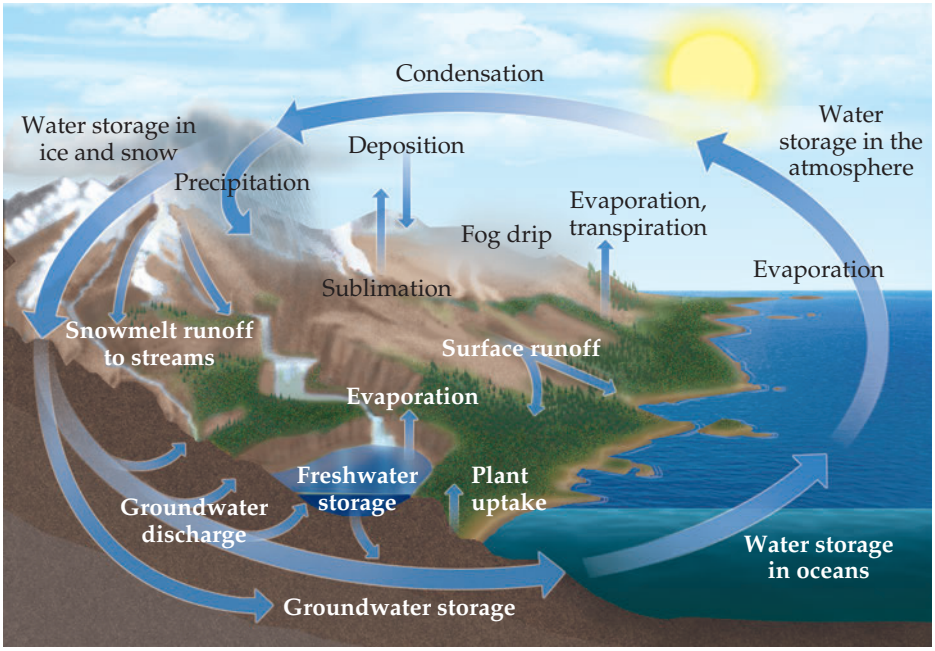
All the water on Earth is connected in a global water cycle (**Figure 18.14**). Most of the processes depicted here rely on the phase changes of water. For instance, warmed by the Sun, liquid water in the oceans evaporates into the atmosphere as water vapor and condenses into liquid water droplets that we see as clouds. Water droplets in the clouds can crystallize to ice, which can precipitate as hail or snow. Once on the ground, the hail or snow melts to liquid water, which soaks into the ground. If conditions are right, it is also possible for ice on the ground to sublime to water vapor in the atmosphere. Because the processes occurring on the surface (evaporation, sublimation) are endothermic and those occurring in the atmosphere (condensation, crystallization) are exothermic they act to transfer heat absorbed by the surface into the atmosphere.

Salt Water: Earth's Oceans and Seas

The vast layer of salty water that covers so much of the planet is in actuality one large connected body and is generally constant in composition. For this reason, oceanographers speak of a *world ocean* rather than of the separate oceans we learn about in geography books.

The world ocean is huge, having a volume of 1.35×10^9 km^3 and containing 97.2% of all the water on Earth. Of the remaining 2.8%, 2.1% is in the form of ice caps and glaciers. All the freshwater—in lakes, in rivers, and in the ground—amounts to only 0.6%.

Go Figure Which processes shown in this figure involve the phase transition $H_2O(l) \longrightarrow H_2O(g)$?



▲ **Figure 18.14** The global water cycle.

TABLE 18.5 Ionic Constituents of Seawater Present in Concentrations Greater than 0.001 g/kg (1 ppm)

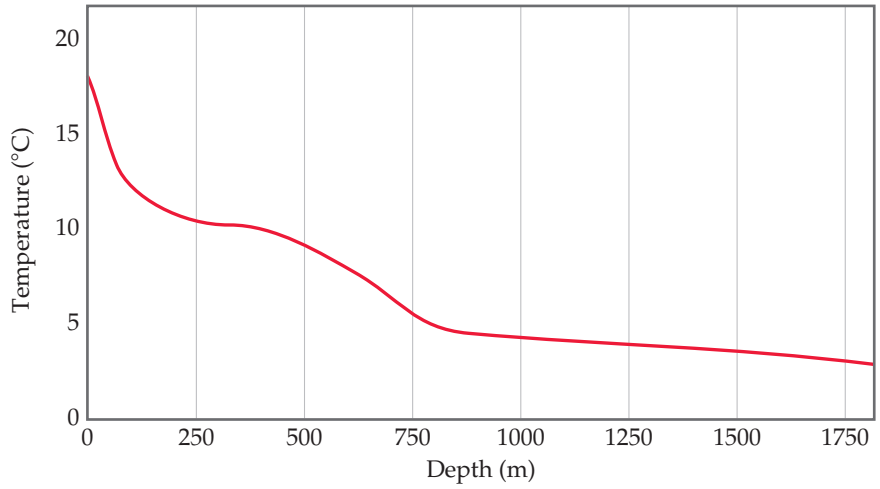
Ionic Constituent	Salinity	Concentration (*M*)
Chloride, Cl^-	19.35	0.55
Sodium, Na^+	10.76	0.47
Sulfate, SO_4^{2-}	2.71	0.028
Magnesium, Mg^{2+}	1.29	0.054
Calcium, Ca^{2+}	0.412	0.010
Potassium, K^+	0.40	0.010
Carbon dioxide*	0.106	2.3×10^{-3}
Bromide, Br^-	0.067	8.3×10^{-4}
Boric acid, H_3BO_3	0.027	4.3×10^{-4}
Strontium, Sr^{2+}	0.0079	9.1×10^{-5}
Fluoride, F^-	0.0013	7.0×10^{-5}

*CO_2 is present in seawater as HCO_3^- and CO_3^{2-}.

Seawater is often referred to as saline water. The **salinity** of seawater is the mass in grams of dry salts present in 1 kg of seawater. In the world ocean, salinity averages about 35. To put it another way, seawater contains about 3.5% dissolved salts by mass. The list of elements present in seawater is very long. Most, however, are present only in very low concentrations. Table 18.5 lists the 11 ionic species most abundant in seawater.

Seawater temperature varies as a function of depth (Figure 18.15), as does salinity and density. Sunlight penetrates well only 200 m into the water; the region between 200 m and 1000 m deep is the "twilight zone," where visible light is faint. Below 1000 m, the ocean is pitch-black and cold, about 4 °C. The transport of heat, salt, and other chemicals throughout the ocean is influenced by these changes in the physical properties of seawater, and in turn the changes in the way heat and substances are transported affects ocean currents and the global climate.

Go Figure Based on the temperature variation here would you expect the density of seawater to increase or decrease as the depth increases?



▲ **Figure 18.15** Typical average temperature of mid-latitude seawater as a function of depth.

The sea is so vast that if the concentration of a substance in seawater is 1 part per billion (1×10^{-6} g/kg of water), there is 1×10^{12} kg of the substance in the world ocean. Nevertheless, because of high extracting costs, only three substances are obtained from seawater in commercially important amounts: sodium chloride, bromine (from bromide salts), and magnesium (from its salts).

Absorption of CO_2 by the ocean plays a large role in global climate. Because carbon dioxide and water form carbonic acid, the H_2CO_3 concentration in the ocean increases as the water absorbs atmospheric CO_2. Most of the carbon in the ocean, however, is in the form of HCO_3^- and CO_3^{2-} ions, which form a buffer system that maintains the ocean's pH between 8.0 and 8.3. The pH of the ocean is predicted to decrease as the concentration of CO_2 in the atmosphere increases, as discussed in the "Chemistry and Life" box on ocean acidification on page 890.

Freshwater and Groundwater

Freshwater is the term used to denote natural waters that have low concentrations (less than 500 ppm) of dissolved salts and solids. Freshwater includes the waters of lakes, rivers, ponds, and streams.

The total amount of freshwater on Earth is not a very large fraction of the total water present. Indeed, freshwater is one of our most precious resources. It forms by evaporation from the oceans and the land. The water vapor that accumulates in the atmosphere is transported by global atmospheric circulation, eventually returning to Earth as rain, snow, and other forms of precipitation (Figure 18.14).

As water runs off the land on its way to the oceans, it dissolves a variety of cations (mainly Na^+, K^+, Mg^{2+}, Ca^{2+}, and Fe^{2+}), anions (mainly Cl^-, SO_4^{2-}, and HCO_3^-), and gases (principally O_2, N_2, and CO_2). As we use water, it becomes laden with additional dissolved material, including the wastes of human society. As our population and output of environmental pollutants increase, ever-increasing amounts of money and resources must be spent to guarantee a supply of freshwater.

Approximately 20% of the world's freshwater is under the soil, in the form of *groundwater*. Groundwater resides in *aquifers*, which are layers of porous rock that hold water. The water in aquifers can be very pure, and accessible for human consumption if near the surface (Figure 18.16). Dense underground formations that do not allow water to readily penetrate can hold groundwater for years or even millennia. When their water is removed by drilling and pumping, such aquifers are slow to recharge via the diffusion of surface water.

The nature of the rock that contains the groundwater has a large influence on the water's chemical composition. If minerals in the rock are water soluble to some extent, ions can leach out of the rock and remain dissolved in the groundwater. Arsenic in the form of $HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4, and $HAsO_3$ is found in many groundwater sources across the world, most infamously in Bangladesh, at concentrations poisonous to humans.

Self-Assessment Exercise

18.19 Consider the phase diagram for water shown in Figure 11.28 (page 544). In what pressure range and in what temperature range must H_2O exist in order for $H_2O(s)$ to sublime to $H_2O(g)$?

(a) $T > 0\,^\circ C$ and $P > 0.6$ kPa
(b) $T < 0\,^\circ C$ and $P > 0.6$ kPa
(c) $T > 0\,^\circ C$ and $P < 0.6$ kPa
(d) $T < 0\,^\circ C$ and $P < 0.6$ kPa

Exercises

18.20 Sulfur is present in seawater to the extent of 0.09 % by mass. Assuming that the sulfur is present as sulfate, SO_4^{2-}, calculate the corresponding molar concentration of SO_4^{2-} in seawater.

18.21 The enthalpy of fusion of water is 6.01 kJ/mol. Sunlight striking Earth's surface supplies 168 W per square meter (1 W = 1 watt = 1 J/s). (**a**) Assuming that melting of ice is due only to energy input from the Sun, calculate how

many grams of ice could be melted from a 1.00 square meter patch of ice over a 12 h day. (**b**) The specific heat capacity of ice is 2.032 J/g °C. If the initial temperature of a 1.00 square meter patch of ice is −5.0 °C, what is its final temperature after being in sunlight for 12 h, assuming no phase changes and assuming that sunlight penetrates uniformly to a depth of 1.00 cm?

18.22 Platinum is found in seawater at very low levels, about 0.23 parts in 10^{12} by mass. How much platinum can be found in the entire ocean (1.3×10^{21} L)? Assume the density of seawater is 1.03 g/mL.

Answers to Self-Assessment Exercises

18.19 (d)

18.4 Human Activities and Water Quality



At least 8 million tons of plastic end up in the oceans every year, resulting in entanglement and ingestion by marine life and sea birds. At the current rate of pollution, there will be more plastic, by weight, than fish in the oceans by 2050.

All life on Earth depends on the availability of suitable water. Many human activities entail waste disposal into natural waters without any treatment. These practices result in contaminated water that is detrimental to both plant and animal aquatic life.

By the end of this section, you should be able to

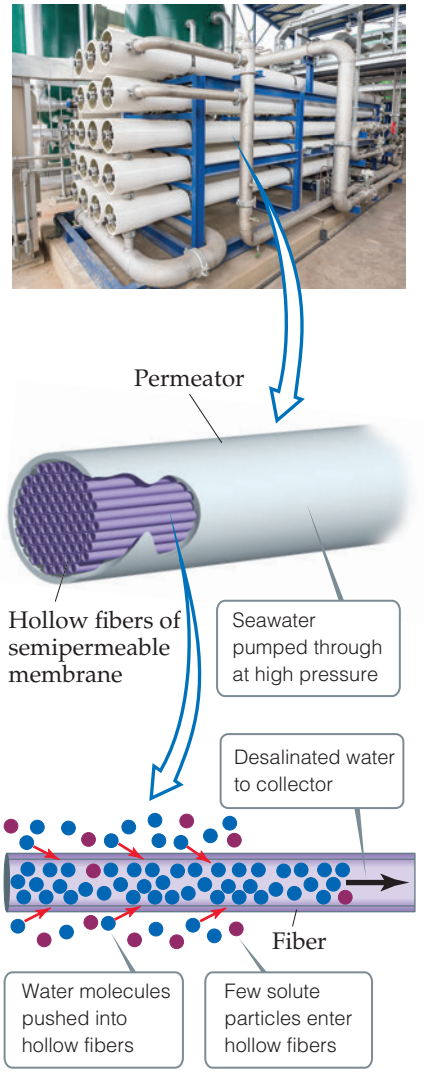
- Understand some main factors that result in the deterioration of water quality and how water can be treated to make it fit for human consumption.

Dissolved Oxygen and Water Quality

The amount of O_2 dissolved in water is an important indicator of water quality. Water fully saturated with air at 101.3 kPa and 20 °C contains about 9 ppm of O_2. Oxygen is necessary for fish and most other aquatic life. Cold-water fish require water containing at



▲ **Figure 18.17 Eutrophication.** This rapid accumulation of dead and decaying plant matter in a body of water uses up the water's oxygen supply, making the water unsuitable for aquatic animals.



▲ **Figure 18.18 Reverse osmosis.**

least 5 ppm of dissolved oxygen for survival. Aerobic bacteria consume dissolved oxygen to oxidize organic materials for energy. The organic material the bacteria are able to oxidize is said to be **biodegradable**.

Excessive quantities of biodegradable organic materials in water are detrimental because they remove the oxygen necessary to sustain aquatic animal life. Typical sources of these biodegradable materials, which are called *oxygen-demanding wastes*, include sewage, industrial wastes from food-processing plants and paper mills, and liquid waste from meatpacking plants.

In the presence of oxygen, the carbon, hydrogen, nitrogen, sulfur, and phosphorus in biodegradable material end up mainly as CO_2, HCO_3^-, H_2O, NO_3^-, SO_4^{2-}, and phosphates. The formation of these oxidation products sometimes reduces the amount of dissolved oxygen to the point where aerobic bacteria can no longer survive. Anaerobic bacteria then take over the decomposition process, forming CH_4, NH_3, H_2S, PH_3, and other products, several of which contribute to the offensive odors of some polluted waters.

Plant nutrients, particularly nitrogen and phosphorus, contribute to water pollution by stimulating excessive growth of aquatic plants. The most visible results of excessive plant growth are floating algae and murky water. What is more significant, however, is that as plant growth becomes excessive, the amount of dead and decaying plant matter increases rapidly, a process called *eutrophication* (**Figure 18.17**). The processes by which plants decay consumes O_2, and without sufficient oxygen, the water cannot sustain animal life.

The most significant sources of nitrogen and phosphorus compounds in water are domestic sewage (phosphate-containing detergents and nitrogen-containing body wastes), runoff from agricultural land (fertilizers contain both nitrogen and phosphorus), and runoff from livestock areas (animal wastes contain nitrogen).

Water Purification: Desalination

Because of its high salt content, seawater is unfit for human consumption and for most of the uses to which we put water. In many countries, the salt content of municipal water supplies is restricted by health codes to no more than about 0.05% by mass. This amount is much lower than the 3.5% dissolved salts present in seawater and the 0.5% or so present in brackish water found underground in some regions. The removal of salts from seawater or brackish water to make the water usable is called **desalination**.

Water can be separated from dissolved salts by *distillation* because water is a volatile substance and the salts are nonvolatile. The principle of distillation is simple enough, but carrying out the process on a large scale presents many problems. As water is distilled from seawater, for example, the salts become more and more concentrated and eventually precipitate out. Distillation is also an energy-intensive process.

Seawater can also be desalinated using **reverse osmosis**. Recall that osmosis is the net movement of solvent molecules, but not solute molecules, through a semipermeable membrane. In osmosis, the solvent passes from the more dilute solution into the more concentrated one. However, if sufficient external pressure is applied, osmosis can be stopped and, at still higher pressures, reversed. When reverse osmosis occurs, solvent passes from the more concentrated into the more dilute solution. In a modern reverse-osmosis facility, hollow fibers are used as the semipermeable membrane (**Figure 18.18**). Saline water (water containing significant salts) is introduced under pressure into the fibers, and desalinated water is recovered.

The world's largest desalination plant, in Jubail, Saudi Arabia, provides 50% of that country's drinking water by using reverse osmosis to desalinate seawater from the Persian Gulf.

Water Purification: Municipal Treatment

The water needed for domestic, agricultural, and industrial use is taken either from lakes, rivers, and underground sources or from reservoirs. Much of the water that finds its way into municipal water systems is "used" water, meaning it has already passed through one or more sewage systems or industrial plants. Consequently, this water must be treated before it is distributed.

Municipal water treatment usually involves five steps (**Figure 18.19**).

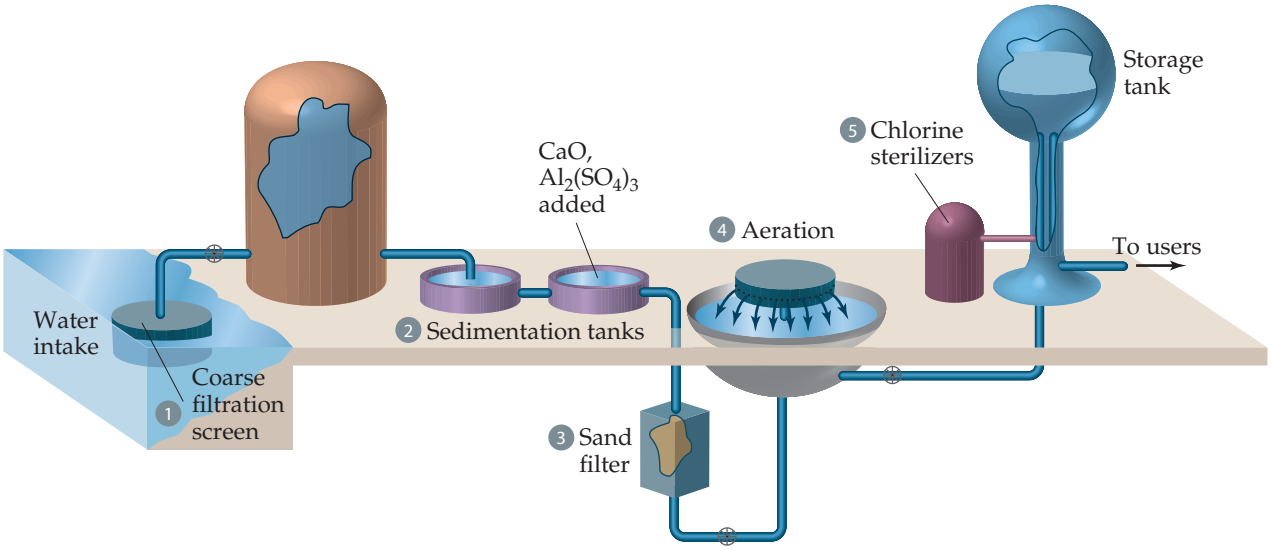
1. After coarse filtration through a screen, the water is allowed to stand in large sedimentation tanks where sand and other minute particles settle out. To aid in removing very small particles, the water may first be made slightly basic with CaO.
2. Then $Al_2(SO_4)_3$ is added and reacts with OH^- ions to form a spongy, gelatinous precipitate of $Al(OH)_3$ ($K_{sp} = 1.3 \times 10^{-33}$). This precipitate settles slowly, carrying suspended particles down with it, thereby removing nearly all finely divided matter and most bacteria.
3. The water is then filtered through a sand bed.
4. Following filtration, the water may be sprayed into the air (aeration) to hasten oxidation of dissolved inorganic ions of iron and manganese, reduce concentrations of any H_2S or NH_3 that may be present, and reduce bacterial concentrations.
5. The final step normally involves treating the water with a chemical agent to ensure the destruction of bacteria. Ozone is more effective, but chlorine is less expensive. Liquefied Cl_2 is dispensed from tanks through a metering device directly into the water supply. The amount used depends on the presence of other substances with which the chlorine might react and on the concentrations of bacteria and viruses to be removed.

The sterilizing action of chlorine is not due to Cl_2 itself but to hypochlorous acid, which forms when chlorine reacts with water:

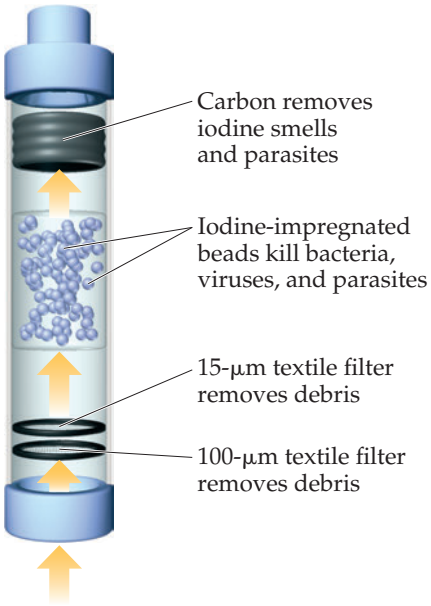
$$Cl_2(aq) + H_2O(l) \longrightarrow HClO(aq) + H^+(aq) + Cl^-(aq) \qquad [18.15]$$

It is estimated that about 800 million people worldwide lack access to clean water. According to the United Nations, 95% of the world's cities still dump raw sewage into

Go Figure What is the primary function of the aeration step in water treatment?



▲ **Figure 18.19** Common steps in treating water for a public water system.



▲ **Figure 18.20** **A LifeStraw purifies water as it is drunk.**

their water supplies. Thus, it should come as no surprise that 80% of all the health maladies in developing countries can be traced to waterborne diseases associated with unsanitary water.

One promising development is a device called the LifeStraw (**Figure 18.20**). When a person sucks water through the straw, the water first encounters a textile filter with a mesh opening of 100 μm followed by a second textile filter with a mesh opening of 15 μm. These filters remove debris and even clusters of bacteria. The water next encounters a chamber of iodine-impregnated beads, where bacteria, viruses, and parasites are killed. Finally, the water passes through granulated active carbon, which removes the smell of iodine as well as the parasites that have not been taken by the filters or killed by the iodine. At present the Lifestraw is too costly to permit widespread use in underdeveloped countries, but there is hope that its cost can be greatly reduced. They have been used in acute situations where a natural disaster such as an earthquake or flooding has resulted in the temporary contamination of the drinking water supply.

Water disinfection is one of the greatest public health innovations in human history. It has dramatically decreased the incidences of waterborne bacterial diseases such as cholera and typhus. However, this great benefit comes at a price. In 1974 scientists in Europe and the United States discovered that chlorination of water produces a group of by-products previously undetected. These by-products are called *trihalomethanes* (THMs) because all have a single carbon atom and three halogen atoms: $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$. These and many other chlorine- and bromine-containing organic substances are produced by the reaction of dissolved chlorine with the organic materials present in nearly all natural waters, as well as with substances that are by-products of human activity. Recall that chlorine dissolves in water to form the oxidizing agent HClO as shown in Equation 18.15.

The HClO in turn reacts with organic substances to form THMs. Bromine enters the reaction sequence through the reaction of HClO with dissolved bromide ion:

$$HClO(aq) + Br^-(aq) \longrightarrow HBrO(aq) + Cl^-(aq) \qquad [18.16]$$

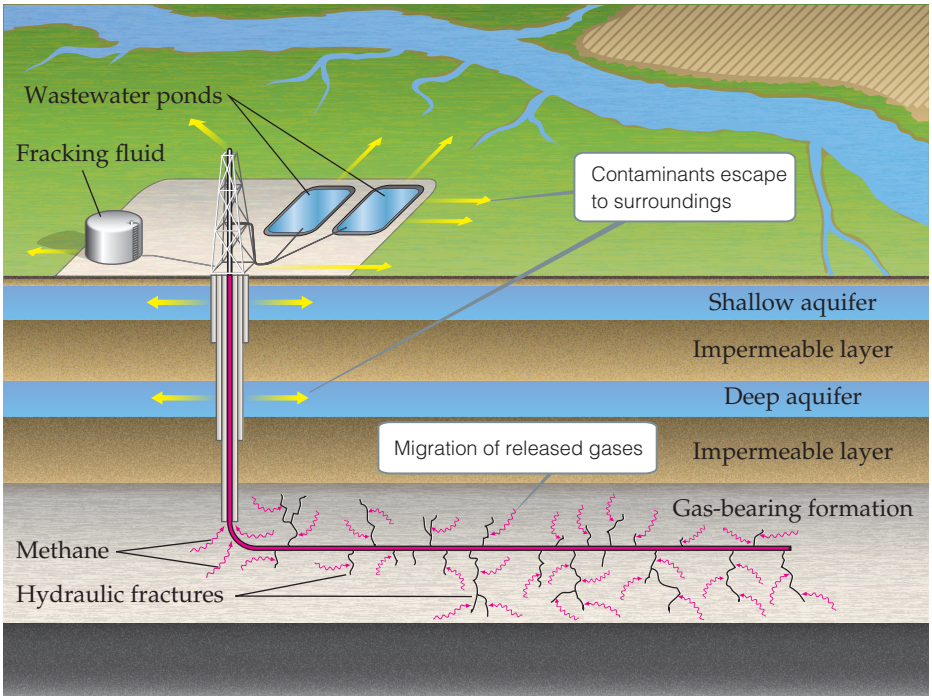
Then both $HBrO(aq)$ and $HClO(aq)$ can halogenate organic substances to form the THMs.

A CLOSER LOOK Fracking and Water Quality

In recent years **fracking**, short for *hydraulic fracturing,* has become widely used to greatly increase the availability of petroleum reserves. In fracking, a large volume of water, typically seven million liters or more, mixed with various additives, is injected at high pressure into wellbores extended horizontally into rock formations (**Figure 18.21**). The water is laden with sand, ceramic materials, and other additives, including gels, foams, and compressed gases, that serve to increase the yield in the process. The high-pressure fluid finds its way into tiny faults in geological formations, releasing petroleum and natural gas. Fracking has greatly increased petroleum reserves, particularly of natural gas, in many parts of the world.

Unfortunately, the potential for environmental damage from fracking is significant. The large volume of fracking fluid required to create a well must be returned to the surface. Without purification the fluid is rendered unfit for other uses, and becomes a large-scale environmental problem. Often the waste water is allowed to sit in open waste water pits. Because fracturing of rock formations increases the pathways for flows of petroleum and various gases, bodies of underground water that have been serving as municipal water supplies or wells for individual homes in some locales have become contaminated with petroleum, hydrogen sulfide and other toxic substances. The escape of a variety of gases, including methane and other hydrocarbons, from the wellheads contributes to air pollution. In a study published in 2013, methane emissions to the atmosphere during hydraulic fracking operations in Utah, USA were estimated to be in the range of 6–12% of the amount of methane produced. As related in the Closer Look box on page 880, methane is a potent greenhouse gas.

The many environmental issues surrounding the practice of fracking have generated widespread concern and adverse public reaction. Fracking represents yet one more instance of the conflict between those who advocate the availability of low cost energy and those who are more focused on sustaining long term the quality of the environment.



▲ **Figure 18.21 A schematic of a well site employing fracking.** The yellow arrows indicate the avenues through which contaminants enter the environment.

Some THMs and other halogenated organic substances are suspected carcinogens; others interfere with the body's endocrine system. As a result, the World Health Organization have placed concentration limits of 80 μg/L (80 ppb) on the total quantity of THMs in drinking water. The goal is to reduce the levels of THMs and other disinfection by-products in the drinking water supply while preserving the antibacterial effectiveness of the water treatment. In some cases, lowering the concentration of chlorine may provide adequate disinfection while reducing the concentrations of THMs formed. Alternative oxidizing agents, such as ozone or chlorine dioxide, produce less of the halogenated substances but have their own disadvantages. For example, each is capable of oxidizing dissolved bromide, as shown here for ozone:

$$O_3(aq) + Br^-(aq) + H_2O(l) \longrightarrow HBrO(aq) + O_2(aq) + OH^-(aq) \qquad [18.17]$$

$$HBrO(aq) + 2\,O_3(aq) \longrightarrow BrO_3^-(aq) + 2\,O_2(aq) + H^+(aq) \qquad [18.18]$$

Bromate ion, BrO_3^-, has been shown to cause cancer in animal tests.

At present, there seem to be no completely satisfactory alternatives to chlorination or ozonation, and we are faced with a consideration of benefit versus risk. In this case, the risks of cancer from THMs and related substances in municipal water are very low relative to the risks of cholera, typhus, and gastrointestinal disorders from untreated water. When the water supply is cleaner to begin with, less disinfectant is needed and thus the risk of THMs is lowered. Once THMs form, their concentrations in the water supply can be reduced by aeration because the THMs are more volatile than water. Alternatively, they can be removed by adsorption onto activated charcoal or other adsorbents.

- Understand some main factors that result in the deterioration of water quality and how water can be treated to make it fit for human consumption.

CHEMISTRY AND LIFE Ocean Acidification

Seawater is a weakly basic solution, with pH values typically between 8.0 and 8.3. This pH range is maintained through a carbonic acid buffer system similar to the one in blood (see Equation 17.10). Because the pH of seawater is higher than that of blood (7.35–7.45), the second dissociation of carbonic acid cannot be neglected and CO_3^{2-} becomes an important aqueous species.

The availability of carbonate ions plays an important role in shell formation for a number of marine organisms, including stony corals (**Figure 18.22**). These organisms, which are referred to as marine *calcifiers* and play an important role in the food chains of nearly all oceanic ecosystems, depend on dissolved Ca^{2+} and CO_3^{2-} ions to form their shells and exoskeletons. The relatively low solubility-product constant of $CaCO_3$,

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \quad K_{sp} = 4.5 \times 10^{-9}$$

and the fact that the ocean contains saturated concentrations of Ca^{2+} and CO_3^{2-} mean that $CaCO_3$ is usually quite stable once formed. In fact, calcium carbonate skeletons of creatures that died millions of years ago are not uncommon in the fossil record.

The concentration of dissolved CO_2 in the ocean is sensitive to changes in atmospheric CO_2 levels. As discussed in Section 18.2, the atmospheric CO_2 concentration has risen by approximately 30% over the past three centuries to the present level of 400 ppm. Human activity has played a prominent role in this increase. Scientists estimate that one-third to one-half of the CO_2 emissions resulting from human activity have been absorbed by Earth's oceans. While this absorption helps mitigate the greenhouse gas effects of CO_2, the extra CO_2 in the ocean produces carbonic acid, which lowers the pH. Because CO_3^{2-} is the conjugate base of the weak acid HCO_3^-, the carbonate ion readily combines with the hydrogen ion:

$$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$$

This consumption of carbonate ion shifts the $CaCO_3$ dissolution equilibrium to the right, increasing the solubility of $CaCO_3$, which can lead to partial dissolution of calcium carbonate shells and exoskeletons. If the amount of atmospheric CO_2 continues to increase at the present rate, scientists estimate that seawater pH will fall to 7.9 sometime over the next 50 years. While this change might sound small, it has dramatic ramifications for oceanic ecosystems.

Related Exercises: 18.39, 18.42, 18.78



▲ **Figure 18.22 Marine calcifiers.** Many sea-dwelling organisms use $CaCO_3$ for their shells and exoskeletons. Examples include stony coral, crustaceans, some phytoplankton, and echinoderms, such as sea urchins and starfish.

Self-Assessment Exercise

18.23 Which two elements are largely responsible for fresh water eutrophication?

(a) S and P
(b) N and P
(c) C and S

Exercises

18.24 Assume that a portable reverse-osmosis apparatus operates on seawater, whose concentrations of constituent ions are listed in Table 18.5, and that the desalinated water output has an effective molarity of about 0.02 *M*. What minimum pressure must be applied by hand pumping at 297 K to cause reverse osmosis to occur? (*Hint:* Refer to Section 13.5.)

18.25 (**a**) Explain why the concentration of dissolved oxygen in freshwater is an important indicator of the quality of the water. (**b**) Find graphical data in the text that show variations of gas solubility with temperature, and estimate to two significant figures the percent solubility of O_2 in water at 30 °C as compared with 20 °C. How do these data relate to the quality of natural waters?

18.26 Sewage causes removal of oxygen from the fresh water into which the sewage is discharged. For a town with a population of 100,000 people, this effluent causes a daily oxygen depletion of 50.0 g per person. How many liters of water at 8 ppm O_2 are 50% depleted of oxygen in a day by the population of this town?

18.27 In the lime soda process once used in large scale municipal water softening, calcium hydroxide prepared from lime and sodium carbonate are added to precipitate Ca^{2+} as $CaCO_3(s)$ and Mg^{2+} as $Mg(OH)_2(s)$:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

$$Mg^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Mg(OH)_2(s)$$

How many moles of $Ca(OH)_2$ and Na_2CO_3 should be added to soften (remove the Ca^{2+} and Mg^{2+}) 1000 L of water in which

$$[Ca^{2+}] = 3.5 \times 10^{-4}\,M$$

$$[Mg^{2+}] = 7.5 \times 10^{-4}\,M$$

18.28 (a) Suppose that tests of a municipal water system reveal the presence of bromate ion, BrO_3^-. What are the likely origins of this ion? (b) Is bromate ion an oxidizing or reducing agent?

Answers to Self-Assessment Exercises

18.23 (b)

18.5 | Green Chemistry



The planet on which we live is, to a large extent, a *closed system*, one that exchanges energy but not matter with its surroundings. If humankind is to thrive in the future, all the processes we carry out should be in balance with Earth's natural processes and physical resources. This goal requires that no toxic materials be released to the environment, that our needs be met with renewable resources, and that we consume the least possible amount of energy. Although the chemical industry is but a small part of human activity, chemical processes are involved in nearly all aspects of modern life. Chemistry is therefore at the heart of efforts to accomplish these goals.

By the end of this section, you should be able to

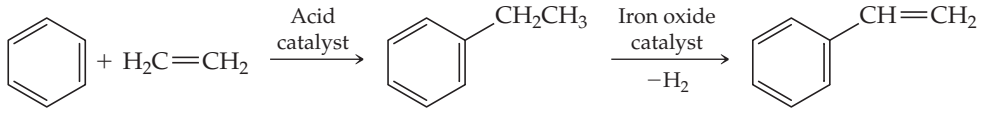
- The basic concepts underpinning green chemistry

Green chemistry is an initiative that promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. Green chemistry rests on a set of 12 principles:

1. **Prevention** It is better to prevent waste than to clean it up after it has been created.
2. **Atom Economy** Methods to make chemical compounds should be designed to maximize the incorporation of all starting atoms into the final product.
3. **Less Hazardous Chemical Syntheses** Wherever practical, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Design of Safer Chemicals** Chemical products should be designed to minimze toxicity and yet maintain their desired function.
5. **Safer Solvents and Auxiliaries** Auxiliary substances (for example, solvents, separation agents, etc.) should be used as little as possible. Those that are used should be as nontoxic as possible.

6. **Design for Energy Efficiency** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, chemical reactions should be conducted at room temperature and pressure.
7. **Use of Renewable Feedstocks** A raw material or feedstock should be renewable whenever technically and economically practical.
8. **Reduction of Derivatives** Unnecessary derivatization (intermediate compound formation, temporary modification of physical/chemical processes) should be minimized or avoided if possible because such steps require additional reagents and can generate waste.
9. **Catalysis** Catalytic reagents (as selective as possible) improve product yields within a given time and with a lower energy cost compared to noncatalytic processes and are, therefore, preferred to noncatalytic alternatives.
10. **Design for Degradation** The end products of chemical processing should break down at the end of their useful lives into innocuous degradation products that do not persist in the environment.
11. **Real-Time Analysis for Pollution Prevention** Analytical methods need to be developed that allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention** Reagents and solvents used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.*

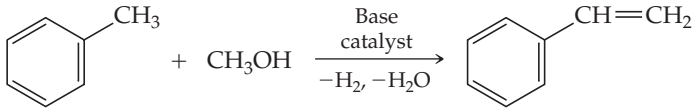
To illustrate how green chemistry works, consider the manufacture of styrene, an important building block for many polymers, including the expanded polystyrene packages used to pack eggs and restaurant takeout food. The global demand for styrene is more than 25 billion kg per year. For many years, styrene has been produced in a two-step process: Benzene and ethene react to form ethyl benzene, followed by the ethyl benzene being mixed with high-temperature steam and passed over an iron oxide catalyst to form styrene:



Benzene Ethene Ethyl benzene Styrene

This process has several shortcomings. One is that both benzene, which is formed from crude oil, and ethene, formed from natural gas, are high-priced starting materials for a product that should be a low-priced commodity. Another is that benzene is a known carcinogen. In a recently developed process that bypasses some of these shortcomings, the two-step process is replaced by a one-step process in which toluene is reacted with methanol at 425 °C over a special catalyst:

*Adapted from P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*. New York: Oxford University Press 1998, p. 30. See also Mike Lancaster, *Green Chemistry: An Introductory Text.* Cambridge, UK: RSC Publishing, 2010, Second Edition, Chapter 1.



Toluene Methanol Styrene

The one-step process saves money both because toluene and methanol are less expensive than benzene and ethene, and because the reaction requires less energy input. Additional benefits are that the methanol could be produced from biomass and that benzene is replaced by less toxic toluene. The hydrogen formed in the reaction can be recycled as a source of energy. This example demonstrates how finding the right catalyst is often key in discovering a new process.

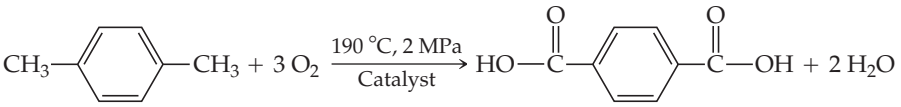
Let's consider some other examples in which green chemistry can operate to improve environmental quality.

Supercritical Solvents

A major area of concern in chemical processes is the use of volatile organic compounds as solvents. Generally, the solvent in which a reaction is run is not consumed in the reaction, and there are unavoidable releases of solvent into the atmosphere even in the most carefully controlled processes. Further, the solvent may be toxic or may decompose to some extent during the reaction, thus creating waste products.

The use of supercritical fluids represents a way to replace conventional solvents. Recall that a supercritical fluid is an unusual state of matter that has properties of both a gas and a liquid. Water and carbon dioxide are the two most popular choices as supercritical fluid solvents. One recently developed industrial process, for example, replaces chlorofluorocarbon solvents with liquid or supercritical CO_2 in the production of polytetrafluoroethene ($[CF_2CF_2]_n$, sold as Teflon®). Though CO_2 is a greenhouse gas, no new CO_2 need be manufactured for use as a supercritical fluid solvent.

As a further example, *para*-xylene is oxidized to form terephthalic acid, which is used to make polyethene terephthalate (PET) plastic and polyester fiber:



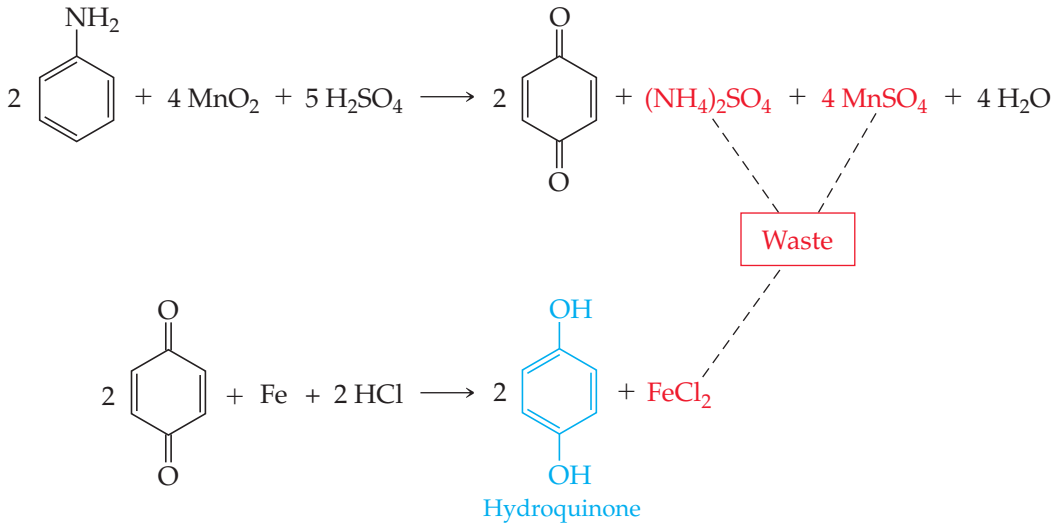
para-Xylene Terephthalic acid

This commercial process requires pressurization and a relatively high temperature. Oxygen is the oxidizing agent, and acetic acid (CH_3COOH) is the solvent. An alternative route employs supercritical water as the solvent and hydrogen peroxide as the oxidant. This alternative process has several potential advantages, most particularly the elimination of acetic acid as solvent.

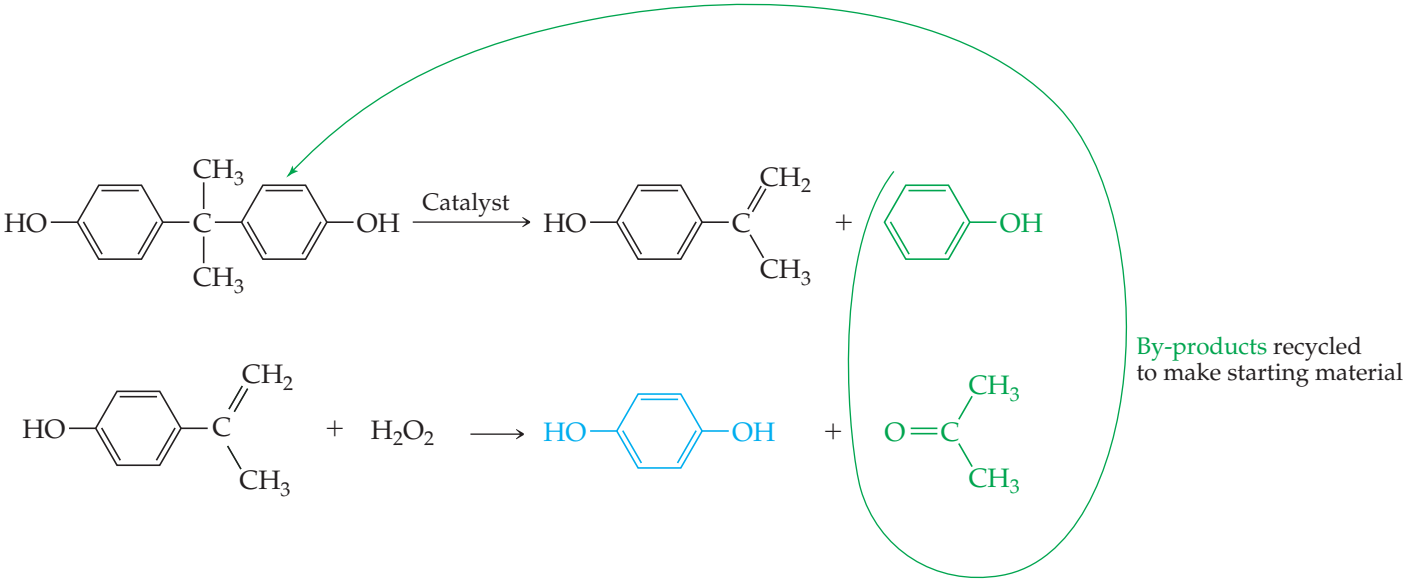
Greener Reagents and Processes

Let us examine two more examples of green chemistry in action.

Hydroquinone, $HO{-}C_6H_4{-}OH$, is a common intermediate used to make polymers. The standard industrial route to hydroquinone, used until recently, yields many by-products that are treated as waste:

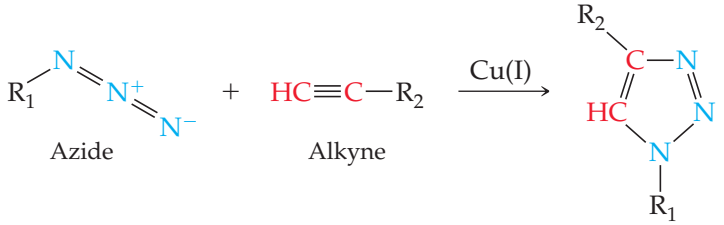


Using the principles of green chemistry, researchers have improved this process. The new process for hydroquinone production uses a new starting material. Two of the by-products of the new reaction (shown in green) can be isolated and used to make the new starting material.



The new process is an example of "atom economy," a phrase that means that a high percentage of the atoms from the starting materials end up in the product.

Another example of atom economy is a reaction in which, at room temperature and in the presence of a copper(I) catalyst, an organic *azide* and an *alkyne* form one product molecule:



This reaction is informally called a *click reaction*. The yield—actual, not just theoretical—is close to 100%, and there are no by-products. Depending on the type of azide and type of alkyne we start with, this very efficient click reaction can be used to create any number of valuable product molecules.

Self-Assessment Exercise

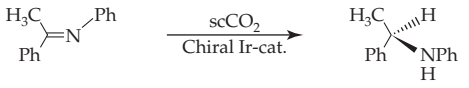
18.29 Assuming the by-products of the green manufacture of hydroquinone (these are: phenol and acetone) are recycled, what atoms, if any, used in this process do not end up in the final products?

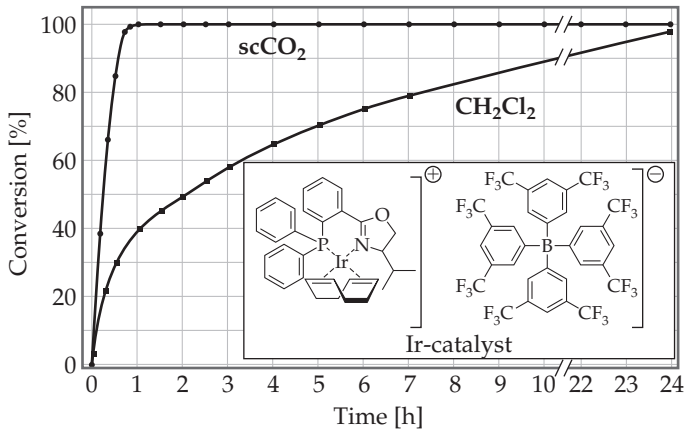
(a) All atoms are used
(b) 3C and 5H remain
(c) 1O and 2H remain

Exercises

18.30 Discuss how catalysts can make processes more energy efficient.

18.31 The hydrogenation reaction shown here was performed with an iridium catalyst, both in supercritical CO_2 ($scCO_2$) and in the chlorinated solvent CH_2Cl_2. The kinetic data for the reaction in both solvents are plotted in the graph. In what respects is the use of $scCO_2$ a good example of a green chemical reaction?





18.32 In the following three instances, which choice is greener in a chemical process? Explain. (**a**) A reaction that can be run at 350 K for 12 h without a catalyst or one that can be run at 300 K for 1 h with a reusable catalyst. (**b**) A reagent for the reaction that can be obtained from corn husks or one that is obtained from petroleum. (**c**) A process that produces no by-products or one in which the by-products are recycled for another process.

Answers to Self-Assessment Exercise

18.29 (c)

Sample Integrative Exercise

Putting Concepts Together

(**a**) Acid rain is no threat to lakes in areas where the rock is limestone (calcium carbonate), which can neutralize the acid. Where the rock is granite, however, no neutralization occurs. How does limestone neutralize acid? (**b**) Acidic water can be treated with basic substances to increase the pH, although such a procedure is usually only a temporary cure. Calculate the minimum mass of lime, CaO, needed to adjust the pH of a small lake ($V = 4 \times 10^9$ L) from 5.0 to 6.5. Why might more lime be needed?

Continued

SOLUTION

Analyze We need to remember what a neutralization reaction is and calculate the amount of a substance needed to effect a certain change in pH.

Plan For (a), we need to think about how acid can react with calcium carbonate, a reaction that evidently does not happen with acid and granite. For (b), we need to think about what reaction between an acid and CaO is possible and do stoichiometric calculations. From the proposed change in pH, we can calculate the change in proton concentration needed and then figure out how much CaO is needed.

Solve

(**a**) The carbonate ion, which is the anion of a weak acid, is basic and so reacts with $H^+(aq)$. If the concentration of $H^+(aq)$ is low, the major product is the bicarbonate ion, HCO_3^-. If the concentration of $H^+(aq)$ is high, H_2CO_3 forms and decomposes to CO_2 and H_2O.

(**b**) The initial and final concentrations of $H^+(aq)$ in the lake are obtained from their pH values:

$$[H^+]_{initial} = 10^{-5.0} = 1 \times 10^{-5}\,M$$

$$[H^+]_{final} = 10^{-6.5} = 3 \times 10^{-7}\,M$$

Using the lake volume, we can calculate the number of moles of $H^+(aq)$ at both pH values:

$$(1 \times 10^{-5}\ \text{mol/L})(4.0 \times 10^{9}\ \text{L}) = 4 \times 10^{4}\ \text{mol}$$

$$(3 \times 10^{-7}\ \text{mol/L})(4.0 \times 10^{9}\ \text{L}) = 1 \times 10^{3}\ \text{mol}$$

Hence, the change in the amount of $H^+(aq)$ is $4 \times 10^4\ \text{mol} - 1 \times 10^3\ \text{mol} \approx 4 \times 10^4\ \text{mol}$.

Let's assume that all the acid in the lake is completely ionized, so that only the free $H^+(aq)$ contributing to the pH needs to be neutralized. We need to neutralize at least that much acid, although there may be a great deal more than that amount in the lake.

The oxide ion of CaO is very basic. In the neutralization reaction, 1 mol of CaO reacts with 2 mol of H^+ to form H_2O and Ca^{2+} ions. Thus, 4×10^4 mol of H^+ requires

$$(4 \times 10^4\ \text{mol H}^+)\left(\frac{1\ \text{mol CaO}}{2\ \text{mol H}^+}\right)\left(\frac{56.1\ \text{g CaO}}{1\ \text{mol CaO}}\right) = 1 \times 10^6\ \text{g CaO}$$

A tonne of CaO costs about $100 when purchased in large quantities, so it relatively inexpensive. This amount of CaO is the minimum amount needed, however, because there are likely to be weak acids in the water that must also be neutralized.

This liming procedure has been used to bring the pH of some small lakes into the range necessary for fish to live. The lake in our example would be about a kilometer long and a kilometer wide and have an average depth of 6 m.

Chapter Summary and Key Terms

EARTH'S ATMOSPHERE (SECTION 18.1) In this section we examined the physical and chemical properties of Earth's atmosphere. The complex temperature variations in the atmosphere give rise to four regions, each with characteristic properties. The lowest of these regions, the **troposphere**, extends from Earth's surface up to an altitude of about 12 km. Above the troposphere, in order of increasing altitude, are the **stratosphere**, mesosphere, and thermosphere. In the upper reaches of the atmosphere, only the simplest chemical species can survive the bombardment of highly energetic particles and radiation from the Sun. The average molecular weight of the atmosphere at high elevations is lower than that at Earth's surface because the lightest atoms and molecules diffuse upward and also because of **photodissociation**, which is the breaking of bonds in molecules because of the absorption of light. Absorption of radiation may also lead to the formation of ions via **photoionization**.

HUMAN ACTIVITIES AND EARTH'S ATMOSPHERE (SECTION 18.2) Ozone is produced in the upper atmosphere from the reaction of atomic oxygen with O_2. Ozone is itself decomposed by absorption of a photon or by reaction with an active species such as Cl. **Chlorofluorocarbons** can undergo photodissociation in the stratosphere, introducing atomic chlorine, which is capable of catalytically destroying ozone. A marked reduction in the ozone level in the upper atmosphere would have serious adverse consequences because the ozone layer filters out certain wavelengths of harmful ultraviolet light that are not removed by any other atmospheric component. In the troposphere the chemistry of trace atmospheric components is of major importance. Many of these minor components are pollutants. Sulfur dioxide is one of the more noxious and prevalent examples. It is oxidized in air to form sulfur trioxide, which, upon dissolving in water, forms sulfuric acid. The oxides of sulfur are major contributors to **acid rain**. One method of preventing the escape of SO_2 from industrial operations is to react it with CaO to form calcium sulfite $CaSO_3$.

Photochemical smog is a complex mixture in which both nitrogen oxides and ozone play important roles. Smog components are generated mainly in automobile engines, and smog control consists largely of controlling auto emissions.

Carbon dioxide and water vapor are the major components of the atmosphere that strongly absorb infrared radiation. CO_2 and H_2O are therefore critical in maintaining Earth's surface temperature. The concentrations of CO_2 and other so-called **greenhouse gases** in the atmosphere are thus important in determining global climate. Because of the extensive combustion of fossil fuels (coal, oil, and natural gas), the concentration of carbon dioxide in the atmosphere is steadily increasing, which in turn appears to be contributing to an increase in the average temperature of the Earth.

EARTH'S WATER (SECTION 18.3) Earth's water is largely in the oceans and seas; only a small fraction is freshwater. Seawater contains about 3.5% by mass of dissolved salts and is described as having a **salinity** (grams of dry salts per 1 kg seawater) of 35. Seawater's density and salinity vary with depth. Because most of the world's water is in the oceans, humans may eventually need to recover freshwater from seawater. The global water cycle involves continuous phase changes of water.

HUMAN ACTIVITIES AND WATER QUALITY (SECTION 18.4) Freshwater contains many dissolved substances including dissolved oxygen, which is necessary for fish and other aquatic life. Substances that are decomposed by bacteria are said to be **biodegradable**. Because the oxidation of biodegradable substances by aerobic

bacteria consumes dissolved oxygen, these substances are called oxygen-demanding wastes. The presence of an excess amount of oxygen-demanding wastes in water can sufficiently deplete the dissolved oxygen to kill fish and produce offensive odors. Plant nutrients can contribute to the problem by stimulating the growth of plants that become oxygen-demanding wastes when they die. **Desalination** is the removal of dissolved salts from seawater or brackish water to make it fit for human consumption. Desalination may be accomplished by distillation or by **reverse osmosis**.

The water available from freshwater sources may require treatment before it can be used domestically. The several steps generally used in municipal water treatment include coarse filtration, sedimentation, sand filtration, aeration, and sterilization.

GREEN CHEMISTRY (SECTION 18.5) The **green chemistry** initiative promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. The areas in which the principles of green chemistry can operate to improve environmental quality include choices of solvents and reagents for chemical reactions, development of alternative processes, and improvements in existing systems and practices.

Learning Outcomes After studying this chapter, you should be able to:

- Describe the regions of Earth's atmosphere in terms of how temperature varies with altitude. (Section 18.1) *Related exercises 18.4, 18.43*
- Describe the composition of the atmosphere in terms of the major components in dry air at sea level. (Section 18.1) *Related exercises 18.6, 18.44*
- Calculate concentrations of gases in parts per million (ppm). (Section 18.1) *Related exercises 18.5, 18.45*
- Describe the processes of photodissociation and photoionization and their role in the upper atmosphere. (Section 18.1) *Related exercises 18.8, 18.47*
- Calculate the minimum frequency or maximum wavelength needed to cause photodissociation or photoionization. (Section 18.1) *Related exercises 18.7, 18.46, 18.48*
- Explain how ozone in the upper atmosphere functions to filter short wavelength solar radiation, and how chlorofluorcarbons (CFCs) cause depletion of the ozone layer. (Sections 18.1 and 18.2) *Related exercises 18.9, 18.13, 18.14, 18.51*
- Describe the origins and behavior of sulfur oxides and nitrogen oxides as air pollutants, including the generation of acid rain and photochemical smog. (Section 18.2) *Related exercises 18.15, 18.17, 18.52, 18.54*
- Describe how water and carbon dioxide cause an increase in atmospheric temperature near Earth's surface. (Section 18.2) *Related exercises 18.18, 18.55*
- Describe the global water cycle. (Section 18.3) *Related exercises 18.21, 18.57*
- Explain what is meant by the salinity of water and describe the process of reverse osmosis as a means of desalination. (Section 18.4) *Related Exercises 18.24, 18.60*
- List the major cations, anions, and gases present in natural waters and describe the relationship between dissolved oxygen and water quality. (Section 18.4) *Related exercises 18.25, 18.26, 18.59, 18.62*
- List the main steps involved in treating water for domestic uses. (Section 18.4) *Related exercises 18.27, 18.28, 18.63, 18.64*
- Describe the main goals of green chemistry. (Section 18.5) *Related exercises 18.30, 18.65*
- Compare reactions and decide which reaction is greener. (Section 18.5) *Related exercises 18.31, 18.32, 18.67*

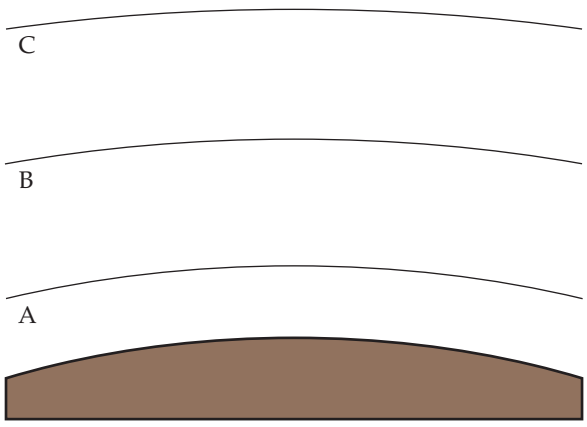
Exercises

Visualizing Concepts

18.33 At 273 K and 101.3 kPa, 1 mol of an ideal gas occupies 22.4 L. (Section 10.4) (**a**) Looking at Figure 18.1, predict whether a 1 mol sample of the atmosphere in the middle of the stratosphere would occupy a greater or smaller volume than 22.4 L (**b**) Looking at Figure 18.1, we see that the temperature is lower at 85 km altitude than at 50 km. Does this mean that one mole of an ideal gas would occupy less volume at 85 km than at 50 km? Explain. (**c**) In which parts of the atmosphere would you expect gases to behave most ideally (ignoring any photochemical reactions)? [Section 18.1]

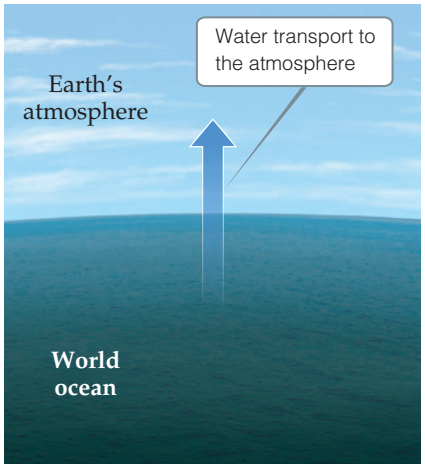
18.34 Molecules in the upper atmosphere tend to contain double and triple bonds rather than single bonds. Suggest an explanation. [Section 18.1]

18.35 The figure shows the three lowest regions of Earth's atmosphere. (**a**) Name each and indicate the approximate elevations at which the boundaries occur. (**b**) In which region is ozone a pollutant? In which region does it filter UV solar radiation? (**c**) In which region is infrared radiation from Earth's surface most strongly reflected back? (**d**) An aurora borealis is due to excitation of atoms and molecules in the atmosphere 55–95 km above Earth's surface. Which regions in the figure are involved in an aurora borealis? (**e**) Compare the changes in relative concentrations of water vapor and carbon dioxide with increasing elevation in these three regions [Section 18.1].



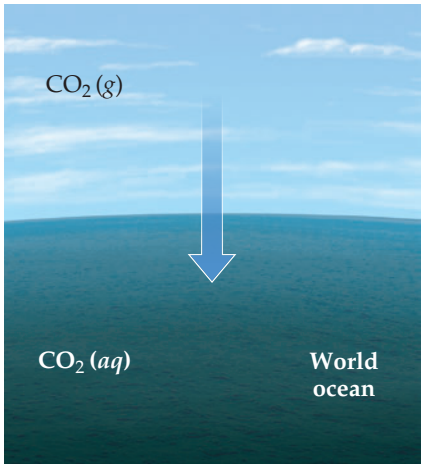
18.36 You are working with an artist who has been commissioned to make a sculpture for a big city. The artist is wondering what material to use to make her sculpture because she has heard that acid rain might destroy it over time. You take samples of granite, marble, bronze, and other materials, and place them outdoors for a long time in the big city. You periodically examine the appearance and measure the mass of the samples. (**a**) What observations would lead you to conclude that one or more of the materials are well-suited for the sculpture? (**b**) What chemical process (or processes) is (are) the most likely responsible for any observed changes in the materials? [Section 18.2]

18.37 Where does the energy come from to evaporate the estimated 425,000 km^3 of water that annually leaves the oceans, as illustrated here? [Section 18.3]

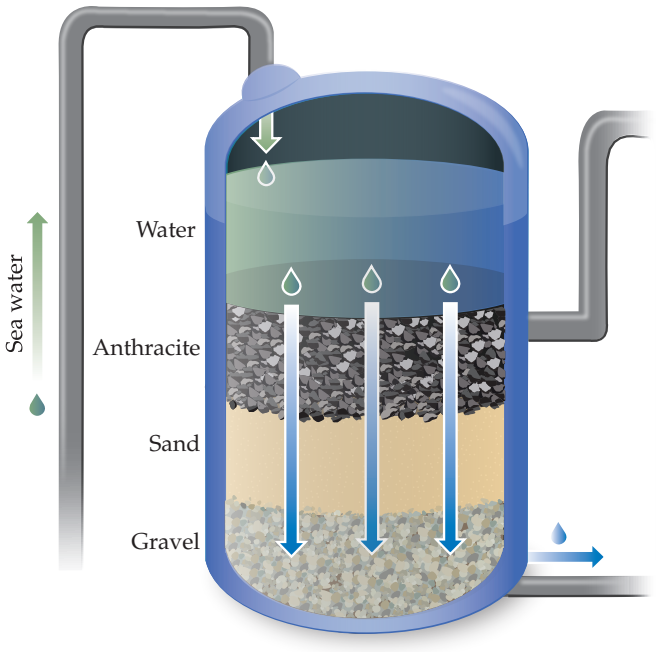


18.38 The Earth's oceans have a salinity of 35. What is the concentration of dissolved salts in seawater when expressed in ppm? What percentage of salts must be removed from seawater before it can be considered freshwater (dissolved salts < 500 ppm)? [Section 18.3]

18.39 Describe what changes occur when atmospheric CO_2 interacts with the world ocean as illustrated here. [Section 18.3]

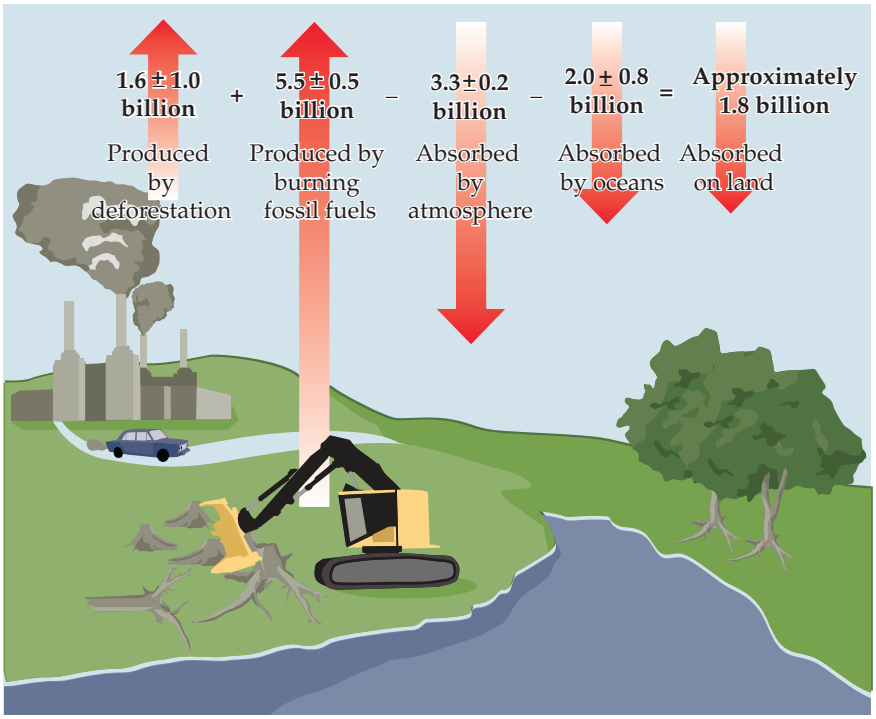


18.40 The first stage of treatment at a reverse osmosis plant is to flow the water through rock, sand, and gravel as shown here. Would this step remove particulate matter? Would this step remove dissolved salts? [Section 18.4]



18.41 From study of Figure 18.21, describe the various ways in which operation of a fracking well site could lead to environmental contamination.

18.42 One mystery in environmental science is the imbalance in the "carbon dioxide budget." Considering only human activities, scientists have estimated that 1.6 billion tonne tons of CO_2 is added to the atmosphere every year because of deforestation (plants use CO_2, and fewer plants will leave more CO_2 in the atmosphere). Another 5.5 billion tonne per year is put into the atmosphere because of burning fossil fuels. It is further estimated (again, considering only human activities) that the atmosphere actually takes up about 3.3 billion tonne of this CO_2 per year, while the oceans take up 2 billion tonne per year, leaving about 1.8 billion tonne of CO_2 per year unaccounted for. Describe a mechanism by which CO_2 is removed from the atmosphere and ultimately ends up below the surface (*Hint:* What is the source of the fossil fuels?). [Sections 18.1–18.3]



Earth's Atmosphere (Section 18.1)

18.43 (**a**) What is the primary basis for the division of the atmosphere into different regions? (**b**) Name the regions of the atmosphere, indicating the altitude interval for each one.

18.44 From the data in Table 18.1, calculate the partial pressures of neon and helium when the total atmospheric pressure is 102.3 kPa.

18.45 The average concentration of carbon monoxide in air in a city in 2007 was 3.0 ppm. Calculate the number of CO molecules in 1.0 L of this air at a pressure of 100 kPa and a temperature of 25 °C.

18.46 The dissociation energy of a carbon–iodine bond is typically about 240 kJ/mol. (**a**) What is the maximum wavelength of photons that can cause C—I bond dissociation? (**b**) Which kind of electromagnetic radiation—ultraviolet, visible, or infrared—does the wavelength you calculated in part (a) correspond to?

18.47 (**a**) Distinguish between *photodissociation* and *photoionization*. (**b**) Use the energy requirements of these two processes to explain why photodissociation of oxygen is more important than photoionization of oxygen at altitudes below about 90 km.

18.48 The dissociation energy of N_2 is very high, 941 kJ/mol. (**a**) Calculate the wavelength of the photons that possess sufficient energy to dissociate N_2. (**b**) In which region of the electromagnetic spectrum does this light fall? Does this light have enough energy to photoionize N_2?

Human Activities and Earth's Atmosphere (Section 18.2)

18.49 Do the reactions involved in ozone depletion involve changes in oxidation state of the O atoms? Explain.

18.50 Draw the Lewis structure for the chlorofluorocarbon CFC-11, $CFCl_3$. What chemical characteristics of this substance allow it to effectively deplete stratospheric ozone?

18.51 The average bond enthalpies of the C—C and C—H bonds are 348 kJ/mol and 413 kJ/mol, respectively. (**a**) What is the maximum wavelength that a photon can possess and still have sufficient energy to break the C—H and C—C bonds, respectively? (**b**) Given the fact that O_2, N_2, and O in the upper atmosphere absorb most of the light with wavelengths shorter than 240 nm, would you expect the photodissociation of C—C and C—H bonds to be significant in the lower atmosphere?

18.52 Nitrogen oxides like NO_2 and NO are a significant source of acid rain. For each of these molecules write an equation that shows how an acid is formed from the reaction with water.

18.53 (**a**) It has been reported, that acid rain with a pH of 3.5 could corrode mild steel. Write a chemical equation that describes the attack of acid rain on an iron (Fe) material. (**b**) If the iron material were covered with a surface layer of copper, would this help to stop the effects of acid rain? Explain.

18.54 Alcohol-based fuels for cars lead to the production of formaldehyde (CH_2O) in exhaust gases. Formaldehyde undergoes photodissociation, which contributes to photochemical smog:

$$CH_2O + h\nu \longrightarrow CHO + H$$

The maximum wavelength of light that can cause this reaction is 335 nm. (**a**) In what part of the electromagnetic spectrum is light with this wavelength found? (**b**) What is the maximum strength of a bond, in kJ/mol, that can be broken by absorption of a photon of 335 nm light? (**c**) Compare your answer from part (b) to the appropriate value from Table 8.3. What do you conclude about C—H bond energy in formaldehyde? (**d**) Write out the formaldehyde photodissociation reaction, showing Lewis-dot structures.

18.55 Consider the Earth's energy balance shown in Figure 18.10. (**a**) How many different sources transfer energy to the atmosphere? Which makes the largest contribution? What is the total amount of energy transferred into the atmosphere in W/m^2? (**b**) To maintain a balance the atmosphere must lose an equal amount of energy by emitting radiation, either into space or back toward the surface. What fraction is radiated back to the surface?

Earth's Water (Section 18.3)

18.56 What is the molarity of Na^+ in a solution of NaCl whose salinity is 25.0 if the solution has a density of 1.04 g/mL?

18.57 The enthalpy of evaporation of water is 40.67 kJ/mol. Sunlight striking Earth's surface supplies 168 W per square meter (1 W = 1 watt = 1 J/s). (**a**) Assuming that evaporation of water is due only to energy input from the Sun, calculate how many grams of water could be evaporated from a 1.00 square meter patch of ocean over a 12 h day. (**b**) The specific heat capacity of liquid water is 4.184 J/g °C. If the initial surface temperature of a 1.00 square meter patch of ocean is 26 °C, what is its final temperature after being in sunlight for 12 h, assuming no phase changes and assuming that sunlight penetrates uniformly to depth of 10.0 cm?

18.58 A first-stage recovery of magnesium from seawater is precipitation of $Mg(OH)_2$ with CaO:

$$Mg^{2+}(aq) + CaO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

What mass of CaO, in grams, is needed to precipitate 1000 kg of $Mg(OH)_2$?

18.59 Although there are many ions in seawater, the overall charges of the dissolved cations and anions must maintain charge neutrality. Consider only the six most abundant ions in seawater, as listed in Table 18.5 (Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and K^+), calculate the total charge in Coulombs of the cations in 1.0 L of seawater. Calculate the total charge in Coulombs of the anions in 1.0 L of seawater. To how many significant figures are the two numbers equal?

Human Activities and Water Quality (Section 18.4)

18.60 Suppose that one wishes to use reverse osmosis to reduce the salt content of brackish water containing 0.265 *M* total salt concentration to a value of 0.015 *M*, thus rendering it usable for human consumption. What is the minimum pressure that needs to be applied in the permeators (Figure 18.18) to achieve this goal, assuming that the operation occurs at 15 °C? (*Hint:* Refer to Section 13.5.)

18.61 List the common products formed when an organic material containing the elements carbon, hydrogen, oxygen, sulfur, and nitrogen decomposes (**a**) under aerobic conditions, (**b**) under anaerobic conditions.

18.62 Sodium stearate ($C_{18}H_{35}O_2Na$) is the most common soap. Assume that the stearate anion undergoes aerobic decomposition in the following manner:

$$C_{18}H_{35}O_2^-(aq) + 26\,O_2(aq) \longrightarrow 17\,CO_2(aq) + 17\,H_2O(l) + HCO_3^-(aq)$$

What is the total mass of O_2 required to biodegrade 3.0 g of this substance?

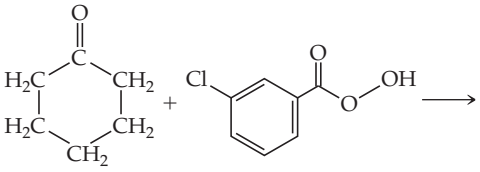
18.63 Hydrogen phosphate (HPO_4^{2-})can be removed in water treatment by the addition of slaked lime, $Ca(OH)_2$. Write a balanced chemical equation for the reaction (using ions as reactant), in which $Ca_5(OH)(PO_4)_3$ forms as a precipitate.

18.64 (**a**) What are *trihalomethanes* (THMs)? (**b**) Draw the Lewis structures of two example THMs.

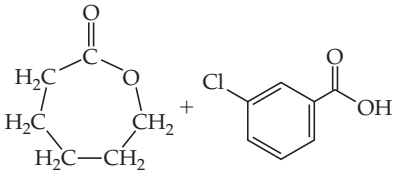
Green Chemistry (Section 18.5)

18.65 One of the principles of green chemistry is that it is better to use as few steps as possible in making new chemicals. In what ways does following this rule advance the goals of green chemistry? How does this principle relate to energy efficiency?

18.66 A reaction for converting ketones to lactones, called the Baeyer–Villiger reaction,



Ketone 3-Chloroperbenzoic acid



Lactone 3-Chlorobenzoic acid

is used in the manufacture of plastics and pharmaceuticals. 3-Chloroperbenzoic acid is shock-sensitive, however, and prone to explode. Also, 3-chlorobenzoic acid is a waste product. An alternative process being developed uses hydrogen peroxide and a catalyst consisting of tin deposited within a solid support. The catalyst is readily recovered from the reaction mixture. (**a**) What would you expect to be the other product of oxidation of the ketone to lactone by hydrogen peroxide? (**b**) What principles of green chemistry are addressed by use of the proposed process?

18.67 In the following three instances, which choice is greener in each situation? Explain. (**a**) Petroleum as a raw material or vegetable oil as a raw material. (**b**) Toluene as a solvent or water as a solvent. (**c**) Catalyzed reaction at 600 K or uncatalyzed reaction at 800 K.

Additional Exercises

18.68 A friend of yours has seen each of the following items in newspaper articles and would like an explanation: (**a**) acid rain, (**b**) greenhouse gas, (**c**) photochemical smog, (**d**) ozone depletion. Give a brief explanation of each term and identify one or two of the chemicals associated with each.

18.69 Suppose that on another planet the atmosphere consists of 10% Kr, 40% CH_4, and 50% O_2. What is the average molar mass at the surface? What is the average molar mass at an altitude at which all the O_2 is photodissociated?

18.70 If an average O_3 molecule "lives" only 100–200 seconds in the stratosphere before undergoing dissociation, how can O_3 offer any protection from ultraviolet radiation?

18.71 Show how Equations 18.7 and 18.9 can be added to give Equation 18.10.

18.72 What properties of CFCs make them ideal for various commercial applications but also make them a long-term problem in the stratosphere?

18.73 *Halons* are fluorocarbons that contain bromine, such as $CBrF_3$. They are used extensively as foaming agents for fighting fires. Like CFCs, halons are very unreactive and ultimately can diffuse into the stratosphere. (**a**) Based on the data in Table 8.3, would you expect photodissociation of Br atoms to occur in the stratosphere? (**b**) Propose a mechanism by which the presence of halons in the stratosphere could lead to the depletion of stratospheric ozone.

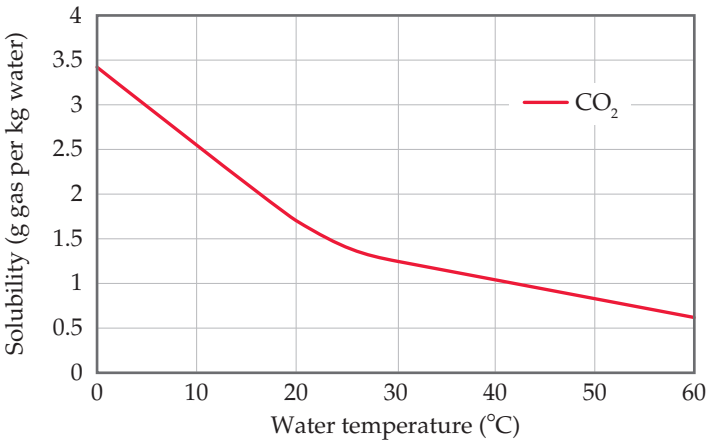
18.74 (**a**) What is the difference between a CFC and an HFC? (**b**) It is estimated that the lifetime for HFCs in the stratosphere is 2–7 years. Why is this number significant? (**c**)Why have HFCs been used to replace CFCs? (**d**) What is the major disadvantage of HFCs as replacements for CFCs?

18.75 Explain, using Le Châtelier's principle, why the equilibrium constant for the formation of NO from N_2 and O_2 increases with increasing temperature, whereas the equilibrium constant for the formation of NO_2 from NO and O_2 decreases with increasing temperature.

18.76 Liquefied petroleum gas (LPG) consists primarily of propane, $C_3H_8(l)$ or butane $C_4H_{10}(l)$. (**a**) Write a balanced chemical equation for the complete combustion of propane to produce $CO_2(g)$ as the only carbon-containing product. (**b**) Write a balanced chemical equation for the incomplete combustion of propane to produce $CO(g)$ as the only carbon-containing product. (**c**) At 25 °C and 101.3 kPa pressure, what is the minimum quantity of dry air needed to combust 10.0 mL of $C_3H_8(l)$ completely to $CO_2(g)$? The density of the LPG is 0.50 g/mL.

18.77 It was estimated that the eruption of the Mount Pinatubo volcano resulted in the injection of 20 million metric tons of SO_2 into the atmosphere. Most of this SO_2 underwent oxidation to SO_3, which reacts with atmospheric water to form an aerosol. (**a**) Write chemical equations for the processes leading to formation of the aerosol. (**b**) The aerosols caused a 0.5–0.6 °C drop in surface temperature in the northern hemisphere. What is the mechanism by which this occurs? (**c**) The sulfate aerosols, as they are called, also cause loss of ozone from the stratosphere. How might this occur?

18.78 One of the possible consequences of climate change is an increase in the temperature of ocean water. The oceans serve as a "sink" for CO_2 by dissolving large amounts of it.



(**a**) The accompanying figure shows the solubility of CO_2 in water as a function of temperature. Does CO_2 behave more or less similarly to other gases in this respect?

(**b**) What are the implications of this figure for the problem of climate change?

18.79 The rate of solar energy striking Earth averages 168 watts per square meter. The rate of energy radiated from Earth's surface averages 390 watts per square meter. Comparing these numbers, one might expect that the planet would cool quickly, yet it does not. Why not?

18.80 In 2008, the global average electricity consumption per head was 3.0 MWh. The solar power striking Earth every day averages 168 watts per square meter. Considering that present technology for solar energy conversion is about 10% efficient, from how many square meters of land must sunlight be collected in order to provide this power?

18.81 Write balanced chemical equations for each of the following reactions: (**a**) The carbon dioxide molecule undergoes photodissociation in the upper atmosphere. (**b**) The carbon dioxide molecule undergoes photoionization in the upper atmosphere. (**c**) Carbon monoxide undergoes oxidation by ozone in the stratosphere. (**d**) Carbon dioxide dissolves in water to form hydrogen carbonate.

18.82 (**a**) When sufficient Na_2CO_3 is added to a solution containing Mg^{2+}, $Mg(OH)_2$ will precipitate. Explain by writing balanced equations of the reactions. (**b**) Will $Mg(OH)_2$ precipitate when 2.0 g of Na_2CO_3 is added to 1.00 L of a solution containing 25 ppm of Mg^{2+}?

18.83 The CDC (Centers for Disease Control and Prevention) published a reference blood lead level (BLL), which is based on the BLL distribution among children. It is currently 5 μg/dL. (**a**) What is the molarity of an aqueous solution with this concentration? (**b**) Express this concentration in ppb.

Integrative Exercises

18.84 The estimated average concentration of NO_2 in air in an urbanized country in 2015 was 0.010 ppm. (**a**) Calculate the partial pressure of the NO_2 in a sample of this air when the atmospheric pressure is 101 kPa. (**b**) How many molecules of NO_2 are present under these conditions at 25 °C in a room that measures 10 m × 8 m × 2.50 m?

18.85 A 500 megawatt electrical power plant typically burned 1,430,000 tonne of coal in a year. (**a**) Assuming that the coal was 80% carbon and 3% sulfur and that combustion was complete, calculate the number of tonne of carbon dioxide and sulfur dioxide produced by the plant during the year. (**b**) If 50% of the SO_2 could be removed by reaction with powdered CaO to form $CaSO_3$, how many tonne of $CaSO_3$ would be produced?

18.86 Figure 14.4 shows the visible spectra of iodine (I_2) solutions at different concentrations (1 mg/L 100 mg/L). The absorption maximum is at 450 nm. (**a**) What color corresponds to a wavelength of 450 nm? (**b**) Calculate the extinction coefficient ε of iodine in this solution at 450 nm. Assume a common spectrometer path length of $b = 1.0$ cm.

18.87 Common lab spectrometers can detect absorbance down to 0.0002 with good reliability. Consider a dissolved harmful organic substance with a molar mass of 120.5 g/mol, which can be detected in this spectrometer. It shows an extinction coefficient of $\varepsilon = 1.43 \times 10^3\, M^{-1}\,cm^{-1}$ at 320 nm, its absorption maximum (A Closer Look, p. 667). (**a**) Calculate the minimum concentration of the organic substance detectable by this spectrometer (path length 1 cm). (**b**) Convert the minimum observable molarity to ppb.

18.88 The concentration of H_2O in the stratosphere is about 5 ppm. It undergoes photodissociation according to:

$$H_2O(g) \longrightarrow H(g) + OH(g)$$

(**a**) Write out the Lewis-dot structures for both products and reactant.

(**b**) Using Table 8.3, calculate the wavelength required to cause this dissociation.

(**c**) The hydroxyl radical, OH, can react with ozone, giving the following reactions:

$$OH(g) + O_3(g) \longrightarrow HO_2(g) + O_2(g)$$
$$HO_2(g) + O(g) \longrightarrow OH(g) + O_2(g)$$

What overall reaction results from these two elementary reactions? What is the catalyst in the overall reaction? Explain.

18.89 Bioremediation is the process by which bacteria repair their environment in response, for example, to an oil spill. The efficiency of bacteria for "eating" hydrocarbons depends on the amount of oxygen in the system, pH, temperature, and many other factors. In a certain oil spill, hydrocarbons from the oil disappeared with a first-order rate constant of $2 \times 10^{-6}\,s^{-1}$. At that rate, how many days would it take for the hydrocarbons to decrease to 10% of their initial value?

18.90 The standard enthalpies of formation of ClO and ClO_2 are 101 and 102 kJ/mol, respectively. Using these data and the thermodynamic data in Appendix C, calculate the overall enthalpy change for each step in the following catalytic cycle:

$$ClO(g) + O_3(g) \longrightarrow ClO_2(g) + O_2(g)$$
$$ClO_2(g) + O(g) \longrightarrow ClO(g) + O_2(g)$$

What is the enthalpy change for the overall reaction that results from these two steps?

18.91 The main reason that distillation is a costly method for purifying water is the high energy required to heat and vaporize water. (**a**) Using the density, specific heat, and heat of vaporization of water from Appendix B, calculate the amount of energy required to vaporize 1.00 L of water beginning with water at 25 °C. (**b**) If the energy is provided by electricity costing \$0.085/kWh, calculate its cost. (**c**) If distilled water sells in a grocery store for \$0.49 per L, what percentage of the sales price is represented by the cost of the energy?

18.92 A reaction that contributes to the depletion of ozone in the stratosphere is the direct reaction of oxygen atoms with ozone:

$$O(g) + O_3(g) \longrightarrow 2\,O_2(g)$$

At 298 K the rate constant for this reaction is $4.8 \times 10^5\, M^{-1}\,s^{-1}$. (**a**) Based on the units of the rate constant, write the likely rate law for this reaction. (**b**) Would you expect this reaction to occur via a single elementary process? Explain why or why not. (**c**) Use ΔH_f° values from Appendix C to estimate the enthalpy change for this reaction. Would this reaction raise or lower the temperature of the stratosphere?

18.93 The following data were collected for the decomposition of O_3 by ($O_3 + H \longrightarrow O_2 + OH$) at very low concentrations:

Trial	$[O_3]$ (M)	[H] (M)	Initial Rate (M/s)
1	3.25×10^{-33}	2.25×10^{-26}	8.10×10^{-15}
2	6.50×10^{-33}	4.50×10^{-26}	3.25×10^{-14}
3	6.48×10^{-33}	2.23×10^{-26}	1.62×10^{-14}

(**a**) Write the rate law for the reaction.

(**b**) Calculate the rate constant.

18.94 The degradation of CF_3CH_2F (an HFC) by OH radicals in the troposphere is first order in each reactant and has a rate constant of $k = 2.1 \times 10^8\, M^{-1}s^{-1}$ at 10 °C. If the tropospheric concentrations of OH and CF_3CH_2F are 1.0×10^{12} and 7.5×10^{14} molecules/m^3, respectively, what is the rate of reaction at this temperature in M/s?

18.95 The Henry's law constant for CO_2 in water at 25 °C is 3.4×10^{-4} mol/m^3-Pa (**a**) What is the solubility of CO_2 in water at this temperature if the solution is in contact with air at normal atmospheric pressure? (**b**) Assume that all of this CO_2 is in the form of H_2CO_3 produced by the reaction between CO_2 and H_2O:

$$CO_2(aq) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

What is the pH of this solution?

18.96 The precipitation of $Al(OH)_3$ ($K_{sp} = 1.3 \times 10^{-33}$) is sometimes used to purify water. (**a**) Estimate the pH at which precipitation of $Al(OH)_3$ will begin if 5.0 kg of $Al_2(SO_4)_3$ is added to 10,000 L of water. (**b**) Approximately how many pounds of CaO must be added to the water to achieve this pH?

18.97 The valuable polymer polyurethane is made by a condensation reaction of alcohols (ROH) with compounds that contain an isocyanate group (RNCO). Two reactions that can generate a urethane monomer are shown here:

(i) $RNH_2 + CO_2 \longrightarrow R{-}N{=}C{=}O + 2\,H_2O$

$$R{-}N{=}C{=}O + R'OH \longrightarrow R{-}\overset{\displaystyle H}{\underset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR'$$

(ii) $RNH_2 + \mathrm{Cl_2C{=}O} \longrightarrow R{-}N{=}C{=}O + 2\,HCl$

$$R{-}N{=}C{=}O + R'OH \longrightarrow R{-}\overset{\displaystyle H}{\underset{|}{N}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR'$$

(**a**) Which process, i or ii, is greener? Explain.
(**b**) What are the hybridization and geometry of the carbon atoms in each C-containing compound in each reaction?
(**c**) If you wanted to promote the formation of the isocyanate intermediate in each reaction, what could you do, using Le Châtelier's principle?

18.98 The pH of a particular raindrop is 5.6. (**a**) Assuming the major species in the raindrop are $H_2CO_3(aq)$, $HCO_3^-(aq)$, and $CO_3^{2-}(aq)$, calculate the concentrations of these species in the raindrop, assuming the total carbonate concentration is $1.0 \times 10^{-5}\,M$. The appropriate K_a values are given in Table 16.3. (**b**) What experiments could you do to test the hypothesis that the rain also contains sulfur-containing species that contribute to its pH? Assume you have a large sample of rain to test.

Design an Experiment

Considerable fracking of petroleum/gas wells (see Closer Look box in Section 18.4) has occurred in recent years in a particular rural area. The residents have complained that the water in the residential wells serving their domestic water needs has become contaminated with chemicals associated with the fracking operations. The well operators respond that the chemicals about which complaints are lodged occur naturally, and are not the result of well-drilling activities.

Describe experiments that you could conduct on the waters from residential wells to help determine whether and to what extent well contaminants are due to fracking operations. Among the chemicals that might be expected to be employed in fracking operations are hydrochloric acid, sodium chloride, ethylene glycol, borate salts, water-soluble gelling agents such as guar gum, citric acid, methanol, and other alcohols such as isopropanol, and methane. Assume that you have available the techniques to make measurements of the concentrations of these substances in the residential wells. What experiments would you conduct, and what analyses of the results would you carry out in an attempt to settle the question of whether fracking operations have led to contamination of the well water? Would simply measuring the concentrations of some or all of these substances in the well waters be sufficient to settle the issue?

WHAT'S AHEAD

19.1 ▶ Spontaneous Processes

19.2 ▶ Entropy and the Second Law of Thermodynamics

19.3 ▶ The Molecular Interpretation of Entropy and the Third Law of Thermodynamics

19.4 ▶ Entropy Changes in Chemical Reactions

19.5 ▶ Gibbs Free Energy

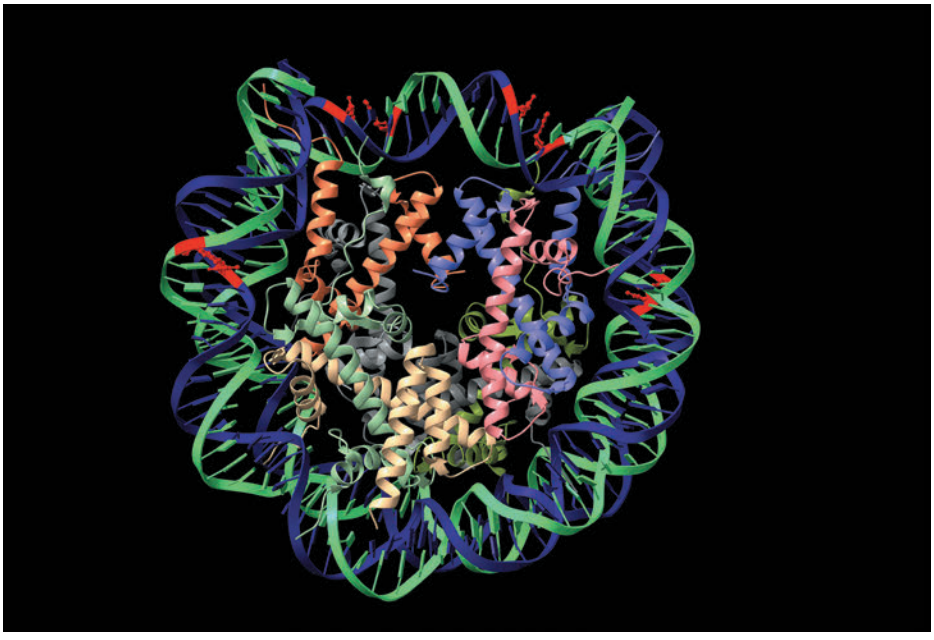
19.6 ▶ Free Energy and Temperature

19.7 ▶ Free Energy and the Equilibrium Constant

19

CHEMICAL THERMODYNAMICS

19.1 | Spontaneous Processes



The nucleosome is a macromolecule inside the nucleus of a living cell: DNA (the gray outer double-helical portion) surrounds eight protein molecules (the colored molecular models). This overall DNA/protein structure, called the nucleosome, is the basic unit of chromosomes in the nuclei of our cells. These structures are highly ordered, yet also must be unraveled for gene expression to take place. Both packaging and unpackaging of DNA in the nucleosome involve changes in the energy of the system.

The amazing organization of living systems, from complex molecular structures such as those of nucleosomes, to cells, to tissues, and finally to whole plants and animals, is an unending source of wonder and delight to the scientists who study them. Energy must be spent, somehow, to form and maintain these organized systems. But how is that energy channeled to accomplish these tasks? We cannot merely take the requisite atoms, put them in a pot, add energy, and get something like a nucleosome.

Understanding natural processes, whether they be DNA replication, photosynthesis, or merely the rusting of a nail, relies on understanding the general laws that govern chemical reactions.

In this chapter, we explore the connection between energy and the extent of a reaction. Doing so requires a deeper look at *chemical thermodynamics*, the area of chemistry that deals with energy relationships. We first considered thermodynamics in Chapter 5, where we discussed the nature of energy, the first law of thermodynamics, and the concept of enthalpy. In this chapter, we discuss the second law of thermodynamics and the concept of *entropy*, a thermodynamic quantity that we encountered briefly in Chapter 13. We start with a few definitions. By the end of this section, you should be able to

- Explain and apply the terms spontaneous process, reversible process, irreversible process, and isothermal process.

If you release a brick from your hand, it will fall. It never jumps back into your hand no matter how long you wait. Likewise, if you let a nail sit in the rain, it will eventually rust. The rusted nail will never convert to its original condition even when the sun shines and time passes. These are but two examples illustrating that there is directionality to events. We say that events like the falling brick and rusting nail occur spontaneously. A **spontaneous process** is one that occurs on its own without any outside assistance.

A spontaneous process occurs in one direction only, and the reverse of any spontaneous process is always *nonspontaneous*. Drop an egg above a hard surface, for example, and it breaks on impact (**Figure 19.1**). Now, imagine seeing a video clip in which a broken egg rises from the floor, reassembles itself, and ends up in someone's hand. You would conclude that the video is running in reverse because you know that broken eggs do not rise and reassemble themselves. An egg falling and breaking is a spontaneous process, whereas the egg rising and reassembling itself is a nonspontaneous process.

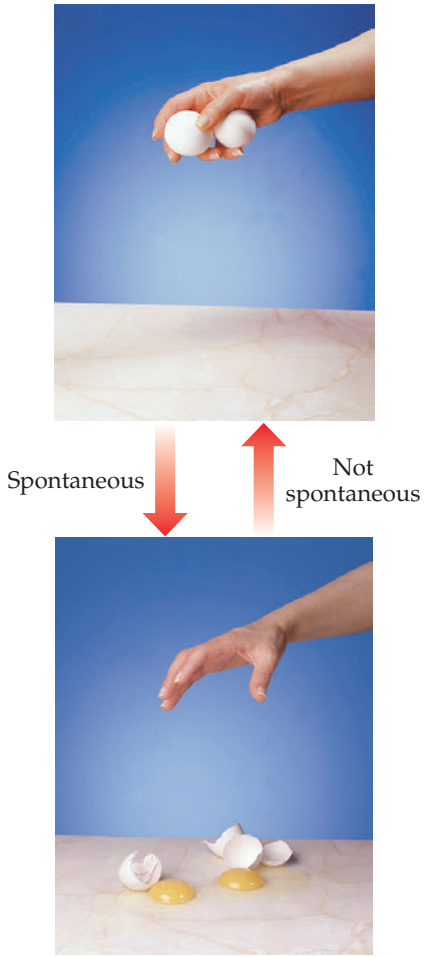
Processes that are spontaneous in one direction are nonspontaneous in the opposite direction.

Experimental conditions, such as temperature and pressure, are often important in determining whether a process is spontaneous. Consider, for example, the melting of ice. Ice melts spontaneously at atmospheric pressure when the temperature of the surroundings is above 0 °C. When the surroundings are below 0 °C, however, liquid water freezes spontaneously. The reverse process, melting, is then nonspontaneous as summarized in **Figure 19.2**.

We must not confuse the *spontaneity* of a process with *speed*. Just because a process is spontaneous does not necessarily mean that it will occur at an observable rate. A spontaneous process can be fast, as in the case of acid–base neutralization, or slow, as in the rusting of iron. Thermodynamics tells us the *direction* and *extent* of reaction but nothing about the rate.

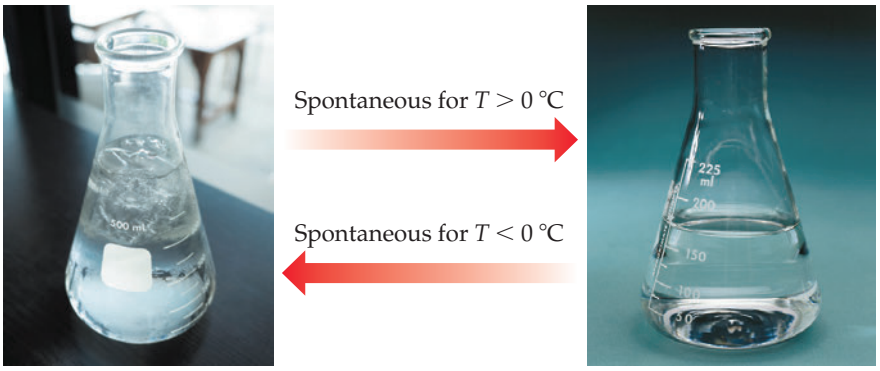
Go Figure

Does the potential energy of the eggs change during this process?



▲ **Figure 19.1** **A spontaneous process!**

Go Figure In which direction is this process exothermic?



▲ **Figure 19.2 Spontaneity can depend on temperature.** At $T > 0$ °C, ice melts spontaneously to liquid water. At $T < 0$ °C, the reverse process, water freezing to ice, is spontaneous. At $T = 0$ °C the two states are in equilibrium.

It is also important to understand that nonspontaneous does not mean impossible. For example, although the decomposition of table salt, NaCl, into sodium and chlorine is nonspontaneous under ordinary conditions, it is possible to decompose molten NaCl by supplying energy from an external source. A spontaneous process occurs without such outside intervention.

Sample Exercise 19.1

Identifying Spontaneous Processes

Predict whether each process is spontaneous as described, spontaneous in the reverse direction, or at equilibrium: (**a**) Water at 40 °C gets hotter when a piece of metal heated to 150 °C is added. (**b**) Water at room temperature decomposes into $H_2(g)$ and $O_2(g)$. (**c**) Benzene vapor, $C_6H_6(g)$, at a pressure of 101.3 kPa condenses to liquid benzene at the normal boiling point of benzene, 80.1 °C.

SOLUTION

Analyze We are asked to judge whether each process is spontaneous in the direction indicated, in the reverse direction, or in neither direction.

Plan We need to think about whether each process is consistent with our experience about the natural direction of events or whether we expect the reverse process to occur.

Solve

(**a**) This process is spontaneous. Whenever two objects at different temperatures are brought into contact, heat is transferred from the hotter object to the colder one. Thus, heat is transferred from the hot metal to the cooler water. The final temperature, after the metal and water achieve the same temperature (thermal equilibrium), will be somewhere between the initial temperatures of the metal and the water.

(**b**) Experience tells us that this process is not spontaneous—we certainly have never seen hydrogen and oxygen gases spontaneously bubbling up out of water! Rather, the *reverse* process—the reaction of H_2 and O_2 to form H_2O—is spontaneous.

(**c**) The normal boiling point is the temperature at which a vapor at 101.3 kPa is in equilibrium with its liquid. Thus, this is an equilibrium situation. If the temperature were below 80.1 °C, condensation would be spontaneous.

Practice Exercise

The process of iron being oxidized to make iron(III) oxide (rust) is spontaneous. Which of these statements about this process is/are true? (**a**) The reduction of iron(III) oxide to iron is also spontaneous. (**b**) Because the process is spontaneous, the oxidation of iron must be fast. (**c**) The oxidation of iron is endothermic. (**d**) Equilibrium is achieved in a closed system when the rate of iron oxidation is equal to the rate of iron(III) oxide reduction. (**e**) The energy of the universe is decreased when iron is oxidized to rust.

Seeking a Criterion for Spontaneity

A marble rolling down an incline or a brick falling from your hand loses potential energy. The loss of some form of energy is a common feature of spontaneous change in mechanical systems. In the 1870s, Marcellin Bertholet (1827–1907) suggested that the direction of spontaneous changes in chemical systems is determined by the loss of energy. He proposed that all spontaneous chemical and physical changes are exothermic. It takes only a few moments, however, to find exceptions to this generalization. For example, the melting of ice at room temperature is spontaneous and endothermic. Similarly, many spontaneous dissolution processes, such as the dissolving of NH_4NO_3, are endothermic, as we discovered in Section 13.1. We conclude that although the majority of spontaneous reactions are exothermic, there are spontaneous endothermic ones as well. Clearly, some other factor must be at work in determining the natural direction of processes.

To understand why certain processes are spontaneous, we need to consider more closely the ways in which the state of a system can change. Recall from Section 5.2 that quantities such as temperature, internal energy, and enthalpy are *state functions*, properties that define a state and do not depend on how we reach that state. The heat transferred between the system and its surroundings, q, and the work done on or by the system, w, are *not* state functions—their values depend on the specific way in which the change occurs. That is, their values depend on the *path* taken between states. Understanding two kinds of paths, those that are *reversible* and those that are *irreversible*, is a key to understanding spontaneity.

Reversible and Irreversible Processes

For any process, we can imagine a hypothetical, ideal path that can be reversed to restore both the system and its surroundings to exactly their original states. This means that after the process is reversed, both the system and surroundings are unchanged. Such an ideal process is said to be reversible.

- A **reversible process** is one for which we can restore the system to its original condition with no change to the surroundings.
- An **irreversible process** is one that leaves the surroundings somehow changed when the system is restored to its original state.

Sometimes these processes are referred to as being *thermodynamically reversible* or *thermodynamically irreversible* to add greater clarity to their meanings.

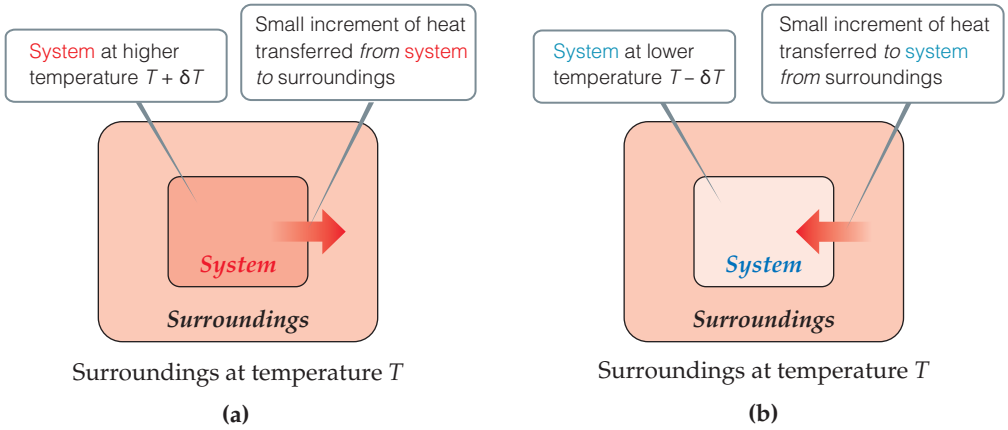
As an example, let's consider a process involving the transfer of heat. When two objects at different temperatures are in contact, heat flows spontaneously from the hotter object to the colder one. Because it is impossible to make the heat flow in the opposite direction, from colder to hotter, this is an irreversible process. Given this fact, can we imagine any hypothetical conditions under which the heat transfer could be reversible? The answer is yes, but only if we consider temperature changes that are infinitesimally small.

Imagine the system and its surroundings at essentially the same temperature, with just an infinitesimal temperature difference, δT, between them (**Figure 19.3**). If the surroundings are at temperature T and the system is at an infinitesimally higher temperature $T + \delta T$, then an infinitesimal amount of heat flows from the system to surroundings. We can reverse the direction of heat flow by making an infinitesimal change of temperature in the opposite direction, lowering the system temperature to $T - \delta T$. Now the direction of heat flow is from surroundings to system. Thus, for the process to be reversible, the amounts of heat must be infinitesimally small and the transfer of heat must occur infinitely slowly.

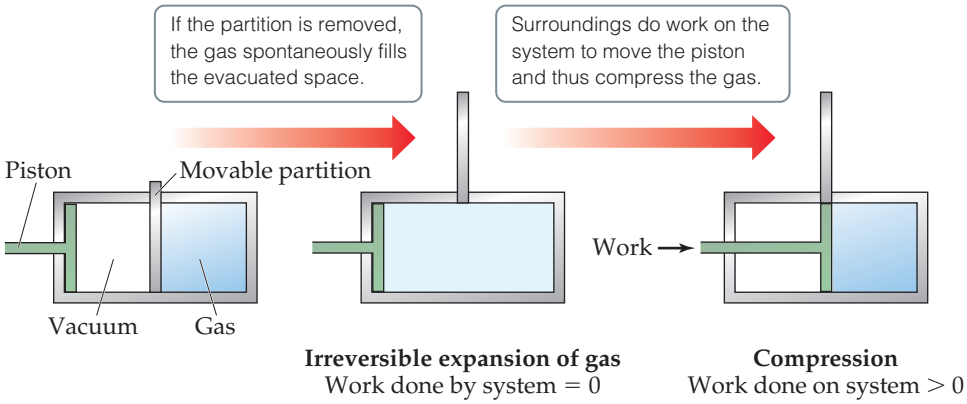
Reversible processes are those that reverse direction whenever an infinitesimal change is made in some property of the system.

Now let's consider another example, the expansion of an ideal gas at constant temperature (referred to as an **isothermal** process). In the cylinder-piston arrangement of **Figure 19.4**, when the partition is removed, the gas expands spontaneously to fill the evacuated space. Can we determine whether this particular isothermal expansion is

Go Figure If the flow of heat into or out of the system is to be reversible, what must be true of δT?



▲ **Figure 19.3 Reversible flow of heat.** Heat can flow reversibly between a system and its surroundings only if the two have an infinitesimally small difference in temperature δT. (**a**) Increasing the temperature of the system by δT causes heat to flow from the hotter system to the colder surroundings. (**b**) Decreasing the temperature of the system by δT causes heat to flow from the hotter surroundings to the colder system.



▲ **Figure 19.4 An irreversible process.** Initially, an ideal gas is confined to the right half of a cylinder. When the partition is removed, the gas spontaneously expands to fill the whole cylinder. No work is done by the system during this expansion. Using the piston to compress the gas back to its original state requires the surroundings to do work on the system.

reversible or irreversible? Because the gas expands into a vacuum with no external pressure, it does no P–V work on the surroundings. Thus, for the expansion, $w = 0$. We can use the piston to compress the gas back to its original state, but doing so requires that the surroundings do work on the system, meaning that $w > 0$ for the compression. In other words, the path that restores the system to its original state requires a different value of w (and, by the first law, a different value of q) than the path by which the system was first changed. The fact that the same path cannot be followed to restore the system to its original state indicates that the process is irreversible.

What might a *reversible* isothermal expansion of an ideal gas be? This process will occur only if initially, when the gas is confined to half the cylinder, the external pressure acting on the piston exactly balances the pressure exerted by the gas on the piston. If the external pressure is reduced infinitely slowly, the piston will move outward, allowing the pressure of the confined gas to readjust to maintain the pressure balance. This infinitely slow process in which the external pressure and internal pressure are always in equilibrium is reversible. If we reverse the process and compress the gas in the same infinitely

slow manner, we can return the gas to its original volume. The complete cycle of expansion and compression in this hypothetical process, moreover, is accomplished without any net change to the surroundings.

From these and other examples we learn two important facts:

- Because real processes can at best only approximate the infinitesimal changes associated with reversible processes, *all real processes are irreversible*.
- Because spontaneous processes are real processes, *all spontaneous processes are irreversible*.

Thus, for any spontaneous change, returning the system to its original condition results in a net change in the surroundings. But what kind of change occurs?

Recall that the first law of thermodynamics states that energy is conserved. In mathematical terms, $\Delta E = q + w$; that is, the change in internal energy of a system is equal to the heat absorbed (or released) by the system plus the work done on (or by) the system. If we return a system to its original condition, no net change in energy takes place, but there is a change in the nature of the energy. Returning the system to its initial condition requires us to do work on the system. Doing work requires a focused, relatively concentrated application of energy. During the process, that focused, concentrated energy gets converted to a more diffuse form. Thus, the net change in the surroundings involves the nature of the energy—it becomes more dispersed and disordered and therefore less able to do work.

What we observe about energy changes is that *energy has a tendency to spread out*. Consider a hot cup of tea. As it cools, energy spreads (or disperses) from the smaller volume of the tea into the greater volume of its surroundings. On a molecular level, the random, chaotic motion of particles (thermal motion) transfers energy through molecular collisions from the higher temperature (greater average kinetic energy) to lower temperature (lesser average kinetic energy) until the tea and its surroundings reach the same temperature. This natural tendency for energy to spread from a more concentrated form to a less concentrated form renders some of the energy unavailable to do work. Interestingly, a reversible process produces the maximum amount of work that can be done by a system on its surroundings.

Self-Assessment Exercise

19.1 Suppose you have a system made up of water only, with the container and everything beyond being the surroundings. Consider a process in which the water is first evaporated and then condensed back into its original container. Is this two-step process necessarily reversible?

(a) Yes

(b) No

Exercises

19.2 Which of the following processes are spontaneous: (**a**) the evaporation of water at STP to form water vapor of 101.3 kPa pressure; (**b**) separation of a mixture of water and oil into two separate phases; (**c**) the souring of milk; (**d**) the neutralization of hydrochloric acid with sodium hydroxide at STP; (**e**) the formation of ice from water at 20 °C and 101.3 kPa?

19.3 (**a**) Can endothermic chemical reactions be spontaneous? (**b**) Can a process be spontaneous at one temperature and nonspontaneous at a different temperature? (**c**) Water can be decomposed to form hydrogen and oxygen, and the hydrogen and oxygen can be recombined to form water. Does this mean that the processes are thermodynamically reversible? (**d**) Does the amount of work that a system can do on its surroundings depend on the path of the process?

19.4 The normal boiling point of *n*-octane (C_8H_{18}) is 125 °C. (**a**) Is the condensation of gaseous *n*-octane to liquid *n*-octane an endothermic or exothermic process? (**b**) In what temperature range is the boiling of *n*-octane a spontaneous process? (**c**) In what temperature range is it a nonspontaneous process? (**d**) Is there any temperature at which liquid *n*-octane and gaseous *n*-octane are in equilibrium? Explain.

19.5 Consider what happens when a sample of the explosive TNT is detonated under atmospheric pressure. (**a**) Is the detonation a reversible process? (**b**) What is the sign of *q* for this process? (**c**) Is *w* positive, negative, or zero for the process?

Answers to Self-Assessment Exercise

19.1 (b)

19.2 | Entropy and the Second Law of Thermodynamics



Refrigeration has had a massive impact on the transportation, storage, and preservation of food. While there are several ways to generate 'cold,' the most common one in modern refrigerators uses a vapor-compression cycle. Here a volatile liquid is evaporated by passing it through an expansion valve. This is an endothermic process with the heat drawn from the surroundings, which are cooled as a consequence. This is connected to the food storage compartment of the refrigerator. The gas is then condensed by passing it into a compressor with the heat generated by this condensation being removed via a heat exchanger to be discharged outside the refrigerator. Effectively, heat is removed from a cold area and added to a hot area. This is a nonspontaneous process but may be driven with the input of energy.

By the end of this section, you should be able to

- Define entropy and state the second law of thermodynamics.
- Calculate ΔS for a phase change.

In order to apply what we have learned about irreversible processes to predict whether an unfamiliar process is spontaneous, we must examine the thermodynamic quantity called entropy.

Entropy is a measure of the tendency for energy to spread or disperse, thereby reducing its ability to accomplish work. In a general sense, it reflects the degree of *randomness* or *disorder* associated with the particles that carry the energy.

In this section, we consider how entropy changes are related to heat transfer and temperature. Our analysis will bring us to a profound statement about entropy changes and spontaneity known as the second law of thermodynamics.

The Relationship between Entropy and Heat

The entropy, S, of a system is a state function just like internal energy, E, and enthalpy, H. As with these other quantities, the value of S is a characteristic of the state of a system. Thus, the change in entropy, ΔS, in a system depends only on the initial and final states of the system and not on the path taken from one state to the other:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \qquad [19.1]$$

For the special case of an isothermal process, ΔS is equal to the heat that would be transferred if the process were reversible, q_{rev}, divided by the absolute temperature at which the process occurs:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad \text{(constant } T\text{)} \qquad [19.2]$$

Although many possible paths can take the system from one state to another, only one path is associated with a reversible process. Thus, the value of q_{rev} is uniquely defined for any two states of the system. Because S is a state function, we can use Equation 19.2 to calculate ΔS for *any* isothermal process between states, not just the reversible one.

ΔS for Phase Changes

The melting of a substance at its melting point and the vaporization of a substance at its boiling point are isothermal processes. Consider the melting of ice. At 101.3 kPa, ice and liquid water are in equilibrium at 0 °C. Imagine melting 1 mol of ice at 0 °C, 101.3 kPa to form 1 mol of liquid water at 0 °C, 101.3 kPa. We can achieve this change by adding heat to the system from the surroundings: $q = \Delta H_{fusion}$, where ΔH_{fusion} is the heat of melting. Imagine adding the heat infinitely slowly, raising the temperature of the surroundings only infinitesimally above 0 °C. When we make the change in this fashion, the process is reversible because we can reverse it by infinitely slowly removing the same amount of heat, ΔH_{fusion}, from the system, using immediate surroundings that are infinitesimally below 0 °C. Thus, $q_{rev} = \Delta H_{fusion}$ for the melting of ice at $T = 0\,°C = 273\,K$.

The enthalpy of fusion for H_2O is $\Delta H_{fusion} = 6.01\,kJ/mol$ (a positive value because melting is an endothermic process). Thus, we can use Equation 19.2 to calculate ΔS_{fusion} for melting 1 mol of ice at 273 K:

$$\Delta S_{fusion} = \frac{q_{rev}}{T} = \frac{\Delta H_{fusion}}{T} = \frac{(1\,\cancel{mol})(6.01 \times 10^3\,J/\cancel{mol})}{273\,K} = 22.0\,J/K$$

Notice that (1) we must use the absolute temperature in Equation 19.2, and (2) the units for ΔS, J/K, are energy divided by absolute temperature, as we expect from Equation 19.2.

Sample Exercise 19.2

Calculating ΔS for a Phase Change

Elemental mercury is a silver liquid at room temperature. Its normal freezing point is −38.9 °C, and its molar enthalpy of fusion is $\Delta H_{fusion} = 2.29\,kJ/mol$. What is the entropy change of the system when 50.0 g of Hg(*l*) freezes at the normal freezing point?

SOLUTION

Analyze We first recognize that freezing is an *exothermic* process, which means heat is transferred from the system to the surroundings and $q < 0$. Because freezing is the reverse of melting, the enthalpy change that accompanies the freezing of 1 mol of Hg is $-\Delta H_{fusion} = -2.29\,kJ/mol$.

Plan We can use $-\Delta H_{fusion}$ and the atomic weight of Hg to calculate q for freezing 50.0 g of Hg. Then we use this value of q as q_{rev} in Equation 19.2 to determine ΔS for the system.

Solve

For q we have:

$$q = (50.0\,\cancel{g\,Hg})\left(\frac{1\,\cancel{mol\,Hg}}{200.59\,\cancel{g\,Hg}}\right)\left(\frac{-2.29\,\cancel{kJ}}{1\,\cancel{mol\,Hg}}\right)\left(\frac{1000\,J}{1\,\cancel{kJ}}\right) = -571\,J$$

Before using Equation 19.2, we must first convert the given Celsius temperature to kelvins:

$$-38.9\,°C = (-38.9 + 273.15)\,K = 234.3\,K$$

We can now calculate ΔS_{sys}:

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{-571\,J}{234.3\,K} = -2.44\,J/K$$

Check The entropy change is negative because our q_{rev} value is negative, which it must be because heat flows out of the system in this exothermic process.

Comment This procedure can be used to calculate ΔS for other isothermal phase changes, such as the vaporization of a liquid at its boiling point.

Practice Exercise

Do all exothermic phase changes have a negative value for the entropy change of the system? (**a**) Yes, because the heat transferred from the system has a negative sign. (**b**) Yes, because the temperature decreases during the phase transition. (**c**) No, because the entropy change depends on the sign of the heat transferred to or from the system. (**d**) No, because the heat transferred to the system has a positive sign. (**e**) More than one of the previous answers is correct.

A CLOSER LOOK The Entropy Change When a Gas Expands Isothermally

In general, the entropy of any system increases as the system becomes more random or more spread out. Thus, we expect the spontaneous expansion of a gas to result in an increase in entropy. To see how this entropy increase can be calculated, consider the expansion of an ideal gas that is initially constrained by a piston, as in the rightmost part of Figure 19.4. Imagine that we allow the gas to undergo a reversible isothermal expansion by infinitesimally decreasing the external pressure on the piston. The work done on the surroundings by the reversible expansion of the system against the piston can be calculated with the aid of calculus (we do not show the derivation):

$$w_{rev} = -nRT \ln \frac{V_2}{V_1}$$

In this equation, n is the number of moles of gas, R is the ideal-gas constant, T is the absolute temperature, V_1 is the initial volume, and V_2 is the final volume. Notice that if $V_2 > V_1$, as it must be in our expansion, then $w_{rev} < 0$, meaning that the expanding gas does work on the surroundings.

One characteristic of an ideal gas is that its internal energy depends only on temperature, not on pressure. Thus, when an ideal gas expands isothermally, $\Delta E = 0$. Because $\Delta E = q_{rev} + w_{rev} = 0$, we see that $q_{rev} = -w_{rev} = nRT \ln(V_2/V_1)$. Then, using Equation 19.2, we can calculate the entropy change in the system:

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T} = nR \ln \frac{V_2}{V_1} \qquad [19.3]$$

Let's calculate the entropy change for 1.00 L of an ideal gas at 101.3 kPa, 0 °C temperature, expanding to 2.00 L. From the ideal-gas equation, we can calculate the number of moles in 1.00 L of an ideal gas at 101.3 kPa and 0 °C as we did in Chapter 10:

$$n = \frac{PV}{RT} = \frac{(101.3\ \text{kPa})(1.00\ \cancel{\text{L}})}{(8.314\ \text{L kPa/mol}\ \cancel{\text{K}})(273\ \cancel{\text{K}})} = 4.46 \times 10^{-2}\ \text{mol}$$

The gas constant, R, can also be expressed as 8.314 J/mol K (Table 10.2), and this is the value we must use in Equation 19.3 because we want our answer to be expressed in terms of J rather than in L kPa. Thus, for the expansion of the gas from 1.00 L to 2.00 L, we have

$$\Delta S_{sys} = (4.46 \times 10^{-2}\ \cancel{\text{mol}})\left(8.314\ \frac{\text{J}}{\cancel{\text{mol}}\ \text{K}}\right)\left(\ln \frac{2.00\ \cancel{\text{L}}}{1.00\ \cancel{\text{L}}}\right)$$

$$= 0.26\ \text{J/K}$$

In Section 19.3 we will see that this increase in entropy is a measure of the increased randomness of the molecules due to the expansion.

Related Exercises: 19.11, 19.66

The Second Law of Thermodynamics

The key idea of the first law of thermodynamics is that energy is conserved in any process. Is entropy also conserved in a spontaneous process in the same way that energy is conserved?

Let's try to answer this question by calculating the entropy change of a system and the entropy change of its surroundings when our system is 1 mol of ice (a piece roughly the size of an ice cube) melting in the palm of your hand, which is part of the surroundings. The process is not reversible because the system and surroundings are at different temperatures. Nevertheless, because ΔS is a state function, its value is the same regardless of whether the process is reversible or irreversible. Earlier (just before Sample Exercise 19.2) we calculated the entropy change of this system:

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{(1\ \cancel{\text{mol}})(6.01 \times 10^3\ \text{J}/\cancel{\text{mol}})}{273\ \text{K}} = 22.0\ \text{J/K}$$

The portion of the surroundings immediately in contact with the ice is your palm, which we assume is at body temperature, 37 °C = 310 K. We will use this as the temperature of the surroundings. The quantity of heat lost by your palm is -6.01×10^3 J/mol, which is equal in magnitude to the quantity of heat gained by the ice but has the opposite sign. Hence, the entropy change of the surroundings is

$$\Delta S_{surr} = \frac{q_{rev}}{T} = \frac{(1\ \cancel{\text{mol}})(-6.01 \times 10^3\ \text{J}/\cancel{\text{mol}})}{310\ \text{K}} = -19.4\ \text{J/K}$$

We can consider that everything in the universe consists of the system of interest and its surroundings. Therefore, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$. Thus, the overall entropy change of the universe is positive in our example:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = (22.0\ \text{J/K}) + (-19.4\ \text{J/K}) = 2.6\ \text{J/K}$$

If the temperature of the surroundings were not 310 K but rather some temperature infinitesimally above 273 K, the melting would be reversible instead of irreversible. In that case, the entropy change of the surroundings would equal −22.0 J/K and ΔS_{univ} would be zero.

In general, any irreversible process results in an increase in the entropy of the universe, whereas any reversible process results in no change in the entropy of the universe:

$$\begin{aligned} &\textit{Reversible Process:} && \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \\ &\textit{Irreversible Process:} && \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \end{aligned} \qquad [19.4]$$

These equations summarize the **second law of thermodynamics**. Because spontaneous processes are irreversible, we can also state the second law this way:

The entropy of the universe increases for any spontaneous process.

The second law of thermodynamics tells us the essential character of any spontaneous change—it is always accompanied by an increase in the entropy of the universe. We can use this law as a criterion to predict whether or not a given process is spontaneous. Before seeing how this is done, however, we will find it useful to explore entropy from a molecular perspective.

A word on notation before we proceed: Throughout most of the remainder of this chapter, we will focus on systems rather than surroundings. To simplify the notation, we will usually refer to the entropy change of the system as ΔS rather than explicitly indicating ΔS_{sys}.

Self-Assessment Exercises

19.6 Sodium metal reacts with chlorine gas to form sodium chloride. This reaction is spontaneous and is accompanied by a decrease in the entropy of the system (the sodium and chlorine). What can we conclude about the entropy change of the surroundings?

(a) The entropy of the surroundings increases

(b) The entropy of the surroundings remains the same

(c) The entropy of the surroundings decreases

19.7 $\Delta S = 1.09$ J/mol K for the transition of solid rhombic sulfur to solid monoclinic sulfur at 95.5 °C. What is the enthalpy change, ΔH, for this transition?

(a) 11.4 J/mol

(b) 104 J/mol

(c) 402 J/mol

Exercises

19.8 Indicate whether each statement is true or false. (**a**) The entropy of the universe increases for any spontaneous process. (**b**) The entropy change of the system is equal and opposite that of the surroundings for any irreversible process. (**c**) The entropy of the system must increase in any spontaneous process. (**d**) The entropy change for an isothermal process depends on both the absolute temperature and the amount of heat reversibly transferred.

19.9 The element sodium (Na) melts at 97.8 °C, and its molar enthalpy of fusion is $\Delta H_{\text{fus}} = 2.60$ kJ/mol. (**a**) When molten sodium solidifies to Na(s), is ΔS positive or negative? (**b**) Calculate the value of ΔS when 50.0 g of Na(l) solidifies at 97.8 °C.

19.10 (**a**) Does the entropy of the surroundings increase for spontaneous processes? (**b**) In a particular spontaneous process the entropy of the system decreases. What can you conclude about the sign and magnitude of ΔS_{surr}? (**c**) During a certain reversible process, the surroundings undergo an entropy change, $\Delta S_{\text{surr}} = -78$ J/K. What is the entropy change of the system for this process?

19.11 (**a**) What sign for ΔS do you expect when the pressure on 0.600 mol of an ideal gas at 350 K is increased isothermally from an initial pressure of 76.0 kPa? (**b**) If the final pressure on the gas is 121.6 kPa, calculate the entropy change for the process. (**c**) Do you need to specify the temperature to calculate the entropy change?

Answers to Self-Assessment Exercises

19.6 (a) **19.7** (c)

19.3 The Molecular Interpretation of Entropy and the Third Law of Thermodynamics



Imagine a major sporting event, the final of a football match perhaps, and the roar of the crowd when the winning goal is kicked. Thousands of individual voices, all slightly different, but resulting in a single sound. In our discussion of entropy so far, we have considered the macroscopic interpretation of entropy and its relation to the system, the surroundings and the universe. In this section, we look at the microscopic interpretation of entropy—that is what is going on at a molecular level.

By the end of this section, you should be able to

- Explain how the entropy of a system is related to the number of possible microstates.
- Describe the kinds of molecular motion that a molecule can possess.
- Predict the sign of ΔS for physical and chemical processes.
- State the third law of thermodynamics.

As chemists, we are interested in molecules. What does entropy have to do with them and with their transformations? What molecular property does entropy reflect? Ludwig Boltzmann (1844–1906) gave another conceptual meaning to the notion of entropy, and to understand his contribution, we need to examine the ways in which we can interpret entropy at the molecular level.

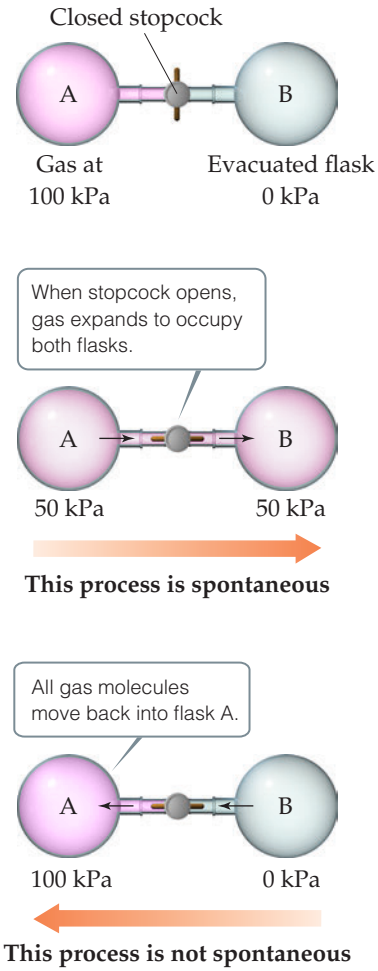
Expansion of a Gas at the Molecular Level

Consider a simple spontaneous process—the expansion of a gas into a vacuum as shown in **Figure 19.5**. Though we now understand that the entropy of the universe increases during the expansion, how can we explain the spontaneity of this process at the molecular level? We can get a sense of what makes this expansion spontaneous by envisioning the gas as a collection of particles in constant motion, as we did in discussing the kinetic-molecular theory of gases. When the stopcock in Figure 19.5 is opened, we can view the expansion of the gas as the ultimate result of the gas molecules moving randomly throughout the larger volume.

Let's look at this idea more closely by tracking two of the gas molecules as they move around. Before the stopcock is opened, both molecules are confined to the left flask, as shown in **Figure 19.6**(**a**). After the stopcock is opened, the molecules travel randomly throughout the entire apparatus. As Figure 19.6(**b**) shows, there are four possible arrangements for the two molecules once both flasks are available to them. Because the molecular motion is random, all four arrangements are equally likely.

Go Figure

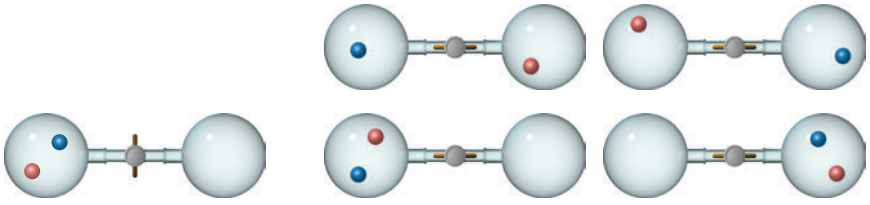
If flask B were smaller than flask A, would the final pressure after the stopcock is opened be greater than, equal to, or less than 50 kPa?



▲ **Figure 19.5 Expansion of a gas into an evacuated space is a spontaneous process.** The reverse process—gas molecules initially distributed evenly in two flasks all moving into one flask—is not spontaneous.

Note that now only one arrangement corresponds to the situation before the stopcock was opened: both molecules in the left flask.

Figure 19.6(b) shows that with both flasks available to the molecules, the probability of the red molecule being in the left flask is two in four (top right and bottom left arrangements), and the probability of the blue molecule being in the left flask is the same (top left and bottom left arrangements). Because the probability is $^2/_4 = {}^1/_2$ that each molecule is in the left flask, the probability that *both* are there is $(^1/_2)^2 = {}^1/_4$. If we apply the same



(a)
The two molecules are colored red and blue to keep track of them.

(b)
Four possible arrangements (microstates) once the stopcock is opened.

◀ **Figure 19.6 Possible arrangements of two gas molecules in two flasks.** (**a**) Before the stopcock is opened, both molecules are in the left flask. (**b**) After the stopcock is opened, there are four possible arrangements of the two molecules.

analysis to *three* gas molecules, we find that the probability that all three are in the left flask at the same time is $(1/2)^3 = 1/8$.

Now let's consider a *mole* of gas. The probability that all the molecules are in the left flask at the same time is $(1/2)^N$, where $N = 6.02 \times 10^{23}$. This is a vanishingly small number! Thus, there is essentially zero likelihood that all the gas molecules will be in the left flask at the same time. This analysis of the microscopic behavior of the gas molecules leads to the expected macroscopic behavior: The gas spontaneously expands to fill both the left and right flasks, and it does not spontaneously all go back in the left flask.

This molecular view of gas expansion shows the tendency of the molecules to "spread out" among the different arrangements they can take. Before the stopcock is opened, there is only one possible arrangement: all molecules in the left flask. When the stopcock is opened, the arrangement in which all the molecules are in the left flask is but one of an extremely large number of possible arrangements. The most probable arrangements by far are those in which there are essentially equal numbers of molecules in the two flasks. When the gas spreads throughout the apparatus, any given molecule can be in either flask rather than confined to the left flask. We say that with the stopcock opened, the arrangement of gas molecules is more dispersed than when the molecules are all confined in the left flask.

We will see that this notion of increasing dispersion helps us understand entropy at the molecular level.

Boltzmann's Equation and Microstates

The science of thermodynamics developed as a means of describing the properties of matter in our macroscopic world without regard to microscopic structure. In fact, thermodynamics was a well-developed field before the modern view of atomic and molecular structure was even known. The thermodynamic properties of water, for example, addressed the behavior of bulk water (or ice or water vapor) as a substance without considering any specific properties of individual H_2O molecules.

To connect the microscopic and macroscopic descriptions of matter, scientists have developed the field of *statistical thermodynamics*, which uses the tools of statistics and probability to link the microscopic and macroscopic worlds. Here we show how entropy, which is a property of bulk matter, can be connected to the behavior of atoms and molecules. Because the mathematics of statistical thermodynamics is complex, our discussion will be largely conceptual.

In our discussion of two gas molecules in the two-flask system in Figure 19.6, we saw that the number of possible arrangements helped explain why the gas expands.

Suppose we now consider one mole of an ideal gas in a particular thermodynamic state, which we can define by specifying the temperature, T, and volume, V, of the gas. What is happening to this gas at the microscopic level, and how does what is going on at the microscopic level relate to the entropy of the gas?

Imagine taking a snapshot of the positions and speeds of all the molecules at a given instant. The speed of each molecule relates to its kinetic energy. That particular set of 6×10^{23} positions and kinetic energies of the individual gas molecules is what we call a *microstate* of the system. A **microstate** is a single possible arrangement of the positions and kinetic energies of the molecules when the molecules are in a specific thermodynamic state. We could envision continuing to take snapshots of our system to see other possible microstates.

As you no doubt see, there would be such a staggeringly large number of microstates that taking individual snapshots of all of them is not feasible. Because we are examining such a large number of particles, however, we can use the tools of statistics and probability to determine the total number of microstates for the thermodynamic state. (That is where the *statistical* part of the name *statistical thermodynamics* comes in.) Each thermodynamic state has a characteristic number of microstates associated with it, and we will use the symbol W for that number.

Students sometimes have difficulty distinguishing between the state of a system and the microstates associated with the state.

- A *state* describes the macroscopic view of the system as characterized, for example, by the pressure and temperature of a sample of gas.

- A *microstate* is a particular microscopic arrangement of the atoms or molecules of the system that corresponds to the given state of the system.

Each of the snapshots we described is a microstate—the positions and kinetic energies of individual gas molecules will change from snapshot to snapshot, but each one is a possible arrangement of the collection of molecules corresponding to a single state. For macroscopically sized systems, such as a mole of gas, there is a very large number of microstates for each state—that is, W is generally an extremely large number.

The connection between the number of microstates of a system, W, and the entropy of the system, S, is expressed in a beautifully simple equation developed by Boltzmann and engraved on his tombstone (**Figure 19.7**):

$$S = k \ln W \qquad [19.5]$$

In this equation, k is the Boltzmann constant, 1.38×10^{-23} J/K. We see from the equation that:

Entropy is a measure of how many microstates are associated with a particular macroscopic state.

From Equation 19.5, we see that the entropy change accompanying any process is

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}} \qquad [19.6]$$

Any change in the system that leads to an increase in the number of microstates ($W_{\text{final}} > W_{\text{initial}}$) leads to a positive value of ΔS:

Entropy increases with the number of microstates of the system.



▲ **Figure 19.7 Ludwig Boltzmann's gravestone.** Boltzmann's gravestone in Vienna is inscribed with his famous relationship between the entropy of a state, S, and the number of available microstates, W. (In Boltzmann's time, "log" was used to represent the natural logarithm.)

Let's consider two modifications to our ideal-gas sample and see how the entropy changes in each case. First, suppose we increase the volume of the system, which is analogous to allowing the gas to expand isothermally. A greater volume means a greater number of positions available to the gas atoms and therefore a greater number of microstates. The entropy therefore increases as the volume increases, as we saw in the "A Closer Look" box in Section 19.2.

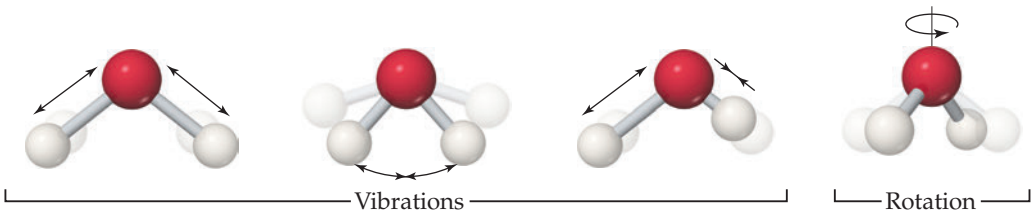
Second, suppose we keep the volume fixed but increase the temperature. How does this change affect the entropy of the system? Recall the distribution of molecular speeds presented in Figure 10.12(a). An increase in temperature increases the most probable speed of the molecules and also broadens the distribution of speeds. Hence, the molecules have a greater number of possible kinetic energies, and the number of microstates increases. Thus, the entropy of the system increases with increasing temperature.

Molecular Motions and Energy

The particles of an ideal gas are idealized points with no volume and no bonds, however—points that we visualize as flitting around through space. Any real molecule can undergo three kinds of more complex motion. The entire molecule can move in one direction, which is the simple motion we visualize for an ideal particle and see in a macroscopic object, such as a thrown ball. We call such movement **translational motion**. The molecules in a gas have more freedom of translational motion than those in a liquid, which have more freedom of translational motion than the molecules of a solid.

A real molecule can also undergo **vibrational motion**, in which the atoms in the molecule move periodically toward and away from one another, and **rotational motion**, in which the molecule spins about an axis. **Figure 19.8** shows the vibrational motions and one of the rotational motions possible for the water molecule. These different forms of motion are ways in which a molecule can store energy.

Go Figure Describe another possible rotational motion for this molecule.



▲ **Figure 19.8** **Vibrational and rotational motions in a water molecule.**

The vibrational and rotational motions possible in real molecules lead to arrangements that a single atom cannot have. A collection of real molecules therefore has a greater number of possible microstates than does the same number of ideal-gas particles. In general, *the number of microstates possible for a system increases with an increase in volume, an increase in temperature, or an increase in the number of molecules because any of these changes increases the possible positions and kinetic energies of the molecules making up the system*. We will also see that the number of microstates increases as the complexity of the molecule increases because there are more vibrational motions available.

Chemists have several ways of describing an increase in the number of microstates possible for a system and therefore an increase in the entropy for the system. Each way seeks to capture a sense of the increased freedom of motion that causes molecules to spread out when not restrained by physical barriers or chemical bonds.

The most common way of describing an increase in entropy is the increase in the *randomness*, or *disorder*, of the system. Another way likens an entropy increase to an increased *dispersion (spreading out) of energy* because there is an increase in the number of ways the positions and energies of the molecules can be distributed throughout the system. Each description (randomness or energy dispersal) is conceptually helpful if applied correctly.

Making Qualitative Predictions about ΔS

It is usually not difficult to estimate qualitatively how the entropy of a system changes during a simple process. As noted earlier, an increase in either the temperature or the volume of a system leads to an increase in the number of microstates, and hence an increase in the entropy. One more factor that correlates with number of microstates is the number of independently moving particles.

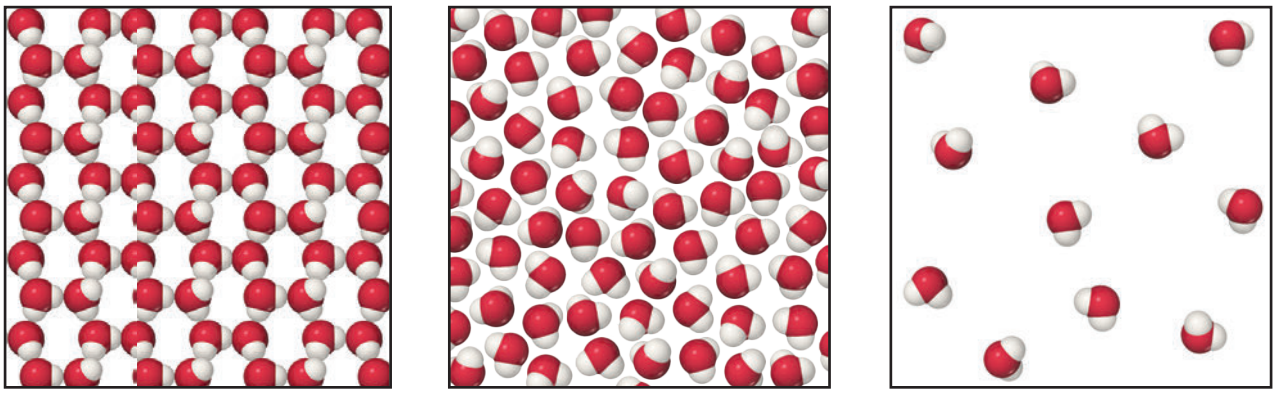
We can usually make qualitative predictions about entropy changes by focusing on these factors. For example, when water vaporizes, the molecules spread out into a larger volume. Because they occupy a larger volume, there is an increase in their freedom of motion, giving rise to a greater number of possible microstates, and hence an increase in entropy.

Now consider the phases of water. In ice, hydrogen bonding leads to the rigid structure shown in **Figure 19.9**. Each molecule in the ice is free to vibrate, but its translational and rotational motions are much more restricted than in liquid water. Although there are hydrogen bonds in liquid water, the molecules can more readily move about relative to one another (translation) and tumble around (rotation). During melting, therefore, the number of possible microstates increases, and so does the entropy. In water vapor, the molecules are essentially independent of one another and have their full range of translational, vibrational, and rotational motions. Thus, water vapor has an even greater number of possible microstates and therefore a higher entropy than liquid water or ice.

When an ionic solid dissolves in water, a mixture of water and ions replaces the pure solid and pure water, as shown for KCl in **Figure 19.10**. The ions in the solution move in a volume that is larger than the volume in which they were able to move in

Go Figure In which phase are water molecules least able to have rotational motion?

Increasing entropy



▲ **Figure 19.9 Entropy and the phases of water.** The larger the number of possible microstates, the higher the entropy of the system.

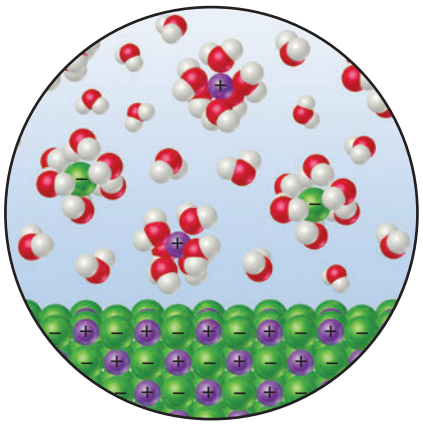
the crystal lattice and so undergo more motion. This increased motion might lead us to conclude that the entropy of the system has increased. We have to be careful, however, because some of the water molecules have lost some freedom of motion because they are now held around the ions as water of hydration. These water molecules are in a *more* ordered state than before because they are now confined to the immediate environment of the ions. Therefore, the dissolving of a salt involves both a disordering process (the ions become less confined) and an ordering process (some water molecules become more confined). The disordering processes are usually dominant, and so the overall effect is an increase in the randomness of the system when most salts dissolve in water.

Now, imagine arranging biomolecules into a highly organized biochemical system, such as the nucleosome in the opening figure of section 19.1. We might expect that the creation of this well-ordered structure would lead to a decrease in the entropy of the system. But this is frequently not the case. Waters of hydration and counterions can be expelled from the interface as two large biomolecules interact, and so the entropy of the system can actually increase—if you consider the water and counterions to be part of the system.

The same ideas apply to chemical reactions. Consider the reaction between nitric oxide gas and oxygen gas to form nitrogen dioxide gas:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \qquad [19.7]$$

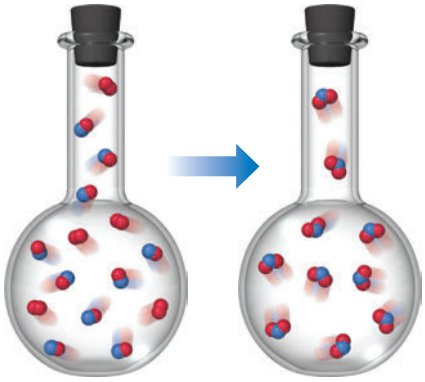
which results in a decrease in the number of molecules—three molecules of gaseous reactants form two molecules of gaseous products (**Figure 19.11**). The formation of new N—O bonds reduces the motions of the atoms in the system. The formation of new bonds decreases the *number of degrees of freedom*, or forms of motion, available to the atoms. That is, the atoms are less free to move in random fashion because of the formation of new bonds. The decrease in the number of molecules and the resultant decrease in motion result in fewer possible microstates and therefore a decrease in the entropy of the system.



▲ **Figure 19.10 Entropy changes when an ionic solid dissolves in water.** The ions become more spread out and disordered, but the water molecules that hydrate the ions become less disordered.

Go Figure

What major factor leads to a decrease in entropy as this reaction takes place?



$2\,NO(g) + O_2(g)$ $2\,NO_2(g)$

▲ **Figure 19.11 Entropy decreases when $NO(g)$ is oxidized by $O_2(g)$ to $NO_2(g)$.** A decrease in the number of gaseous molecules leads to a decrease in the entropy of the system.

In summary, we generally expect the entropy of a system to increase for processes in which

1. Gases form from either solids or liquids.
2. Liquids or solutions form from solids.
3. The number of gas molecules increases during a chemical reaction.

The Third Law of Thermodynamics

If we decrease the thermal energy of a system by lowering the temperature, the energy stored in translational, vibrational, and rotational motion decreases. As less energy is stored, the entropy of the system decreases because it has fewer and fewer microstates available. If we keep lowering the temperature, do we reach a state in which these motions are essentially shut down, a point described by a single microstate? This question is addressed by the **third law of thermodynamics**:

The entropy of a pure, perfect crystalline substance at absolute zero is zero: $S(0\,K) = 0$.

Consider a pure, perfect crystalline solid. At absolute zero, the individual atoms or molecules in the lattice would be perfectly ordered in position. Because none of them would have thermal motion, there is only one possible microstate. As a result, Equation 19.5 becomes $S = k \ln W = k \ln 1 = 0$. As the temperature is increased from absolute zero, the atoms or molecules in the crystal gain energy in the form of vibrational motion about their lattice positions. This means that the degrees of freedom and the entropy both increase. What happens to the entropy, however, as we continue to heat the crystal? We consider this important question in the next section.

Sample Exercise 19.3

Predicting the Sign of ΔS

Predict whether ΔS is positive or negative for each process, assuming each occurs at constant temperature:

(**a**) $H_2O(l) \longrightarrow H_2O(g)$

(**b**) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

(**c**) $4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$

(**d**) $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$

SOLUTION

Analyze We are given four reactions and asked to predict the sign of ΔS for each.

Plan We expect ΔS to be positive if there is an increase in temperature, increase in volume, or increase in number of gas particles. The question states that the temperature is constant, and so we need to concern ourselves only with volume and number of particles.

Solve

(**a**) Evaporation involves a large increase in volume as liquid changes to gas. One mole of water (18 g) occupies about 18 mL as a liquid, and if it could exist as a gas at STP it would occupy 22.4 L. Because the molecules are distributed throughout a much larger volume in the gaseous state, an increase in motional freedom accompanies vaporization and ΔS is positive.

(**b**) In this process, ions, which are free to move throughout the volume of the solution, form a solid, in which they are confined to a smaller volume and restricted to more highly constrained positions. Thus, ΔS is negative.

(**c**) The particles of a solid are confined to specific locations and have fewer ways to move (fewer microstates) than do the molecules of a gas. Because O_2 gas is converted into part of the solid product Fe_2O_3, ΔS is negative.

(**d**) The number of moles of reactant gases is the same as the number of moles of product gases, and so the entropy change is expected to be small. The sign of ΔS is impossible to predict based on our discussions thus far, but we can predict that ΔS will be close to zero.

Practice Exercise

Indicate whether each process produces an increase or decrease in the entropy of the system:

(**a**) $CO_2(s) \longrightarrow CO_2(g)$

(**b**) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

(**c**) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

(**d**) $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

Sample Exercise 19.4

Predicting Relative Entropies

In each pair, choose the system that has greater entropy and explain your choice: (**a**) 1 mol of NaCl(*s*) or 1 mol of HCl(*g*) at 25 °C, (**b**) 2 mol of HCl(*g*) or 1 mol of HCl(*g*) at 25 °C, (**c**) 1 mol of HCl(*g*) or 1 mol of Ar(*g*) at 298 K.

SOLUTION

Analyze We need to select the system in each pair that has the greater entropy.

Plan We examine the state of each system and the complexity of the molecules it contains.

Solve (**a**) HCl(*g*) has the higher entropy because the particles in gases are more disordered and have more freedom of motion than the particles in solids. (**b**) When these two systems are at the same pressure, the sample containing 2 mol of HCl has twice the number of molecules as the sample containing 1 mol. Thus, the 2-mol sample has twice the number of microstates and twice the entropy. (**c**) The HCl system has the higher entropy because the number of ways in which an HCl molecule can store energy is greater than the number of ways in which an Ar atom can store energy. (Molecules can rotate and vibrate; atoms cannot.)

Practice Exercise

Choose the system with the greater entropy in each case: (**a**) 1 mol of $H_2(g)$ at STP or 1 mol of $SO_2(g)$ at STP, (**b**) 1 mol of $N_2O_4(g)$ at STP or 2 mol of $NO_2(g)$ at STP.

CHEMISTRY AND LIFE Entropy and Human Society

Any living organism is a complex, highly organized, well-ordered system, even at the molecular level like the nucleosome we saw at the beginning of section 19.1. Our entropy content is much lower than it would be if we were completely decomposed into carbon dioxide, water, and several other simple chemicals. Does this mean that life is a violation of the second law? No, because the thousands of chemical reactions necessary to produce and maintain life have caused a large increase in the entropy of the rest of the universe. Thus, as the second law requires, the overall entropy change during the lifetime of a human, or any other living system, is positive.

The second law of thermodynamics applies also to the way we humans order our surroundings. In addition to being complex living systems ourselves, we are masters of producing order in the world around us. We manipulate and order matter at the nanoscale level in order to produce the technological breakthroughs that have become so commonplace in the twenty-first century. We use tremendous quantities of raw materials to produce highly ordered materials. In so doing, we expend a great deal of energy to, in essence, "fight" the second law of thermodynamics.

For every bit of order we produce, however, we produce an even greater amount of disorder. Petroleum, coal, and natural gas are burned to provide the energy necessary for us to achieve highly ordered structures, but their combustion increases the entropy of the universe by releasing $CO_2(g)$, $H_2O(g)$, and heat. Thus, even as we strive to create more impressive discoveries and greater order in our society, we drive the entropy of the universe higher, as the second law says we must.

We humans are, in effect, using up our storehouse of energy-rich materials to create order and advance technology. As noted in Chapter 5, we must learn to harness new energy sources, such as solar energy and thereby reduce our dependence on nonrenewable sources.

Self-Assessment Exercises

19.12 What is the entropy of a system that has only a single microstate?

(a) $S = 0$ J/K

(b) $S = 1$ J/K

(c) $S = 6.02 \times 10^{23}$ J/K

19.13 Can an argon atom undergo vibrational motion?

(a) Yes

(b) No

19.14 Predict the sign of ΔS for the oxidation of glucose at constant temperature: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

(a) $\Delta S > 0$

(b) $\Delta S < 0$

Exercises

19.15 (**a**) What is the difference between a *state* and a *microstate* of a system? (**b**) As a system goes from state A to state B, its entropy decreases. What can you say about the number of microstates corresponding to each state? (**c**) In a particular spontaneous process, the number of microstates available to the system decreases. What can you conclude about the sign of ΔS_{surr}?

19.16 (**a**) Using the heat of vaporization in Appendix B, calculate the entropy change for the vaporization of water at 25 °C and at 100 °C. (**b**) From your knowledge of microstates and the structure of liquid water, explain the difference in these two values.

19.17 (**a**) In a chemical reaction, two gases combine to form a solid. What do you expect for the sign of ΔS? (**b**) How does the entropy of the system change in the processes described in Exercise 19.2?

19.18 Does the entropy of the system increase, decrease, or stay the same when (**a**) the temperature of the system increases, (**b**) the volume of a gas increases, (**c**) equal volumes of ethanol and water are mixed to form a solution?

19.19 Indicate whether each statement is true or false. (**a**) Unlike enthalpy, where we can only ever know changes in H, we can know absolute values of S. (**b**) If you heat a gas such as CO_2, you will increase its degrees of translational, rotational and vibrational motions. (**c**) $CO_2(g)$ and Ar(g) have nearly the same molar mass. At a given temperature, they will have the same number of microstates.

19.20 For each of the following pairs, predict which substance possesses the larger entropy per mole: (**a**) 1 mol of $O_2(g)$ at 300 °C, 1.013 kPa, or 1 mol of $O_3(g)$ at 300 °C, 1.013 kPa; (**b**) 1 mol of $H_2O(g)$ at 100 °C, 101.3 kPa, or 1 mol of $H_2O(l)$ at 100 °C, 101.3 kPa; (**c**) 0.5 mol of $N_2(g)$ at 298 K, 20-L volume, or 0.5 mol $CH_4(g)$ at 298 K, 20-L volume; (**d**) 100 g $Na_2SO_4(s)$ at 30 °C or 100 g $Na_2SO_4(aq)$ at 30 °C.

19.21 Predict the sign of ΔS_{sys} for each of the following processes: (**a**) Gaseous H_2 reacts with liquid palmitoleic acid ($C_{16}H_{30}O_2$, unsaturated fatty acid) to form liquid palmitic acid ($C_{16}H_{32}O_2$ saturated fatty acid). (**b**) Liquid palmitic acid solidifies at 1 °C to solid palmitic acid. (**c**) Silver chloride precipitates upon mixing $AgNO_3(aq)$ and $NaCl(aq)$. (**d**) Gaseous H_2 dissociates in an electric arc to form gaseous H atoms (used in atomic hydrogen welding).

Answers to Self-Assessment Exercises

19.12 (a) **19.13** (b) **19.14** (a)

19.4 Entropy Changes in Chemical Reactions



Some reactions, such as the burning of jet fuel to give gaseous products, have an obvious entropy change associated with them, but can we measure entropy changes in all chemical reactions?

By the end of this section, you should be able to

- Use standard molar entropy values to calculate the entropy change of a chemical reaction.

In Section 5.5, we discussed how calorimetry can be used to measure ΔH for chemical reactions. No comparable method exists for measuring ΔS for a reaction. However, because the third law establishes a zero point for entropy, we can use experimental measurements to determine the *absolute value of the entropy*, S. To see schematically how this is done, let's review in greater detail the variation in the entropy of a substance with temperature.

Temperature Variation of Entropy

We know that the entropy of a pure, perfect crystalline solid at 0 K is zero and that the entropy increases as the temperature of the crystal is increased. **Figure 19.12** shows that the entropy of the solid increases steadily with increasing temperature up to the melting point of the solid. When the solid melts, the atoms or molecules are free to move about the entire volume of the sample. The added degrees of freedom increase the randomness of the substance, thereby increasing its entropy. We therefore see a sharp increase in the entropy at the melting point. After all the solid has melted, the temperature again increases and with it, the entropy.

At the boiling point of the liquid, another abrupt increase in entropy occurs. We can understand this increase as resulting from the increased volume available to the atoms or molecules as they enter the gaseous state. When the gas is heated further, the entropy increases steadily as more energy is stored in the translational motion of the gas atoms or molecules.

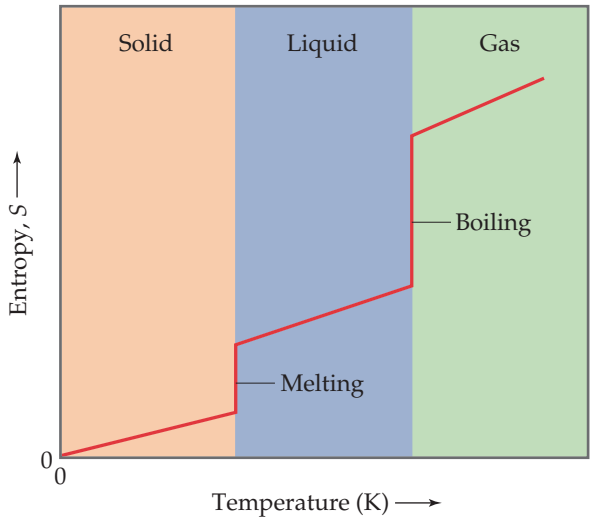
Another change occurring at higher temperatures is the skewing of molecular speeds toward higher values (Figure 10.12(a)). The expansion of the range of speeds leads to increased kinetic energy and increased disorder and, hence, increased entropy. The conclusions we reach in examining Figure 10.12 are consistent with what we noted earlier: Entropy generally increases with increasing temperature because the increased motional energy leads to a greater number of possible microstates.

Entropy versus temperature graphs such as Figure 19.12 can be obtained by carefully measuring how the heat capacity of a substance varies with temperature, and we can use the data to obtain the absolute entropies at different temperatures. (The theory and methods used for these measurements and calculations are beyond the scope of this text.) Entropies are usually tabulated as molar quantities, in units of joules per mole kelvin (J/mol K).

Standard Molar Entropies

Molar entropies for substances in their standard states are known as **standard molar entropies** and denoted $S°$. The standard state for any substance is defined as the pure

Go Figure Why does the plot show vertical jumps at the melting and boiling points?



▲ **Figure 19.12** **Entropy increases with increasing temperature.**

TABLE 19.1 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S°$ (J/mol K)
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

substance at 1 atm pressure. Table 19.1 lists the values of $S°$ for a number of substances at 298 K; Appendix C gives a more extensive list.

We can make several observations about the $S°$ values in Table 19.1:

1. Unlike enthalpies of formation, standard molar entropies of elements at the reference temperature of 298 K are *not* zero.
2. The standard molar entropies of gases are greater than those of liquids and solids, consistent with our interpretation of experimental observations, as represented in Figure 19.12.
3. Standard molar entropies generally increase with increasing molar mass.
4. Standard molar entropies generally increase with an increasing number of atoms in the formula of a substance.

Point 4 is related to the molecular motion discussed in Section 19.3. In general, as the number of atoms increases, the number of possible microstates also increases. Figure 19.13 compares the standard molar entropies of three hydrocarbons in the gas phase. Notice how the entropy increases as the number of atoms in the molecule increases.

Calculating the Standard Entropy Change for a Reaction

The entropy change in a chemical reaction equals the sum of the entropies of the products minus the sum of the entropies of the reactants:

$$\Delta S° = \sum nS°(\text{products}) - \sum mS°(\text{reactants}) \qquad [19.8]$$

As in Equation 5.31, the coefficients n and m are the coefficients in the balanced chemical equation for the reaction.

Entropy Changes in the Surroundings

We can use tabulated absolute entropy values to calculate the standard entropy change in a system, such as a chemical reaction, as just described. But what about the entropy change in the surroundings? We encountered this situation in Section 19.2, but it is good to revisit it now that we are examining chemical reactions.

We should recognize that the surroundings for any system serve essentially as a large, constant-temperature heat source (or heat sink if the heat flows from the system to the surroundings). The change in entropy of the surroundings depends on how much heat is absorbed or given off by the system.

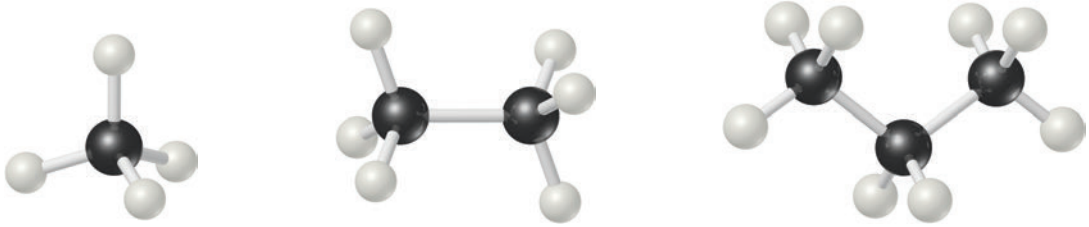
For an isothermal process, the entropy change of the surroundings is given by

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{-q_{sys}}{T}$$

Because in a constant-pressure process, q_{sys} is simply the enthalpy change for the reaction, ΔH, we can write

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} \quad [\text{at constant P}] \qquad [19.9]$$

Go Figure What might you expect for the value of $S°$ for butane, C_4H_{10}?



Methane, CH_4
$S° = 186.3$ J/mol K

Ethane, C_2H_6
$S° = 229.6$ J/mol K

Propane, C_3H_8
$S° = 270.3$ J/mol K

▲ **Figure 19.13** Entropy increases with increasing molecular complexity.

Sample Exercise 19.5

Calculating ΔS° from Tabulated Entropies

Calculate the change in the standard entropy of the system, ΔS°, for the synthesis of ammonia from $N_2(g)$ and $H_2(g)$ at 298 K:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

SOLUTION

Analyze We are asked to calculate the standard entropy change for the synthesis of $NH_3(g)$ from its constituent elements.

Plan We can make this calculation using Equation 19.8 and the standard molar entropy values in Table 19.1 and Appendix C.

Solve

Using Equation 19.8, we have:

$$\Delta S^\circ = 2\,S^\circ(NH_3) - [S^\circ(N_2) + 3\,S^\circ(H_2)]$$

Substituting the appropriate S° values from Table 19.1 yields:

$$\begin{aligned}\Delta S^\circ &= (2\,\text{mol})(192.5\,\text{J/mol K}) - [(1\,\text{mol})(191.5\,\text{J/mol K}) \\ &\quad + (3\,\text{mol})(130.6\,\text{J/mol K})] \\ &= -198.3\,\text{J/K}\end{aligned}$$

Check: The value for ΔS° is negative, in agreement with our qualitative prediction based on the decrease in the number of molecules of gas during the reaction.

Practice Exercise

Using the standard molar entropies in Appendix C, calculate the standard entropy change, ΔS°, for the "water-splitting" reaction at 298 K:

$$2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$$

(**a**) 326.3 J/K (**b**) 265.7 J/K (**c**) 163.2 J/K (**d**) 88.5 J/K (**e**) −326.3 J/K

For the ammonia synthesis reaction in Sample Exercise 19.5, q_{sys} is the enthalpy change for the reaction under standard conditions, ΔH°, so the changes in entropy will be standard entropy changes, ΔS°. Therefore, using the procedures described in Section 5.7, we have

$$\begin{aligned}\Delta H^\circ_{rxn} &= 2\,\Delta H_f^\circ[NH_3(g)] - 3\,\Delta H_f^\circ[H_2(g)] - \Delta H_f^\circ[N_2(g)] \\ &= 2(-46.19\,\text{kJ}) - 3(0\,\text{kJ}) - (0\,\text{kJ}) = -92.38\,\text{kJ}\end{aligned}$$

The negative value tells us that at 298 K the formation of ammonia from $H_2(g)$ and $N_2(g)$ is exothermic. The surroundings absorb the heat given off by the system, which means an increase in the entropy of the surroundings:

$$\Delta S^\circ_{surr} = \frac{92.38\,\text{kJ}}{298\,\text{K}} = 0.310\ \text{kJ/K} = 310\,\text{J/K}$$

Notice that the magnitude of the entropy gained by the surroundings is greater than that lost by the system, calculated as −198.3 J/K in Sample Exercise 19.5.

The overall entropy change for the reaction is

$$\Delta S^\circ_{univ} = \Delta S^\circ_{sys} + \Delta S^\circ_{surr} = -198.3\,\text{J/K} + 310\,\text{J/K} = 112\,\text{J/K}$$

Because ΔS°_{univ} is positive for any spontaneous reaction, this calculation indicates that when $NH_3(g)$, $H_2(g)$, and $N_2(g)$ are together at 298 K in their standard states (each at 101.3 kPa pressure), the reaction moves spontaneously toward formation of $NH_3(g)$.

Keep in mind that while the thermodynamic calculations indicate that formation of ammonia is spontaneous, they do not tell us anything about the rate at which ammonia is formed. Establishing equilibrium in this system within a reasonable period requires a catalyst, as discussed in Section 15.5.

Self-Assessment Exercise

19.22 If a process (the system) is exothermic, what happens to the entropy of the surroundings?

(a) It always increases

(b) It always decreases

(c) It sometimes increases and sometimes decreases, depending on the process

Exercises

19.23 Propanol (C_3H_7OH) melts at −126.5 °C and boils at 97.4 °C. Sketch how the entropy changes as propanol is heated from −150 °C to 150 °C at 101.3 kPa. (Use Figure 19.12 as a model.)

19.24 In each of the following pairs, which compound would you expect to have the higher standard molar entropy: (**a**) $C_3H_8(g)$ or $C_4H_{10}(g)$, (**b**) $C_4H_{10}(l)$ or $C_4H_{10}(g)$.

19.25 Predict which member of each of the following pairs has the greater standard entropy at 25°C: (**a**) $C_6H_6(l)$ or $C_6H_6(g)$, (**b**) $CO(g)$ or $CO_2(g)$, (**c**) 1 mol $N_2O_4(g)$ or 2 mol $NO_2(g)$ (**d**) $HCl(g)$ or $HCl(aq)$. Use Appendix C to find the standard entropy of each substance.

19.26 Three of the forms of elemental carbon are graphite, diamond, and buckminsterfullerene. The entropies at 298 K for graphite and diamond are listed in Appendix C. (**a**) Account for the difference in the $S°$ values of graphite and diamond in light of their structures (Figure 12.29, p. 586). (**b**) What would you expect for the $S°$ value of buckminsterfullerene (Figure 12.48, p. 601) relative to the values for graphite and diamond? Explain.

19.27 Calculate $\Delta S°$ values for the following reactions by using tabulated $S°$ values from Appendix C. In each case, explain the sign of $\Delta S°$.

(**a**) $2\,C_2H_4(g) \longrightarrow C_2H_6(g) + C_2H_2(g)$

(**b**) $Si(s) + 2\,Cl_2(g) \longrightarrow SiCl_4(l)$

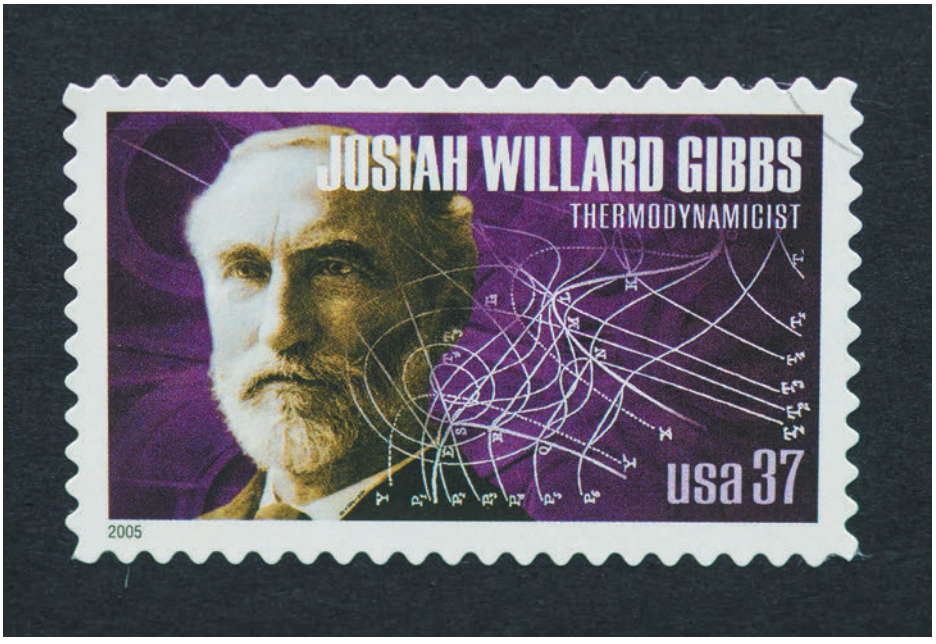
(**c**) $PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$

(**d**) $2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,SO_2(g) + 2\,H_2O(g)$

Answers to Self-Assessment Exercise

19.22 (a)

19.5 Gibbs Free Energy



Josiah Willard Gibbs (1839–1902) was the first person to be awarded a PhD in science from an American university (Yale 1863). From 1871 until his death, he held the chair of mathematical physics at Yale. He developed much of the theoretical foundation that led to the development of chemical thermodynamics.

By the end of this section, you should be able to

- Perform calculations involving Gibbs free energy
- Use the Gibbs free energy to predict if a reaction is spontaneous

We have seen examples of endothermic processes that are spontaneous, such as the dissolution of ammonium nitrate in water. We learned in our discussion of the solution process that a spontaneous process that is endothermic must be accompanied by an increase in the entropy of the system. However, we have also encountered processes that are spontaneous and yet proceed with a *decrease* in the entropy of the system, such as the highly exothermic formation of sodium chloride from its constituent elements. Spontaneous processes that result in a decrease in the system's entropy are always exothermic. Thus, the spontaneity of a reaction seems to involve two thermodynamic concepts, enthalpy and entropy.

How can we use ΔH and ΔS to predict whether a given reaction occurring at constant temperature and pressure will be spontaneous? The means for doing so was first developed by J. Willard Gibbs who proposed a new state function, the **Gibbs free energy** (or just **free energy**)*, G, and defined as

$$G = H - TS \qquad [19.10]$$

where T is the absolute temperature. For an isothermal process, the change in the free energy of the system, ΔG, is

$$\Delta G = \Delta H - T\Delta S \qquad [19.11]$$

Under standard conditions, this equation becomes

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad [19.12]$$

To see how the state function G relates to reaction spontaneity, recall that for a reaction occurring at constant temperature and pressure

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \left(\frac{-\Delta H_{sys}}{T}\right)$$

where Equation 19.9 substitutes for ΔS_{surr}. Multiplying both sides by $-T$ gives

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys} \qquad [19.13]$$

Comparing Equations 19.11 and 19.13, we see that in a process occurring at constant temperature and pressure, the free-energy change, ΔG, is equal to $-T\Delta S_{univ}$. We know that for spontaneous processes, ΔS_{univ} is always positive and, therefore, $-T\Delta S_{univ}$ is always negative. Thus, the sign of ΔG provides us with extremely valuable information about the spontaneity of processes that occur at constant temperature and pressure. If both T and P are constant, the relationship between the sign of ΔG and the spontaneity of a reaction is:

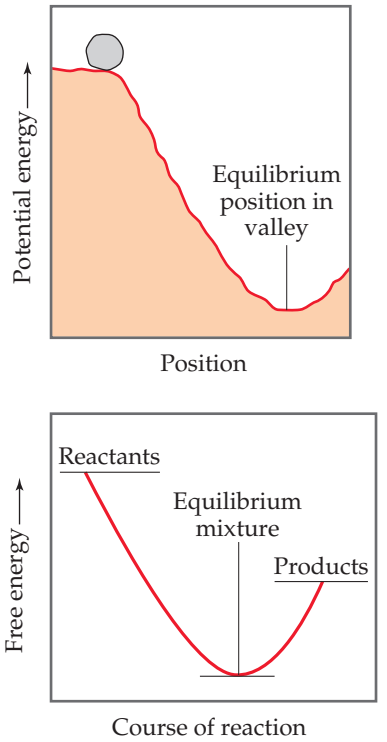
- If $\Delta G < 0$, the reaction is spontaneous in the forward direction.
- If $\Delta G = 0$, the reaction is at equilibrium.
- If $\Delta G > 0$, the reaction is nonspontaneous in the forward direction (work must be done to make it occur) but the reverse reaction is spontaneous.

It is more convenient to use ΔG as a criterion for spontaneity than to use ΔS_{univ} because ΔG relates to the system alone and avoids the complication of having to examine the surroundings.

An analogy is often drawn between the free-energy change during a spontaneous reaction and the potential-energy change when a boulder rolls down a hill (**Figure 19.14**).

Go Figure

Are the processes that move a system toward equilibrium spontaneous or nonspontaneous?



▲ Figure 19.14 Potential energy and free energy. An analogy is shown between the gravitational potential-energy change of a boulder rolling down a hill and the free-energy change in a spontaneous reaction. Free energy always decreases in a spontaneous process when pressure and temperature are held constant.

*Although IUPAC convention now assigns Gibbs energy as the preferred name for Gibbs free energy or free energy, all three terms are in common usage.

In some countries *Gibbs free energy G* is also called "free enthalpy" (Germany: "*freie Enthalpie G*"; France "*enthalpie libre G*")

Potential energy in a gravitational field "drives" the boulder until it reaches a state of minimum potential energy in the valley. Similarly, the free energy of a chemical system decreases until it reaches a minimum value. When this minimum is reached, a state of equilibrium exists. *In any spontaneous process carried out at constant temperature and pressure, the free energy always decreases.*

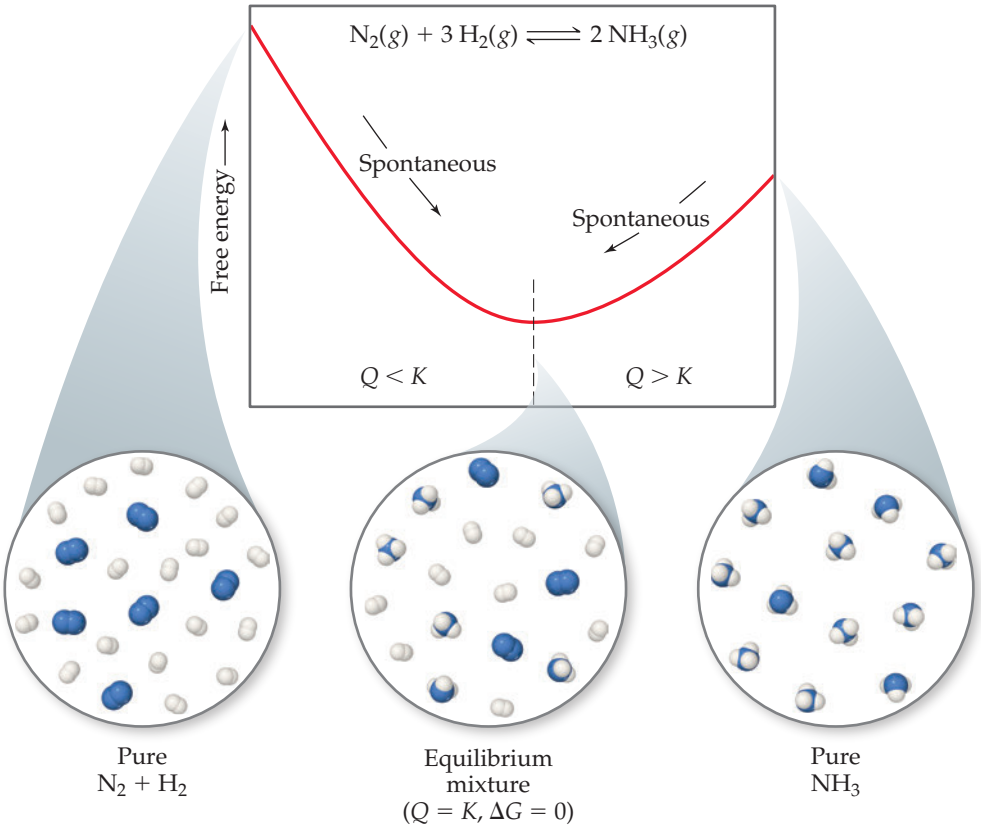
To illustrate these ideas, let's return to the Haber process for the synthesis of ammonia from nitrogen and hydrogen, which we discussed extensively in Chapter 15:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

Imagine that we have a reaction vessel that allows us to maintain a constant temperature and pressure and that we have a catalyst that allows the reaction to proceed at a reasonable rate. What happens when we load the vessel with a certain number of moles of N_2 and three times that number of moles of H_2? As we saw in Figure 15.3, the N_2 and H_2 react spontaneously to form NH_3 until equilibrium is achieved. Similarly, Figure 15.3 shows that if we load the vessel with pure NH_3, it decomposes spontaneously to N_2 and H_2 until equilibrium is reached. In each case, the free energy of the system gets progressively lower and lower as the reaction moves toward equilibrium, which represents a minimum in the free energy. We illustrate these cases in **Figure 19.15**.

This is a good time to remind ourselves of the significance of the reaction quotient, Q, for a system that is not at equilibrium. Recall that when $Q < K$, there is an excess of

Go Figure Why are the spontaneous processes shown sometimes said to be "downhill" in free energy?



▲ **Figure 19.15 Free energy and approaching equilibrium.** In the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, if the reaction mixture has too much N_2 and H_2 relative to NH_3 (left), $Q < K$ and NH_3 forms spontaneously. If there is more NH_3 in the mixture relative to the reactants N_2 and H_2 (right), $Q > K$ and the NH_3 decomposes spontaneously into N_2 and H_2.

Sample Exercise 19.6

Calculating Free-Energy Change from $\Delta H°$, T, and $\Delta S°$

Calculate the standard free-energy change for the formation of NO(g) from $N_2(g)$ and $O_2(g)$ at 298 K:

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$$

given that $\Delta H° = 180.7$ kJ and $\Delta S° = 24.7$ J/K. Is the reaction spontaneous under these conditions?

SOLUTION

Analyze We are asked to calculate $\Delta G°$ for the indicated reaction (given $\Delta H°$, $\Delta S°$, and T) and to predict whether the reaction is spontaneous under standard conditions at 298 K.

Plan To calculate $\Delta G°$, we use Equation 19.12, $\Delta G° = \Delta H° - T\Delta S°$. To determine whether the reaction is spontaneous under standard conditions, we look at the sign of $\Delta G°$.

Solve

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= 180.7\ \text{kJ} - (298\ \text{K})(24.7\ \text{J/K})\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right) \\ &= 180.7\ \text{kJ} - 7.4\ \text{kJ} \\ &= 173.3\ \text{kJ}\end{aligned}$$

Because $\Delta G°$ is positive, the reaction is not spontaneous under standard conditions at 298 K.

Comment Notice that we converted the units of the $T\Delta S°$ term to kJ so that they could be added to the $\Delta H°$ term, whose units are kJ.

Practice Exercise

Which of these statements is true? (**a**) All spontaneous reactions have a negative enthalpy change (**b**) All spontaneous reactions have a positive entropy change (**c**) All spontaneous reactions have a positive free-energy change (**d**) All spontaneous reactions have a negative free-energy change (**e**) All spontaneous reactions have a negative entropy change

reactants relative to products, and the reaction proceeds spontaneously in the forward direction to reach equilibrium, as noted in Figure 19.15. When $Q > K$, the reaction proceeds spontaneously in the reverse direction. At equilibrium $Q = K$.

Standard Free Energy of Formation

Recall that we defined *standard enthalpies of formation*, $\Delta H_f°$, as the enthalpy change when a substance is formed from its elements under defined standard conditions. We can define **standard free energies of formation**, $\Delta G_f°$, in a similar way: $\Delta G_f°$ for a substance is the free-energy change for its formation from its elements under standard conditions. As is summarized in Table 19.2, standard state means 100.0 kPa for gases, the pure solid for solids, and the pure liquid for liquids. For substances in solution, the standard state is normally a concentration of 1 M. (In very accurate work it may be necessary to make certain corrections, but we need not worry about these.)

The temperature usually chosen for purposes of tabulating data is 25 °C, but we will calculate ΔG at other temperatures as well. Just as for the standard heats of formation, the free energies of elements in their standard states are set to zero. This arbitrary choice of a reference point has no effect on the quantity in which we are interested, which is the *difference* in free energy between reactants and products.

A listing of standard free energies of formation is given in Appendix C.

Standard free energies of formation are useful in calculating the *standard free-energy change* for chemical processes. The procedure is analogous to the calculation of $\Delta H°$ (Equation 5.31) and $\Delta S°$ (Equation 19.8):

$$\Delta G° = \sum n\Delta G_f°(\text{products}) - \sum m\Delta G_f°(\text{reactants}) \qquad [19.14]$$

TABLE 19.2 Conventions Used in Establishing Standard Free Energies

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	100.0 kPa pressure
Solution	1 M concentration
Element	$\Delta G_f° = 0$ for element in standard state

- Perform calculations involving Gibbs free energy
- Use the Gibbs free energy to predict is a reaction is spontaneous

Sample Exercise 19.7

Calculating Standard Free-Energy Change from Free Energies of Formation

(**a**) Use data from Appendix C to calculate the standard free energy change for the reaction $P_4(g) + 6\,Cl_2(g) \longrightarrow 4\,PCl_3(g)$ at 298 K. (**b**) What is $\Delta G°$ for the reverse of this reaction?

SOLUTION

Analyze We are asked to calculate the free-energy change for a reaction and then to determine the free-energy change for the reverse reaction.

Plan We look up the free-energy values for the products and reactants and use Equation 19.14. We multiply the molar quantities by the coefficients in the balanced equation and subtract the total for the reactants from that for the products.

Solve

(**a**) $Cl_2(g)$ is in its standard state, so $\Delta G_f°$ is zero for this reactant. $P_4(g)$, however, is not in its standard state, so $\Delta G_f°$ is not zero for this reactant. From the balanced equation and values from Appendix C, we have

$$\begin{aligned}\Delta G°_{rxn} &= 4\,\Delta G_f°[PCl_3(g)] - \Delta G_f°[P_4(g)] - 6\,\Delta G_f°[Cl_2(g)] \\ &= (4\,\text{mol})(-269.6\,\text{kJ/mol}) - (1\,\text{mol})(24.4\,\text{kJ/mol}) - 0 \\ &= -1102.8\,\text{kJ}\end{aligned}$$

That $\Delta G°$ is negative tells us that a mixture of $P_4(g)$, $Cl_2(g)$, and $PCl_3(g)$ at 25 °C, each present at a partial pressure of 101.3 kPa, would react spontaneously in the forward direction to form more PCl_3. Remember, however, that the value of $\Delta G°$ tells us nothing about the rate at which the reaction occurs.

(**b**) When we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of ΔG in Equation 19.14, just as reversing the reaction changes the sign of ΔH. Hence, using the result from part (a), we have

$$4\,PCl_3(g) \longrightarrow P_4(g) + 6\,Cl_2(g) \quad \Delta G° = +1102.8\,\text{kJ}$$

Practice Exercise

The following chemical equations describe the same chemical reaction. How do the free energies of these two chemical equations compare?

(**1**) $2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$

(**2**) $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}\,O_2(g)$

(**a**) $\Delta G_1° = \Delta G_2°$ (**b**) $\Delta G_1° = 2\,\Delta G_2°$ (**c**) $2\,\Delta G_1° = \Delta G_2°$ (**d**) None of these

Sample Exercise 19.8

Predicting and Calculating $\Delta G°$

In Section 5.7 we used Hess's law to calculate $\Delta H°$ for the combustion of propane gas at 298 K:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \quad \Delta H° = -2220\,\text{kJ}$$

(**a**) *Without using data from Appendix C*, predict whether $\Delta G°$ for this reaction is more negative or less negative than $\Delta H°$.

(**b**) Use data from Appendix C to calculate $\Delta G°$ for the reaction at 298 K. Is your prediction from part (a) correct?

SOLUTION

Analyze In part (a) we must predict the value for $\Delta G°$ relative to that for $\Delta H°$ on the basis of the balanced equation for the reaction. In part (b) we must calculate the value for $\Delta G°$ and compare this value with our qualitative prediction.

Plan The free-energy change incorporates both the change in enthalpy and the change in entropy for the reaction (Equation 19.11), so under standard conditions

$$\Delta G° = \Delta H° - T\Delta S°$$

To determine whether $\Delta G°$ is more negative or less negative than $\Delta H°$, we need to determine the sign of the term $T\Delta S°$. Because T is the absolute temperature, 298 K, it is always a positive number. We can predict the sign of $\Delta S°$ by looking at the reaction.

Solve

(**a**) The reactants are six molecules of gas, and the products are three molecules of gas and four molecules of liquid. Thus, the number of molecules of gas has decreased significantly during the reaction. By using the general rules discussed in Section 19.3, we expect a decrease in the number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer possible microstates than the reactants. We therefore expect $\Delta S°$ and $T\Delta S°$ to be negative. Because we are subtracting $T\Delta S°$, which is a negative number, we predict that $\Delta G°$ is *less negative* than $\Delta H°$.

(**b**) Using Equation 19.14 and values from Appendix C, we have

$$\begin{aligned}\Delta G° &= 3\,\Delta G_f°[CO_2(g)] + 4\,\Delta G_f°[H_2O(l)] \\ &\quad - \Delta G_f°[C_3H_8(g)] - 5\,\Delta G_f°[O_2(g)] \\ &= 3\,\text{mol}(-394.4\,\text{kJ/mol}) + 4\,\text{mol}(-237.13\,\text{kJ/mol}) - \\ &\quad 1\,\text{mol}(-23.47\,\text{kJ/mol}) - 5\,\text{mol}(0\,\text{kJ/mol}) = -2108\,\text{kJ}\end{aligned}$$

Notice that we have been careful to use the value of $\Delta G_f°$ for $H_2O(l)$. As in calculating ΔH values, the phases of the reactants and products are important. As we predicted, $\Delta G°$ is less negative than $\Delta H°$ because of the decrease in entropy during the reaction.

Practice Exercise

If a reaction is exothermic and its entropy change is positive, which statement is true? (**a**) The reaction is spontaneous at all temperatures (**b**) The reaction is nonspontaneous at all temperatures (**c**) The reaction is spontaneous only at higher temperatures (**d**) The reaction is spontaneous only at lower temperatures

A CLOSER LOOK What's "Free" About Free Energy?

The Gibbs free energy is a remarkable thermodynamic quantity. Because so many chemical reactions are carried out under conditions of near-constant pressure and temperature, chemists, biochemists, and engineers consider the sign and magnitude of ΔG as exceptionally useful tools in the design of chemical and biochemical reactions. We will see examples of the usefulness of ΔG throughout the remainder of this chapter and this text.

When first learning about ΔG, two common questions often arise: Why is the sign of ΔG an indicator of the spontaneity of reactions? And what is "free" about free energy?

In Section 19.2, we saw that the second law of thermodynamics governs the spontaneity of processes. In order to apply the second law (Equation 19.4), however, we must determine ΔS_{univ}, which is often difficult to evaluate. When T and P are constant, however, we can relate ΔS_{univ} to the changes in entropy and enthalpy of just the *system* by substituting the Equation 19.9 expression for ΔS_{surr} in Equation 19.4:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \left(\frac{-\Delta H_{sys}}{T}\right) \qquad \text{(constant } T, P\text{)} \qquad [19.15]$$

Thus, at constant temperature and pressure, the second law becomes

$$\textit{Reversible process:} \quad \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} = 0$$

$$\textit{Irreversible process:} \quad \Delta S_{univ} = \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0 \qquad [19.16]$$

$$\text{(constant } T, P\text{)}$$

Now we can see the relationship between ΔG_{sys} (which we call simply ΔG) and the second law. From Equation 19.11 we know that $\Delta G = \Delta H_{sys} - T\Delta S_{sys}$. If we multiply Equations 19.16 by $-T$ and rearrange, we reach the following conclusion:

$$\textit{Reversible process:} \quad \Delta G = \Delta H_{sys} - T\Delta S_{sys} = 0$$

$$\textit{Irreversible process:} \quad \Delta G = \Delta H_{sys} - T\Delta S_{sys} < 0 \qquad [19.17]$$

$$\text{(constant } T, P\text{)}$$

Equations 19.17 allow us to use the sign of ΔG to conclude whether a reaction is spontaneous, nonspontaneous, or at equilibrium. When $\Delta G < 0$, a process is irreversible and, therefore, spontaneous. When $\Delta G = 0$, the process is reversible and, therefore, at equilibrium. If a process has $\Delta G > 0$, then the reverse process will have $\Delta G < 0$; thus, the process as written is nonspontaneous, but its reverse reaction will be irreversible and spontaneous.

The magnitude of ΔG is also significant. A reaction for which ΔG is large and negative, such as the burning of gasoline, is much more capable of doing work on the surroundings than is a reaction for which ΔG is small and negative, such as ice melting at room temperature. In fact, thermodynamics tells us that *the change in free energy for a process, ΔG, equals the maximum useful work that can be done by the system on its surroundings in a spontaneous process occurring at constant temperature and pressure:*

$$\Delta G = -w_{max} \qquad [19.18]$$

(Remember our sign convention from Table 5.1: Work done *by* a system is negative.) In other words, ΔG gives the theoretical limit to how much work can be done by a process.

The relationship in Equation 19.18 explains why ΔG is called the *free* energy change—it is the portion of the energy change of a spontaneous reaction that is free to do useful work. The remainder of the energy enters the environment as heat. For example, the theoretical maximum work obtained for the combustion of petrol is given by the value of ΔG for the combustion reaction. On average, standard internal combustion engines are inefficient in utilizing this potential work—more than 60% of the potential work is lost (primarily as heat) in converting the chemical energy of the petrol to mechanical energy to move the vehicle. When other losses are considered—idling time, braking, aerodynamic drag, and so forth—only about 15% of the potential work from the petrol is used to move the car. Advances in automobile design—such as hybrid technology, and new lightweight materials—have the potential to increase the percentage of useful work obtained from the petrol.

Self-Assessment Exercises

19.28 For the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta G_f^\circ(NH_3(g)) = -16.7$ kJ/mol. Calculate the standard free energy change for the reaction.

(a) $\Delta G^\circ = -16.7$ kJ

(b) $\Delta G^\circ = -33.4$ kJ

(c) $\Delta G^\circ = 16.7$ kJ

(d) $\Delta G^\circ = 33.4$ kJ

19.29 Is the reaction shown in Exercise 19.28 spontaneous or nonspontaneous in the forward direction?

(a) Spontaneous

(b) Nonspontaneous

Exercises

19.30 (**a**) For a process that occurs at constant temperature, does the change in Gibbs free energy depend on changes in the enthalpy and entropy of the system? (**b**) For a certain process that occurs at constant T and P, the value of ΔG is positive. Is the process spontaneous? (**c**) If ΔG for a process is large, is the rate at which it occurs fast?

19.31 A certain reaction has $\Delta H^\circ = +20.0\,\text{kJ}$ and $\Delta S^\circ = +100.0\,\text{J/K}$. (**a**) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? (**b**) Does the reaction lead to an increase or decrease in the randomness or disorder of the surroundings? (**c**) Calculate ΔG° for the reaction at 298 K. (**d**) Is the reaction spontaneous at 298 K under standard conditions?

19.32 Use data in Appendix C to calculate ΔH°, ΔS°, and ΔG° at 25 °C for each of the following reactions.

(**a**) $4\,Cr(s) + 3\,O_2(g) \longrightarrow 2\,Cr_2O_3(s)$

(**b**) $BaCO_3(s) \longrightarrow BaO(s) + CO_2(g)$

(**c**) $2\,P(s) + 10\,HF(g) \longrightarrow 2\,PF_5(g) + 5\,H_2(g)$

(**d**) $K(s) + O_2(g) \longrightarrow KO_2(s)$

19.33 Using data from Appendix C, calculate the change in Gibbs free energy for each of the following reactions. In each case, indicate whether the reaction is spontaneous at 298 K under standard conditions.

(**a**) $2\,Ag(s) + Cl_2(g) \longrightarrow 2\,AgCl(s)$

(**b**) $P_4O_{10}(s) + 16\,H_2(g) \longrightarrow 4\,PH_3(g) + 10\,H_2O(g)$

(**c**) $CH_4(g) + 4\,F_2(g) \longrightarrow CF_4(g) + 4\,HF(g)$

(**d**) $2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g)$

19.34 Sulfur dioxide reacts with strontium oxide as follows:

$$SO_2(g) + SrO(g) \longrightarrow SrSO_3(s)$$

(**a**) Without using thermochemical data, predict whether ΔG° for this reaction is more negative or less negative than ΔH°. (**b**) If you had only standard enthalpy data for this reaction, how would you estimate the value of ΔG° at 298 K, using data from Appendix C on other substances.

Answers to Self-Assessment Exercises

19.28 (b) 19.29 (a)

19.6 Free Energy and Temperature



An ice cube melts in the hand, while water in a glass crystallizes when left in a freezer. The transition between solid and liquid phases has a spontaneous direction that depends on temperature. In this section, we discuss the linkage between free energy and temperature.

By the end of this section, you should be able to

- Predict the effect of temperature on spontaneity given ΔH and ΔS.

Tabulations of ΔG_f°, such as those in Appendix C, make it possible to calculate ΔG° for reactions at the standard temperature of 25 °C, but we are often interested in examining reactions at other temperatures. To see how ΔG is affected by temperature, let's look again at Equation 19.11:

$$\Delta G = \underbrace{\Delta H}_{\substack{\text{Enthalpy}\\ \text{term}}} - T\Delta S = \Delta H + \underbrace{(-T\Delta S)}_{\substack{\text{Entropy}\\ \text{term}}}$$

Notice that the expression for ΔG as a sum of two contributions, an enthalpy term, ΔH, and an entropy term, $-T\Delta S$. Because the value of $-T\Delta S$ depends directly on the absolute temperature T, ΔG varies with temperature. We know that the enthalpy term, ΔH, can be either positive or negative and that T is positive at all temperatures other than absolute zero. The entropy term, $-T\Delta S$, can also be positive or negative. When ΔS is positive, which means the final state has greater randomness (a greater number of microstates) than the initial state, the term $-T\Delta S$ is negative. When ΔS is negative, $-T\Delta S$ is positive.

The sign of ΔG, which tells us whether a process is spontaneous, depends on the signs and magnitudes of ΔH and $-T\Delta S$. The various combinations of ΔH and $-T\Delta S$ signs are given in **Table 19.3**.

Note in Table 19.3 that when ΔH and $-T\Delta S$ have opposite signs, the sign of ΔG depends on the magnitudes of these two terms. In these instances, temperature is an important consideration. Generally, ΔH and ΔS change very little with temperature. However, the value of T directly affects the magnitude of $-T\Delta S$. As the temperature increases, the magnitude of $-T\Delta S$ increases, and this term becomes relatively more important in determining the sign and magnitude of ΔG.

As an example, let's consider once more the melting of ice to liquid water at 101.3 kPa:

$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H > 0,\ \Delta S > 0$$

This process is endothermic, which means that ΔH is positive. Because the entropy increases during the process, ΔS is positive, which makes $-T\Delta S$ negative. At temperatures below 0 °C (273 K), the magnitude of ΔH is greater than that of $-T\Delta S$. Hence, the positive enthalpy term dominates, and ΔG is positive. This positive value of ΔG means that ice melting is not spontaneous at $T < 0$ °C, just as our everyday experience tells us; rather, the reverse process, the freezing of liquid water into ice, is spontaneous at these temperatures.

What happens at temperatures greater than 0 °C? As T increases, so does the magnitude of $-T\Delta S$. When $T > 0$ °C, the magnitude of $-T\Delta S$ is greater than the magnitude of ΔH, which means that the $-T\Delta S$ term dominates and ΔG is negative. The negative value of ΔG tells us that ice melting is spontaneous at $T > 0$ °C.

At the normal melting point of water, $T = 0$ °C, the two phases are in equilibrium. Recall that $\Delta G = 0$ at equilibrium; at $T = 0$ °C, ΔH and $-T\Delta S$ are equal in magnitude and opposite in sign, so they cancel and give $\Delta G = 0$.

Our discussion of the temperature dependence of ΔG is also relevant to standard free-energy changes. We can calculate the values of ΔH° and ΔS° at 298 K from the data in Appendix C. If we assume that these values do not change with temperature, we can then use Equation 19.12 to estimate ΔG at temperatures other than 298 K.

TABLE 19.3 How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

Sample Exercise 19.9

Determining the Effect of Temperature on Spontaneity

The Haber process for the production of ammonia involves the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

For this reaction, $\Delta H^\circ = -92.38$ kJ and $\Delta S^\circ = -198.3$ J/K. Assume that ΔH° and ΔS° for this reaction do not change with temperature. (**a**) Predict the direction in which ΔG for the reaction changes with increasing temperature. (**b**) Calculate ΔG at 25 °C and at 500 °C.

SOLUTION

Analyze In part (a) we are asked to predict the direction in which ΔG changes as temperature increases. In part (b) we need to determine ΔG for the reaction at two temperatures.

Plan We can answer part (a) by determining the sign of ΔS for the reaction and then using that information to analyze Equation 19.12. In part (b) we use the given ΔH° and ΔS° values for the reaction together with Equation 19.12 to calculate ΔG.

Solve

(**a**) The temperature dependence of ΔG comes from the entropy term in Equation 19.12, $\Delta G = \Delta H - T\Delta S$. We expect ΔS for this reaction to be negative because the number of molecules of gas is smaller in the products. Because ΔS is negative, $-T\Delta S$ is positive and increases with increasing temperature. As a result, ΔG becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of NH_3 becomes smaller with increasing temperature.

(**b**) If we assume that the values for ΔH° and ΔS° do not change with temperature, we can calculate ΔG at any temperature by using Equation 19.12. At $T = 25\ ^\circ\text{C} = 298$ K, we have

$$\Delta G^\circ = -92.38\ \text{kJ} - (298\ \text{K})(-198.3\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -92.38\ \text{kJ} + 59.1\ \text{kJ} = -33.3\ \text{kJ}$$

At $T = 500\ ^\circ\text{C} = 773$ K, we have

$$\Delta G = -92.38\ \text{kJ} - (773\ \text{K})(-198.3\ \text{J/K})\left(\frac{1\ \text{kJ}}{1000\ \text{J}}\right)$$

$$= -92.38\ \text{kJ} + 153\ \text{kJ} = 61\ \text{kJ}$$

Notice that we had to convert the units of $-T\Delta S^\circ$ to kJ in both calculations so that this term can be added to the ΔH° term, which has units of kJ.

Comment Increasing the temperature from 298 K to 773 K changes ΔG from −33.3 kJ to +61 kJ. Of course, the result at 773 K assumes that ΔH° and ΔS° do not change with temperature. Although these values do change slightly with temperature, the result at 773 K should be a reasonable approximation.

The positive increase in ΔG with increasing T agrees with our prediction in part (a). Our result indicates that in a mixture of $N_2(g)$, $H_2(g)$, and $NH_3(g)$, each present at a partial pressure of 101.3 kPa, the $N_2(g)$ and $H_2(g)$ react spontaneously at 298 K to form more $NH_3(g)$. At 773 K, the positive value of ΔG tells us that the reverse reaction is spontaneous. Thus, when the mixture of these gases, each at a partial pressure of 101.3 kPa, is heated to 773 K, some of the $NH_3(g)$ spontaneously decomposes into $N_2(g)$ and $H_2(g)$.

Practice Exercise

What is the temperature above which the Haber ammonia process becomes nonspontaneous?

(**a**) 25 °C (**b**) 47 °C (**c**) 61 °C (**d**) 193 °C (**e**) 500 °C

Self-Assessment Exercise

19.35 The normal boiling point of toluene is 110 °C. At 100 °C and 101.3 kPa, which term is greater in magnitude for the vaporization of toluene, ΔH_{vap} or $T\Delta S_{vap}$?

(**a**) $\Delta H_{vap} > T\Delta S_{vap}$

(**b**) $T\Delta S_{vap} > \Delta H_{vap}$

Exercises

19.36 Classify each of the following reactions as one of the four possible types summarized in Table 19.3: (i) spontanous at all temperatures; (ii) not spontaneous at any temperature; (iii) spontaneous at low T but not spontaneous at high T; (iv) spontaneous at high T but not spontaneous at low T.

(**a**) $N_2(g) + 3\,F_2(g) \longrightarrow 2\,NF_3(g)$
$\Delta H^\circ = -249$ kJ; $\Delta S^\circ = -278$ J/K

(**b**) $N_2(g) + 3\,Cl_2(g) \longrightarrow 2\,NCl_3(g)$
$\Delta H^\circ = 460$ kJ; $\Delta S^\circ = -275$ J/K

(**c**) $N_2F_4(g) \longrightarrow 2\,NF_2(g)$
$\Delta H^\circ = 85$ kJ; $\Delta S^\circ = 198$ J/K

19.37 A certain constant-pressure reaction is barely nonspontaneous at 45 °C. The entropy change for the reaction is 72 J/K. Estimate ΔH.

19.38 Reactions in which a substance decomposes by losing CO are called *decarbonylation* reactions. The decarbonylation of acetic acid proceeds according to:

$$CH_3COOH(l) \longrightarrow CH_3OH(g) + CO(g)$$

By using data from Appendix C, calculate the minimum temperature at which this process will be spontaneous under standard conditions. Assume that $\Delta H°$ and $\Delta S°$ do not vary with temperature.

19.39 Methanol (CH_3OH) can be made by the controlled oxidation of methane:

$$CH_4(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(g)$$

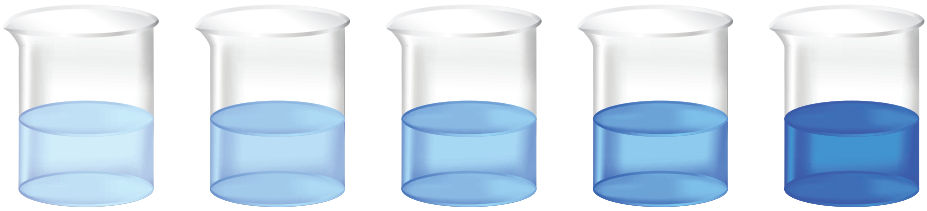
(**a**) Use data in Appendix C to calculate $\Delta H°$ and $\Delta S°$ for this reaction. (**b**) Will ΔG for the reaction increase, decrease, or stay unchanged with increasing temperature? (**c**) Calculate $\Delta G°$ at 298 K. Under standard conditions, is the reaction spontaneous at this temperature? (**d**) Is there a temperature at which the reaction would be at equilibrium under standard conditions and that is low enough so that the compounds involved are likely to be stable?

19.40 The fuel in high-efficiency natural-gas vehicles consists primarily of methane (CH_4). (**a**) How much heat is produced in burning 1 mol of $CH_4(g)$ under standard conditions if reactants and products are brought to 298 K and $H_2O(l)$ is formed? (**b**) What is the maximum amount of useful work that can be accomplished under standard conditions by this system?

Answers to Self-Assessment Exercise

19.35 (a)

19.7 Free Energy and the Equilibrium Constant



Standard conditions form an excellent datum from which to work, but often we find ourselves under conditions that are not standard.

In Section 19.5 we saw a special relationship between ΔG and equilibrium: For a system at equilibrium, $\Delta G = 0$. We have also seen how to use tabulated thermodynamic data to calculate values of the standard free energy change, $\Delta G°$. In this final section, we learn two more ways in which we can use free energy to analyze chemical reactions: using $\Delta G°$ to calculate ΔG under *nonstandard* conditions and relating the values of $\Delta G°$ and K for a reaction.

By the end of this section, you should be able to:

- Calculate ΔG under nonstandard conditions and relate $\Delta G°$ and equilibrium constant.

Free Energy under Nonstandard Conditions

The set of standard conditions for which $\Delta G°$ values pertain is given in Table 19.2. Most chemical reactions occur under nonstandard conditions. For any chemical process, the relationship between the free energy change under standard conditions, $\Delta G°$, and the free-energy change under any other conditions, ΔG, is given by

$$\Delta G = \Delta G° + RT \ln Q \qquad [19.19]$$

In this equation R is the ideal gas constant, 8.314 J/mol K; T is the absolute temperature; and Q is the reaction quotient for the reaction mixture of interest. Recall that the reaction quotient Q is calculated like an equilibrium constant, except that you use the concentrations at any point of interest in the reaction; if $Q = K$, then the reaction is at equilibrium. Under standard conditions, the concentrations of all the reactants and products are equal to 1 M. Thus, under standard conditions $Q = 1$, $\ln Q = 0$, and Equation 19.19 reduces to $\Delta G = \Delta G^\circ$ under standard conditions, as it should.

Remember, this does not mean that equilibrium has been established; that occurs when $\Delta G = 0$.

When the concentrations of reactants and products are nonstandard, we must calculate Q in order to determine ΔG. We illustrate how this is done in Sample Exercise 19.11. At this stage in our discussion, therefore, it becomes important to note the units used to calculate Q when using Equation 19.19. The convention used for standard states is used when applying this equation: In determining the value of Q, the concentrations of gases are always expressed as partial pressures in atmospheres and solutes are expressed as their concentrations in molarities.

Sample Exercise 19.10

Relating ΔG to a Phase Change at Equilibrium

(**a**) Write the chemical equation that defines the normal boiling point of liquid tetrachloromethane, $CCl_4(l)$. (**b**) What is the value of ΔG° for the equilibrium in part (a)? (**c**) Use data from Appendix C and Equation 19.12 to estimate the normal boiling point of CCl_4.

SOLUTION

Analyze (**a**) We must write a chemical equation that describes the physical equilibrium between liquid and gaseous CCl_4 at the normal boiling point. (**b**) We must determine the value of ΔG° for CCl_4, in equilibrium with its vapor at the normal boiling point. (**c**) We must estimate the normal boiling point of CCl_4, based on available thermodynamic data.

Plan (**a**) The chemical equation is the change of state from liquid to gas. For (**b**), we need to analyze Equation 19.19 at equilibrium ($\Delta G = 0$), and for (**c**) we can use Equation 19.12 to calculate T when $\Delta G = 0$.

Solve

(**a**) The normal boiling point is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 101.3 kPa:

$$CCl_4(l) \rightleftharpoons CCl_4(g) \quad P = 101.3\ \text{kPa}$$

(**b**) At equilibrium, $\Delta G = 0$. In any normal boiling point equilibrium, both liquid and vapor are in their standard state of pure liquid and vapor at 101.3 kPa (Table 19.2). Consequently, $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G^\circ$ for this process. We conclude that $\Delta G^\circ = 0$ for the equilibrium representing the normal boiling point of any liquid. (We would also find that $\Delta G^\circ = 0$ for the equilibria relevant to normal melting points and normal sublimation points.)

$$\Delta G^\circ = 0$$

(**c**) Combining Equation 19.12 with the result from part (b), we see that the equality at the normal boiling point, T_b, of $CCl_4(l)$ (or any other pure liquid) is:

$$\Delta G^\circ = \Delta H^\circ - T_b \Delta S^\circ = 0$$

Solving the equation for T_b, we obtain:

$$T_b = \Delta H^\circ / \Delta S^\circ$$

Strictly speaking, we need the values of ΔH° and ΔS° for the $CCl_4(l)/CCl_4(g)$ equilibrium at the normal boiling point to do this calculation. However, we can *estimate* the boiling point by using the values of ΔH° and ΔS° for the phases of CCl_4 at 298 K, which we obtain from Appendix C and Equations 5.31 and 19.8:

$$\Delta H^\circ = (1\ \text{mol})(-106.7\ \text{kJ/mol}) - (1\ \text{mol})(-139.3\ \text{kJ/mol}) = +32.6\ \text{kJ}$$

$$\Delta S^\circ = (1\ \text{mol})(309.4\ \text{J/mol K}) - (1\ \text{mol})(214.4\ \text{J/mol K}) = +95.0\ \text{J/K}$$

As expected, the process is endothermic ($\Delta H > 0$) and produces a gas, thus increasing the entropy ($\Delta S > 0$). We now use these values to estimate T_b for $CCl_4(l)$:

$$T_b = \frac{\Delta H^\circ}{\Delta S^\circ} = \left(\frac{32.6\ \text{kJ}}{95.0\ \text{J/K}}\right)\left(\frac{1000\ \text{J}}{1\ \text{kJ}}\right) = 343\ \text{K} = 70\ ^\circ\text{C}$$

Note that we have used the conversion factor between joules and kilojoules to make the units of ΔH° and ΔS° match.

Check The experimental normal boiling point of $CCl_4(l)$ is 76.5 °C. The small deviation of our estimate from the experimental value is due to the assumption that ΔH° and ΔS° do not change with temperature.

Practice Exercise

If the normal boiling point of a liquid is 67 °C, and the standard molar entropy change for the boiling process is +100 J/K, estimate the standard molar enthalpy change for the boiling process.

(**a**) +6700 J (**b**) −6700 J (**c**) +34,000 J (**d**) −34,000 J

Sample Exercise 19.11

Calculating the Free-Energy Change under Nonstandard Conditions

Calculate ΔG at 298 K for a mixture of 1.00 atm N_2, 3.00 atm H_2, and 0.500 atm NH_3 being used in the Haber process:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

SOLUTION

Analyze We are asked to calculate ΔG under nonstandard conditions.

Plan We can use Equation 19.19 to calculate ΔG. Doing so requires that we calculate the value of the reaction quotient Q for the specified partial pressures, for which we use the partial pressures form of Equation 15.24 (the equilibrium constant expression). We then use a table of standard free energies of formation to evaluate ΔG°.

Solve

The partial-pressures form of Equation 15.24 gives:

$$Q = \frac{P_{NH_3}{}^2}{P_{N_2} P_{H_2}{}^3} = \frac{(0.500)^2}{(1.00)(3.00)^3} = 9.26 \times 10^{-3}$$

In Sample Exercise 19.9 we calculated $\Delta G^\circ = -33.3$ kJ for this reaction. We will have to change the units of this quantity in applying Equation 19.19, however. For the units in Equation 19.19 to work out, we will use kJ/mol as our units for ΔG°, where "per mole" means "per mole of the reaction as written." Thus, $\Delta G^\circ = -33.3$ kJ/mol implies per 1 mol of N_2, per 3 mol of H_2, and per 2 mol of NH_3.

We now use Equation 19.19 to calculate ΔG for these nonstandard conditions:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln Q \\ &= (-33.3\ \text{kJ/mol}) \\ &\quad + (8.314\ \text{J/mol K})(298\ \text{K})(1\ \text{kJ}/1000\ \text{J})\ln(9.26 \times 10^{-3}) \\ &= (-33.3\ \text{kJ/mol}) + (-11.6\ \text{kJ/mol}) = -44.9\ \text{kJ/mol}\end{aligned}$$

Comment We see that ΔG becomes more negative as the pressures of N_2, H_2, and NH_3 are changed from 1.00 atm (standard conditions, ΔG°) to 1.00 atm, 3.00 atm, and 0.500 atm, respectively. The larger negative value for ΔG indicates a larger "driving force" to produce NH_3.

We would make the same prediction based on Le Châtelier's principle. Relative to standard conditions, we have increased the pressure of a reactant (H_2) and decreased the pressure of the product (NH_3). Le Châtelier's principle predicts that both changes shift the reaction to the product side, thereby forming more NH_3.

Practice Exercise

Which of the following statements is true? (**a**) The larger the Q, the larger the ΔG°. (**b**) If $Q = 0$, the system is at equilibrium. (**c**) If a reaction is spontaneous under standard conditions, it is spontaneous under all conditions. (**d**) The free-energy change for a reaction is independent of temperature. (**e**) If $Q > 1$, $\Delta G > \Delta G^\circ$.

Relationship between ΔG° and K

We can now use Equation 19.19 to derive the relationship between ΔG° and the equilibrium constant, K. At equilibrium, $\Delta G = 0$ and $Q = K$. Thus, at equilibrium, Equation 19.19 transforms as follows:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ 0 &= \Delta G^\circ + RT \ln K \\ \Delta G^\circ &= -RT \ln K \end{aligned} \qquad [19.20]$$

Equation 19.20 is a very important one, with broad significance in chemistry. By relating K to ΔG°, we can also relate K to entropy and enthalpy changes for a reaction.

We can also solve Equation 19.20 for K, to yield an expression that allows us to calculate K if we know the value of ΔG°:

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

$$K = e^{-\Delta G^\circ/RT} \qquad [19.21]$$

As usual, we must be careful in our choice of units. In Equations 19.20 and 19.21 we again express ΔG° in kJ/mol. In the equilibrium expression, we use atmospheres for gas pressures, molarities for solutions; and solids, liquids, and solvents do not appear in the expression. Thus, the equilibrium constant is K_p for gas-phase reactions and K_c for reactions in solution.

From Equation 19.20 we see that if ΔG° is negative, $\ln K$ must be positive, which means $K > 1$. Therefore, the more negative ΔG° is, the larger K is. Conversely, if ΔG° is positive, $\ln K$ is negative, which means $K < 1$. Finally, if ΔG° is zero, $K = 1$.

Sample Exercise 19.12

Calculating an Equilibrium Constant from ΔG°

The standard free-energy change for the Haber process at 25 °C was obtained in Sample Exercise 19.9 for the Haber reaction:

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \qquad \Delta G^\circ = -33.3\ \text{kJ/mol} = -33{,}300\ \text{J/mol}$$

Use this value of ΔG° to calculate the equilibrium constant for the process at 25 °C.

SOLUTION

Analyze We are asked to calculate K for a reaction, given ΔG°.

Plan We can use Equation 19.21 to calculate K.

Solve Remembering to use the absolute temperature for T in Equation 19.21 and the form of R that matches our units, we have

$$K = e^{-\Delta G^\circ/RT} = e^{-(-33{,}300\ \text{J/mol})/(8.314\ \text{J/mol K})(298\ \text{K})} = e^{13.4} = 7 \times 10^5$$

Comment This is a large equilibrium constant, which indicates that the product, NH_3, is greatly favored in the equilibrium mixture at 25 °C. The equilibrium constants for the Haber reaction at temperatures in the range 300 °C to 600 °C, given in Table 15.2, are much smaller than the value at 25 °C. Clearly, a low-temperature equilibrium favors the production of ammonia more than a high-temperature one. Nevertheless, the Haber process is carried out at high temperatures because the reaction is extremely slow at room temperature.

Remember Thermodynamics can tell us the direction and extent of a reaction but tells us nothing about the rate at which it will occur. If a catalyst were found that would permit the reaction to proceed at a rapid rate at room temperature, high pressures would not be needed to force the equilibrium toward NH_3.

Practice Exercise

The K_{sp} for a very insoluble salt is 4.2×10^{-47} at 298 K. What is ΔG° for the dissolution of the salt in water?
(**a**) −265 kJ/mol (**b**) −115 kJ/mol (**c**) −2.61 kJ/mol
(**d**) +115 kJ/mol (**e**) +265 kJ/mol

CHEMISTRY AND LIFE Driving Nonspontaneous Reactions: Coupling Reactions

Many desirable chemical reactions, including a large number that are central to living systems, are nonspontaneous as written. For example, consider the extraction of copper metal from the mineral *chalcocite*, which contains Cu_2S. The decomposition of Cu_2S to its elements is nonspontaneous:

$$Cu_2S(s) \longrightarrow 2\ Cu(s) + S(s) \qquad \Delta G^\circ = +86.2\ kJ$$

Because ΔG° is very positive, we cannot obtain Cu(*s*) directly via this reaction. Instead, we must find some way to "do work" on the reaction to force it to occur as we wish. We can do this by coupling the reaction to another one so that the overall reaction *is* spontaneous. For example, we can envision the S(*s*) reacting with $O_2(g)$ to form $SO_2(g)$:

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta G^\circ = -300.4\ kJ$$

By coupling (adding together) these reactions, we can extract much of the copper metal via a spontaneous reaction:

$$Cu_2S(s) + O_2(g) \longrightarrow 2\ Cu(s) + SO_2(g)$$
$$\Delta G^\circ = (+86.2\ kJ) + (-300.4\ kJ) = -214.2\ kJ$$

In essence, we have used the spontaneous reaction of S(*s*) with $O_2(g)$ to provide the free energy needed to extract the copper metal from the mineral.

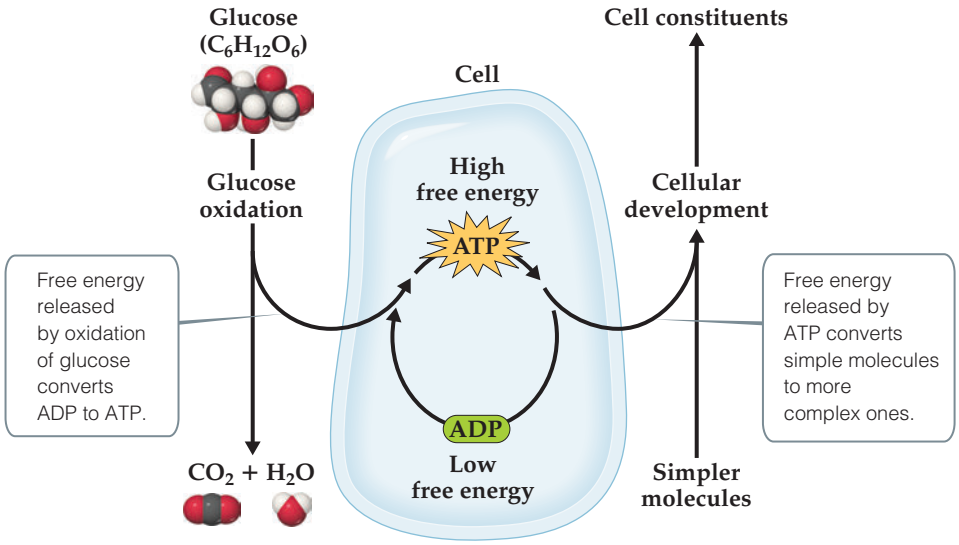
Biological systems employ the same principle of using spontaneous reactions to drive nonspontaneous ones. Many of the biochemical reactions that are essential for the formation and maintenance of highly ordered biological structures are not spontaneous. These necessary reactions are made to occur by coupling them with spontaneous reactions that release energy. The metabolism of food is the usual source of the free energy needed to do the work of maintaining biological systems. For example, complete oxidation of the sugar glucose, $C_6H_{12}O_6$, to CO_2 and H_2O yields substantial free energy:

$$C_6H_{12}O_6(s) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(l) \qquad \Delta G^\circ = -2880\ kJ$$

This energy can be used to drive nonspontaneous reactions in the body. However, a means is necessary to transport the energy released by glucose metabolism to the reactions that require energy. One way, shown in **Figure 19.16**, involves the interconversion of adenosine triphosphate (ATP) and adenosine diphosphate (ADP), molecules that are related to the building blocks of nucleic acids. The conversion of ATP to ADP releases free energy ($\Delta G^\circ = -30.5$ kJ) that can be used to drive other reactions.

In the human body, the metabolism of glucose occurs via a complex series of reactions, most of which release free energy. The free energy released during these steps is used in part to reconvert lower-energy ADP back to higher-energy ATP. Thus, the ATP–ADP interconversions are used to store energy during metabolism and to release it as needed to drive nonspontaneous reactions in the body.

Related Exercises: 19.111, 19.112



▲ **Figure 19.16 Schematic representation of free-energy changes during cell metabolism.** The oxidation of glucose to CO_2 and H_2O produces free energy that is then used to convert ADP into the more energetic ATP. The ATP is then used, as needed, as an energy source to drive nonspontaneous reactions, such as the conversion of simple molecules into more complex cell constituents.

Self-Assessment Exercise

19.41 A reaction has a large positive value of ΔG°. In what numerical range do you expect the value of K to be?

(a) $K >> 1$
(b) $0 < K < 1$
(c) $K << 0$

Exercises

19.42 Indicate whether ΔG increases, decreases, or does not change when the partial pressure of H_2 is increased in each of the following reactions:

(**a**) $H_2(g) + NiO(s) \longrightarrow Ni(s) + H_2O(g)$

(**b**) $H_2(g) + S(s) \longrightarrow H_2S(g)$

(**c**) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

19.43 Consider the reaction $CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(g) + 4\,HCl(g)$. (**a**) Using data from Appendix C, calculate $\Delta G°$ at 298 K. (**b**) Calculate ΔG at 298 K if the reaction mixture consists of 0.500 atm of $CH_4(g)$, 0.250 atm of $Cl_2(g)$, 0.100 atm of $CCl_4(g)$ and 0.150 atm of $HCl(g)$.

19.44 Using data from Appendix C, write the equilibrium-constant expression and calculate the value of the equilibrium constant and the free-energy change for these reactions at 298 K:

(**a**) $NaHCO_3(s) \rightleftharpoons NaOH(s) + CO_2(g)$

(**b**) $2\,HBr(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g) + Br_2(g)$

(**c**) $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$

19.45 Consider the reaction

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)$$

Using data in Appendix C, calculate the equilibrium pressure of CO_2 in the system at (**a**) 400 °C and (**b**) 180 °C.

19.46 The K_b for methylamine (CH_3NH_2) at 25 °C is given in Appendix D. (**a**) Write the chemical equation for the equilibrium that corresponds to K_b. (**b**) By using the value of K_b, calculate $\Delta G°$ for the equilibrium in part (a). (**c**) What is the value of ΔG at equilibrium? (**d**) What is the value of ΔG when $[H^+] = 6.7 \times 10^{-9}\,M$, $[CH_3NH_3^+] = 2.4 \times 10^{-3}\,M$, and $[CH_3NH_2] = 0.098\,M$?

Answers to Self-Assessment Exercise

19.41 (b)

Sample Integrative Exercise

Putting Concepts Together

Consider the simple salts NaCl(*s*) and AgCl(*s*). We will examine the equilibria in which these salts dissolve in water to form aqueous solutions of ions:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

(**a**) Calculate the value of $\Delta G°$ at 298 K for each of the preceding reactions. (**b**) The two values from part (a) are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change? (**c**) Use the values of $\Delta G°$ to calculate the K_{sp} values for the two salts at 298 K. (**d**) Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part (c)? (**e**) How will $\Delta G°$ for the solution process of these salts change with increasing T? What effect should this change have on the solubility of the salts?

SOLUTION

(**a**) We will use Equation 19.14 along with $\Delta G_f°$ values from Appendix C to calculate the $\Delta G°_{soln}$ values for each equilibrium. (As we did in Section 13.1, we use the subscript "soln" to indicate that these are thermodynamic quantities for the formation of a solution.) We find

$$\begin{aligned}\Delta G°_{soln}(NaCl) &= (-261.9\ kJ/mol) + (-131.2\ kJ/mol) \\ &\quad - (-384.0\ kJ/mol) \\ &= -9.1\ kJ/mol\end{aligned}$$

$$\begin{aligned}\Delta G°_{soln}(AgCl) &= (+77.11\ kJ/mol) + (-131.2\ kJ/mol) \\ &\quad - (-109.70\ kJ/mol) \\ &= +55.6\ kJ/mol\end{aligned}$$

(**b**) We can write $\Delta G°_{soln}$ as the sum of an enthalpy term, $\Delta H°_{soln}$, and an entropy term, $-T\Delta S°_{soln}$: $\Delta G°_{soln} = \Delta H°_{soln} + (-T\Delta S°_{soln})$. We can calculate the values of $\Delta H°_{soln}$ and $\Delta S°_{soln}$ by using Equations 5.31 and 19.8. We can then calculate $-T\Delta S°_{soln}$ at $T = 298$ K. The results are summarized in the following table:

Salt	$\Delta H°_{soln}$	$\Delta S°_{soln}$	$T\Delta S°_{soln}$
NaCl	+3.6 kJ/mol	+43.2 J/mol K	−12.9 kJ/mol
AgCl	+65.7 kJ/mol	+34.3 J/mol K	−10.2 kJ/mol

The entropy terms for the solution of the two salts are very similar. That seems sensible because each solution process should lead to a similar increase in randomness as the salt dissolves, forming hydrated ions. In contrast, we see a very large difference in the enthalpy term for the solution of the two salts. The difference in the values of $\Delta G°_{soln}$ is dominated by the difference in the values of $\Delta H°_{soln}$.

(**c**) The solubility product, K_{sp}, is the equilibrium constant for the solution process. As such, we can relate K_{sp} directly to ΔG°_{soln} by using Equation 19.21:

$$K_{sp} = e^{-\Delta G^\circ_{soln}/RT}$$

We can calculate the K_{sp} values in the same way we applied Equation 19.21 in Sample Exercise 19.12. We use the ΔG°_{soln} values we obtained in part (a), remembering to convert them from kJ/mol to J/mol:

$$\text{NaCl: } K_{sp} = [Na^+][Cl^-] = e^{-(-9100)/[(8.314)(298)]}$$
$$= e^{+3.7} = 40$$
$$\text{AgCl: } K_{sp} = [Ag^+][Cl^-] = e^{-(+55{,}600)/[(8.314)(298)]}$$
$$= e^{-22.4}$$
$$= 1.9 \times 10^{-10}$$

The value calculated for the K_{sp} of AgCl is very close to that listed in Appendix D.

(**d**) A soluble salt is one that dissolves appreciably in water. The K_{sp} value for NaCl is greater than 1, indicating that NaCl dissolves to a great extent. The K_{sp} value for AgCl is very small, indicating that very little dissolves in water. Silver chloride should indeed be considered an insoluble salt.

(**e**) As we expect, the solution process has a positive value of ΔS for both salts (see the table in part b). As such, the entropy term of the free-energy change, $-T\Delta S^\circ_{soln}$, is negative. If we assume that ΔH°_{soln} and ΔS°_{soln} do not change much with temperature, then an increase in T will serve to make ΔG°_{soln} more negative. Thus, the driving force for dissolution of the salts will increase with increasing T, and we therefore expect the solubility of the salts to increase with increasing T. In Figure 13.14, we see that the solubility of NaCl (and that of nearly any other salt) increases with increasing temperature.

Chapter Summary and Key Terms

SPONTANEOUS PROCESSES (SECTION 19.1) Most reactions and chemical processes have an inherent directionality: They are **spontaneous** in one direction and nonspontaneous in the reverse direction. The spontaneity of a process is related to the thermodynamic path the system takes from the initial state to the final state. In a **reversible process**, both the system and its surroundings can be restored to their original state by exactly reversing the change. In an **irreversible process**, the system cannot return to its original state without a permanent change in the surroundings. Any spontaneous process is irreversible. A process that occurs at a constant temperature is said to be **isothermal**.

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS (SECTION 19.2) The spontaneous nature of processes is related to a thermodynamic state function called **entropy**, denoted S. For a process that occurs at constant temperature, the entropy change of the system is given by the heat absorbed by the system along a reversible path, divided by the temperature: $\Delta S = q_{rev}/T$. For any process, the entropy change of the universe equals the entropy change of the system plus the entropy change of the surroundings: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$. The way entropy controls the spontaneity of processes is given by the **second law of thermodynamics**, which states that in an irreversible (spontaneous) process $\Delta S_{univ} > 0$. Entropy values are usually expressed in units of joules per kelvin, J/K.

THE MOLECULAR INTERPRETATION OF ENTROPY AND THE THIRD LAW OF THERMODYNAMICS (SECTION 19.3) A particular combination of motions and locations of the atoms and molecules of a system at a particular instant is called a **microstate**. The entropy of a system is a measure of its randomness or disorder. The entropy is related to the number of microstates, W, corresponding to the state of the system: $S = k \ln W$. Molecules can undergo three kinds of motion: In **translational motion** the entire molecule moves in space. Molecules can also undergo **vibrational motion**, in which the atoms of the molecule move toward and away from one another in periodic fashion, and **rotational motion**, in which the entire molecule spins like a top. The number of available microstates, and therefore the entropy, increases with an increase in volume, temperature, or motion of molecules because any of these changes increases the possible motions and locations of the molecules. As a result, entropy generally increases when liquids or solutions are formed from solids, gases are formed from either solids or liquids, or the number of molecules of gas increases during a chemical reaction. The **third law of thermodynamics** states that the entropy of a pure crystalline solid at 0 K is zero.

ENTROPY CHANGES IN CHEMICAL REACTIONS (SECTION 19.4) The third law allows us to assign entropy values for substances at different temperatures. Under standard conditions, the entropy of a mole of a substance is called its **standard molar entropy**, denoted S°. From tabulated values of S°, we can calculate the entropy change for any process under standard conditions. For an isothermal process, the entropy change in the surroundings is equal to $-\Delta H/T$.

GIBBS FREE ENERGY (SECTION 19.5) The **Gibbs free energy** (or just **free energy**), G, is a thermodynamic state function that combines the two state functions enthalpy and entropy: $G = H - TS$. For processes that occur at constant temperature, $\Delta G = \Delta H - T\Delta S$. For a process occurring at constant temperature and pressure, the sign of ΔG relates to the spontaneity of the process. When ΔG is negative, the process is spontaneous. When ΔG is positive, the process is nonspontaneous, but the reverse process is spontaneous. At equilibrium the process is reversible and ΔG is zero. The free energy is also a measure of the maximum useful work that can be performed by a system in a spontaneous process. The standard free-energy change, ΔG°, for any process can be calculated from tabulations of **standard free energies of formation**, ΔG°_f, which are defined in a fashion analogous to standard enthalpies of formation, ΔH°_f. The value of ΔG°_f for a pure element in its standard state is defined to be zero.

FREE ENERGY, TEMPERATURE, AND THE EQUILIBRIUM CONSTANT (SECTIONS 19.6 AND 19.7) The values of ΔH and ΔS for a chemical process generally do not vary much with temperature. Therefore, the dependence of ΔG with temperature is governed mainly by the value of T in the expression $\Delta G = \Delta H - T\Delta S$. The entropy term $-T\Delta S$ has the greater effect on the temperature dependence of ΔG and, hence, on the spontaneity of the process. For example, a process for which $\Delta H > 0$ and $\Delta S > 0$, such as the melting of ice, can be nonspontaneous ($\Delta G > 0$) at low temperatures and spontaneous ($\Delta G < 0$) at higher temperatures. Under nonstandard conditions, ΔG is related to ΔG° and the value of the reaction quotient, Q: $\Delta G = \Delta G^\circ + RT \ln Q$. At equilibrium ($\Delta G = 0, Q = K$), $\Delta G^\circ = -RT \ln K$. Thus, the standard free-energy change is directly related to the equilibrium constant for the reaction. This relationship expresses the temperature dependence of equilibrium constants.

Learning Outcomes After studying this chapter, you should be able to:

- Explain and apply the terms spontaneous process, reversible process, irreversible process, and isothermal process. (Section 19.1) *Related Exercises: 19.2, 19.3, 19.57, 19.58*
- Define entropy and state the second law of thermodynamics. (Section 19.2) *Related Exercises: 19.8, 19.63*
- Calculate ΔS for a phase change. (Section 19.2) *Related Exercises: 19.9, 19.64*
- Explain how the entropy of a system is related to the number of possible microstates. (Section 19.3) *Related Exercises: 19.15, 19.69*
- Describe the kinds of molecular motion that a molecule can possess. (Section 19.3) *Related Exercise: 19.72*
- Predict the sign of ΔS for physical and chemical processes. (Section 19.3) *Related Exercises: 19.18, 19.21, 19.71, 19.74*
- State the third law of thermodynamics. (Section 19.3) *Related Exercise: 19.72*
- Compare the values of standard molar entropies. (Section 19.4) *Related Exercises: 19.24, 19.25, 19.76, 19.77*
- Calculate standard entropy changes for a system from standard molar entropies. (Section 19.4) *Related Exercises: 19.30, 19.80*
- Calculate the Gibbs free energy from the enthalpy change and entropy change at a given temperature. (Section 19.5) *Related Exercises: 19.31, 19.32, 19.81, 19.82*
- Use free-energy changes to predict whether reactions are spontaneous. (Section 19.5) *Related Exercises: 19.31, 19.81*
- Calculate standard free-energy changes using standard free energies of formation. (Section 19.5) *Related Exercises: 19.33, 19.83*
- Predict the effect of temperature on spontaneity given ΔH and ΔS. (Section 19.6) *Related Exercises: 19.36, 19.39, 19.85, 19.88*
- Calculate ΔG under nonstandard conditions. (Section 19.7) *Related Exercises: 19.92, 19.43*
- Relate $\Delta G°$ and equilibrium constant. (Section 19.7) *Related Exercises: 19.44, 19.45, 19.93, 19.94*

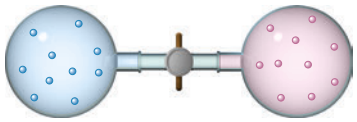
Key Equations

$\Delta S = \frac{q_{rev}}{T}$ (constant T)	[19.2]	Relating entropy change to the heat absorbed or released in a reversible process
Reversible process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$ *Irreversible process*: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$	[19.4]	The second law of thermodynamics
$S = k \ln W$	[19.5]	Relating entropy to the number of microstates
$\Delta S° = \sum nS°(\text{products}) - \sum mS°(\text{reactants})$	[19.8]	Calculating the standard entropy change from standard molar entropies
$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$	[19.9]	The entropy change of the surroundings for a process at constant temperature and pressure
$\Delta G = \Delta H - T\Delta S$	[19.11]	Calculating the Gibbs free-energy change from enthalpy and entropy changes at constant temperature
$\Delta G° = \sum n\Delta G_f°(\text{products}) - \sum m\Delta G_f°(\text{reactants})$	[19.14]	Calculating the standard free-energy change from standard free energies of formation
Reversible process: $\Delta G = \Delta H_{sys} - T\Delta S_{sys} = 0$ *Irreversible process*: $\Delta G = \Delta H_{sys} - T\Delta S_{sys} < 0$	[19.17]	Relating the free-energy change to the reversibility of a process at constant temperature and pressure
$\Delta G = -w_{max}$	[19.18]	Relating the free-energy change to the maximum work a system can perform
$\Delta G = \Delta G° + RT \ln Q$	[19.19]	Calculating the free-energy change under nonstandard conditions
$\Delta G° = -RT \ln K$	[19.20]	Relating the standard free-energy change and the equilibrium constant

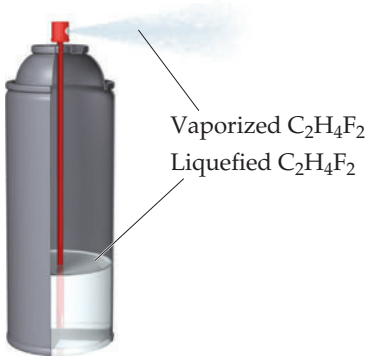
Exercises

Visualizing Concepts

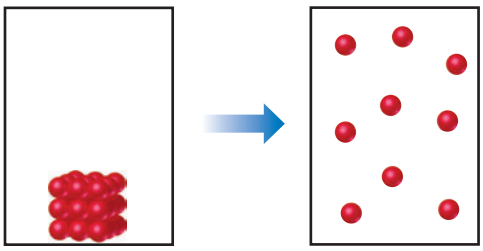
19.47 Two different gases occupy the two bulbs shown here. Consider the process that occurs when the stopcock is opened, assuming the gases behave ideally. (**a**) Draw the final (equilibrium) state. (**b**) Predict the signs of ΔH and ΔS for the process. (**c**) Is the process that occurs when the stopcock is opened a reversible one? (**d**) How does the process affect the entropy of the surroundings? [Sections 19.1 and 19.2]



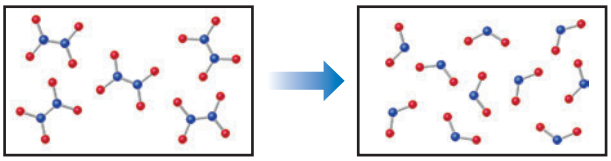
19.48 As shown here, one type of computer keyboard cleaner contains liquefied 1,1-difluoroethane ($C_2H_4F_2$), which is a gas at atmospheric pressure. When the nozzle is squeezed, the 1,1-difluoroethane vaporizes out of the nozzle at high pressure, blowing dust out of objects. (**a**) Based on your experience, is the vaporization a spontaneous process at room temperature? (**b**) Defining the 1,1-difluoroethane as the system, do you expect q_{sys} for the process to be positive or negative? (**c**) Predict whether ΔS is positive or negative for this process. (**d**) Given your answers to (a), (b), and (c), do you think the operation of this product depends more on enthalpy or entropy? [Sections 19.1 and 19.2]



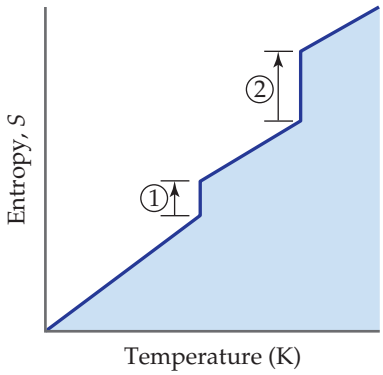
19.49 (**a**) What are the signs of ΔS and ΔH for the process depicted here? (**b**) If energy can flow in and out of the system to maintain a constant temperature during the process, what can you say about the entropy change of the surroundings as a result of this process? [Sections 19.2 and 19.5]



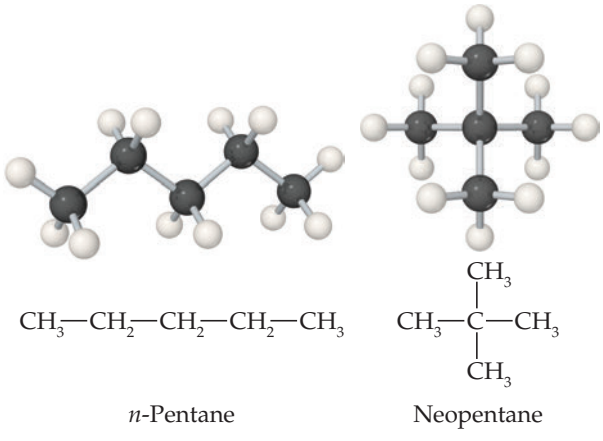
19.50 Predict the signs of ΔH and ΔS for this reaction. Explain your choice. [Section 19.3]



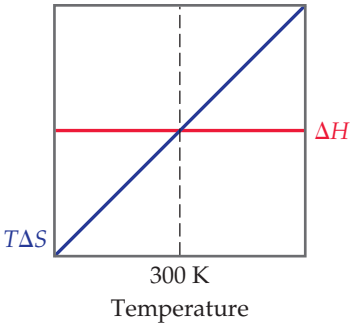
19.51 The accompanying diagram shows how entropy varies with temperature for a substance that is a gas at the highest temperature shown. (**a**) What processes correspond to the entropy increases along the vertical lines labeled 1 and 2? (**b**) Why is the entropy change for 2 larger than that for 1? (**c**) If this substance is a perfect crystal at $T = 0$ K, what is the value of S at this temperature? [Section 19.3]



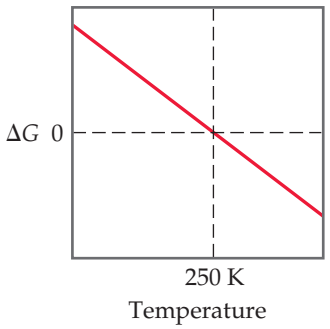
19.52 *Isomers* are molecules that have the same chemical formula but different arrangements of atoms, as shown here for two isomers of pentane, C_5H_{12}. (**a**) Do you expect a significant difference in the enthalpy of combustion of the two isomers? Explain. (**b**) Which isomer do you expect to have the higher standard molar entropy? Explain. [Section 19.4]



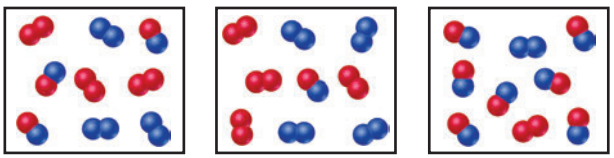
19.53 The accompanying diagram shows how ΔH (red line) and $T\Delta S$ (blue line) change with temperature for a hypothetical reaction. (**a**) What is the significance of the point at 300 K, where ΔH and $T\Delta S$ are equal? (**b**) In what temperature range is this reaction spontaneous? [Section 19.6]



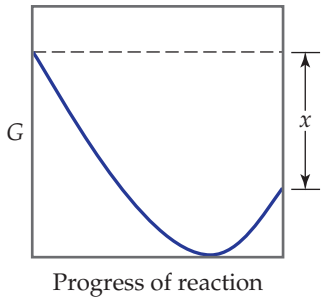
19.54 The accompanying diagram shows how ΔG for a hypothetical reaction changes as temperature changes. (**a**) At what temperature is the system at equilibrium? (**b**) In what temperature range is the reaction spontaneous? (**c**) Is ΔH positive or negative? (**d**) Is ΔS positive or negative? [Sections 19.5 and 19.6]



19.55 Consider a reaction $A_2(g) + B_2(g) \rightleftharpoons 2\,AB(g)$, with atoms of A shown in red in the diagram and atoms of B shown in blue. (**a**) If $K_c = 1$, which box represents the system at equilibrium? (**b**) If $K_c = 1$, which box represents the system at $Q < K_c$? (**c**) Rank the boxes in order of increasing magnitude of ΔG for the reaction. [Sections 19.5 and 19.7]



19.56 The accompanying diagram shows how the free energy, G, changes during a hypothetical reaction $A(g) + B(g) \longrightarrow C(g)$. On the left are pure reactants A and B, each at 101.3 kPa, and on the right is the pure product, C, also at 101.3 kPa. Indicate whether each of the following statements is true or false. (**a**) The minimum of the graph corresponds to the equilibrium mixture of reactants and products for this reaction. (**b**) At equilibrium, all of A and B have reacted to give pure C. (**c**) The entropy change for this reaction is positive. (**d**) The "x" on the graph corresponds to ΔG for the reaction. (**e**) ΔG for the reaction corresponds to the difference between the top left of the curve and the bottom of the curve. [Section 19.7]



Spontaneous Processes (Section 19.1)

19.57 Which of the following processes are spontaneous and which are nonspontaneous: (**a**) mixing of water and ethanol, (**b**) dissolution of sugar in a cup of hot coffee, (**c**) formation of oxygen atoms from O_2 molecules at STP, (**d**) rusting of iron, (**e**) formation of glucose from CO_2 and H_2O at STP?

19.58 Indicate whether each statement is true or false. (**a**) A reaction that is spontaneous in one direction will be nonspontaneous in the reverse direction under the same reaction conditions. (**b**) All spontaneous processes are fast. (**c**) Most spontaneous processes are reversible. (**d**) An isothermal process is one in which the system loses no heat. (**e**) The maximum amount of work can be accomplished by an irreversible process rather than a reversible one.

19.59 Consider the melting of ice (solid water) to liquid water at a pressure of 101.3 kPa. (**a**) Is this process endothermic or exothermic? (**b**) In what temperature range is it a spontaneous process? (**c**) In what temperature range is it a nonspontaneous process? (**d**) At what temperature are the two phases in equilibrium?

19.60 Consider the following process: a system changes from state 1 (initial state) to state 2 (final state) in such a way that its temperature changes from 300 K to 400 K. (**a**) Is this process isothermal? (**b**) Does the temperature change depend on the particular pathway taken to carry out this change of state? (**c**) Does the change in the internal energy, ΔE, depend on whether the process is reversible or irreversible?

19.61 A system goes from state 1 to state 2 and back to state 1. (**a**) Is ΔE the same in magnitude for both the forward and reverse processes? (**b**) Without further information, can you conclude that the amount of heat transferred to the system as it goes from state 1 to state 2 is the same or different as compared to that upon going from state 2 back to state 1? (**c**) Suppose the changes in state are reversible processes. Is the work done by the system upon going from state 1 to state 2 the same or different as compared to that upon going from state 2 back to state 1?

19.62 Consider a system consisting of an ice cube. (**a**) Under what conditions can the ice cube melt reversibly? (**b**) If the ice cube melts reversibly, is ΔH zero for the process?

Entropy and the Second Law of Thermodynamics (Section 19.2)

19.63 Indicate whether each statement is true or false. (**a**) ΔS depends on whether the process is reversible or irreversible. (**b**) If a system undergoes an irreversible change, the entropy of the universe increases. (**c**) Only if the change in entropy of the system is exactly matched by an equal and opposite change in the entropy of the surroundings, the system undergoes a reversible process. (**d**) If the entropy change of the system is zero, the system undergoes a reversible process.

19.64 The normal boiling point of the element mercury (Hg) is 356.7 °C, and its molar enthalpy of vaporization is $\Delta H_{vap} = 59.11$ kJ/mol. (**a**) When Hg boils at its normal boiling point, does its entropy increase or decrease? (**b**) Calculate the value of ΔS when 2.00 mol of Hg is vaporized at 356.7 °C.

19.65 Indicate whether each statement is true or false. (**a**) The second law of thermodynamics says that entropy can only be produced but cannot not be destroyed. (**b**) In a certain process the entropy of the system changes by 1.2 J/K (increase) and the entropy of the surroundings changes by −1.2 J/K (decrease). Thus, this process must be spontaneous. (**c**) In a certain process the entropy of the system changes by 1.3 J/K (increase) and the entropy of the surroundings changes by −1.2 J/K (decrease). Thus, this process must be reversible.

19.66 (**a**) What sign for ΔS do you expect when the volume of 0.200 mol of an ideal gas at 27 °C is increased isothermally from an initial volume of 10.0 L? (**b**) If the final volume is 18.5 L, calculate the entropy change for the process. (**c**) Do you need to specify the temperature to calculate the entropy change?

19.67 (**a**) Use data in Appendix C to estimate the boiling point of bromine, Br_2. (**b**) Use a reference source, such as the CRC Handbook of Chemistry and Physics, to find the experimental boiling point of bromine.

The Molecular Interpretation of Entropy and the Third Law of Thermodynamics (Section 19.3)

19.68 For the isothermal expansion of a gas into a vacuum, $\Delta E = 0, q = 0$, and $w = 0$. (**a**) Is this a spontaneous process? (**b**) Explain why no work is done by the system during this process. (**c**) What is the "driving force" for the expansion of the gas: enthalpy or entropy?

19.69 Would each of the following changes increase, decrease, or have no effect on the number of microstates available to a system: (**a**) increase in temperature, (**b**) decrease in volume, (**c**) change of state from liquid to gas?

19.70 (**a**) What do you expect for the sign of ΔS in a chemical reaction in which 3 mol of gaseous reactants are converted to 2 mol of gaseous products? (**b**) For which of the processes in Exercise 19.57 does the entropy of the system increase?

19.71 Does the entropy of the system increase, decrease, or stay the same when (**a**) a solid melts, (**b**) a gas liquefies, (**c**) a solid sublimes?

19.72 Indicate whether each statement is true or false. (**a**) The third law of thermodynamics says that the entropy of a perfect, pure crystal at absolute zero increases with the mass of the crystal. (**b**) "Translational motion" of molecules refers to their change in spatial location as a function of time. (**c**) "Rotational" and "vibrational" motions contribute to the entropy in atomic gases like He and Xe. (**d**) The larger the number of atoms in a molecule, the more degrees of freedom of rotational and vibrational motion it likely has.

19.73 For each of the following pairs, predict which substance has the higher entropy per mole at a given temperature: (**a**) $I_2(s)$ or $I_2(g)$ (**b**) $O_2(g)$ at 50.7 kPa or O_2 at 101.3 kPa (**c**) 1 mol of N_2 in 22.4 L or 1 mol of N_2 in 44.8 L. (**d**) $CH_3OH(l)$ or $CH_3OH(s)$.

19.74 Predict the sign of the entropy change of the system for each of the following reactions:

(**a**) $CO(g) + H_2(g) \longrightarrow C(s) + H_2O(g)$

(**b**) $2\,O_2(g) + N_2(g) \longrightarrow 2\,NO_2(g)$

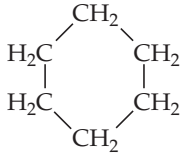
(**c**) $NH_4Cl(s) \longrightarrow HCl(g) + NH_3(g)$

(**d**) $2\,C_2H_4(g) + O_2(g) \longrightarrow 2\,C_2H_4O(g)$

Entropy Changes in Chemical Reactions (Section 19.4)

19.75 (**a**) Using Figure 19.12 as a model, sketch how the entropy of water changes as it is heated from −50 °C to 110 °C at sea level. Show the temperatures at which there are vertical increases in entropy. (**b**) Which process has the larger entropy change: melting ice or boiling water? Explain.

19.76 Cyclohexane and 1-hexene are isomers that both have the formula, C_6H_{12}. Based on the molecular structures shown, which of these isomers would you expect to have the higher standard molar entropy at 25 °C?



Cyclohexane

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3$

1-hexene

19.77 Predict which member of each of the following pairs has the greater standard entropy at 25 °C: (**a**) $HNO_3(g)$ or $HNO_3(aq)$, (**b**) $PCl_3(l)$ or $PCl_3(g)$, (**c**) $Fe_2O_3(s)$ or $Fe_3O_4(s)$, (**d**) Li(*s*) or Li(*g*). Use Appendix C to find the standard entropy of each substance.

19.78 The standard entropies at 298 K for certain Group 14 elements are: C(*s*, diamond) = 2.43 J/mol K, Si(*s*) = 18.81 J/mol K, Ge(*s*) = 31.09 J/mol K, and Sn(*s*) = 51.818 J/mol K. All but Sn have the same (diamond) structure. How do you account for the trend in the $S°$ values?

19.79 Using $S°$ values from Appendix C, calculate $\Delta S°$ values for the following reactions. In each case, account for the sign of $\Delta S°$.

(**a**) $NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

(**b**) $CH_3OH(g) \longrightarrow CO(g) + 2\,H_2(g)$

(**c**) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$

(**d**) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$

Gibbs Free Energy (Sections 19.5 and 19.6)

19.80 (**a**) Is the standard free energy change, $\Delta G°$, always larger than ΔG? (**b**) For any process that occurs at constant

temperature and pressure, what is the significance of $\Delta G = 0$? (**c**) For a certain process, ΔG is large and negative. Does this mean that the process necessarily has a low activation barrier?

19.81 For a certain chemical reaction, $\Delta H° = -40.0\,\text{kJ}$ and $\Delta S° = -150.0\,\text{J/K}$. (**a**) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? (**b**) Does the reaction lead to an increase or decrease in the randomness or disorder of the surroundings? (**c**) Calculate $\Delta G°$ for the reaction at 298 K. (**d**) Is the reaction spontaneous at 298 K under standard conditions?

19.82 Using data in Appendix C, calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 298 K for each of the following reactions.

(**a**) $\text{Ti}(s) + 2\,\text{Cl}_2(g) \longrightarrow \text{TiCl}_4(l)$

(**b**) $\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

(**c**) $\text{CF}_4(g) + 2\,\text{H}_2(l) \longrightarrow \text{C}(s) + 4\,\text{HF}(g)$

(**d**) $\text{Na}_2\text{CO}_3(s) + 2\,\text{HNO}_3(aq) \longrightarrow 2\,\text{NaNO}_3(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$

19.83 Using data from Appendix C, calculate $\Delta G°$ for the following reactions. Indicate whether each reaction is spontaneous at 298 K under standard conditions.

(**a**) $2\,\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\,\text{ZnO}(s)$

(**b**) $2\,\text{NaBr}(s) \longrightarrow 2\,\text{Na}(g) + \text{Br}_2(g)$

(**c**) $\text{CH}_3\text{OH}(g) + \text{CH}_4(g) \longrightarrow \text{C}_2\text{H}_5\text{OH}(g) + \text{H}_2(g)$

(**d**) $2\,\text{AgNO}_3(s) \longrightarrow \text{Ag}_2\text{O}(s) + \text{N}_2\text{O}(g) + 2\,\text{O}_2(g)$

19.84 Today, most candles are made of paraffin wax. A typical component of paraffin wax is the hydrocarbon $\text{C}_{31}\text{H}_{64}$ which is solid at room temperature. (**a**) Write a balanced equation for the combustion of $\text{C}_{31}\text{H}_{64}(s)$ to form $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$. (**b**) Without using thermochemical data, predict whether $\Delta G°$ for this reaction is more negative or less negative than $\Delta H°$.

19.85 From the values given for $\Delta H°$ and $\Delta S°$, calculate $\Delta G°$ for each of the following reactions at 298 K. If the reaction is not spontaneous under standard conditions at 298 K, at what temperature (if any) would the reaction become spontaneous?

(**a**) $2\,\text{PbS}(s) + 3\,\text{O}_2(g) \longrightarrow 2\,\text{PbO}(s) + 2\,\text{SO}_2(g)$
$\Delta H° = -844\,\text{kJ}; \Delta S° = -165\,\text{J/K}$

(**b**) $2\,\text{POCl}_3(g) \longrightarrow 2\,\text{PCl}_3(g) + \text{O}_2(g)$
$\Delta H° = 572\,\text{kJ}; \Delta S° = 179\,\text{J/K}$

19.86 A particular constant pressure reaction is barely spontaneous at 320 K. The enthalpy change for the reaction is +15.2 kJ. Estimate ΔS for the reaction.

19.87 For a particular reaction, $\Delta H = 30.0\,\text{kJ}$ and $\Delta S = 90.0\,\text{J/K}$. Assume that ΔH and ΔS do not vary with temperature. (**a**) At what temperature will the reaction have $\Delta G = 0$? (**b**) If T is increased from that in part (a), will the reaction be spontaneous or nonspontaneous?

19.88 Consider the following reaction between oxides of nitrogen:

$$\text{NO}_2(g) + \text{N}_2\text{O}(g) \longrightarrow 3\,\text{NO}(g)$$

(**a**) Use data in Appendix C to predict how ΔG for the reaction varies with increasing temperature. (**b**) Calculate ΔG at 800 K, assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature. Under standard conditions is the reaction spontaneous at 800 K? (**c**) Calculate ΔG at 1000 K. Is the reaction spontaneous under standard conditions at this temperature?

19.89 (**a**) Using data in Appendix C, estimate the temperature at which the free-energy change for the transformation from $\text{I}_2(s)$ to $\text{I}_2(g)$ is zero. (**b**) Use a reference source, such as Web Elements (www.webelements.com), to find the experimental melting and boiling points of I_2. (**c**) Which of the values in part (b) is closer to the value you obtained in part (a)?

19.90 Acetylene gas, $\text{C}_2\text{H}_2(g)$, is used in welding. (**a**) Write a balanced equation for the combustion of acetylene gas to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$. (**b**) How much heat is produced in burning 1 mol of C_2H_2 under standard conditions if both reactants and products are brought to 298 K? (**c**) What is the maximum amount of useful work that can be accomplished under standard conditions by this reaction?

Free Energy and Equilibrium (Section 19.7)

19.91 Indicate whether ΔG increases, decreases, or stays the same for each of the following reactions as the partial pressure of O_2 is increased:

(**a**) $\text{HgO}(s) \longrightarrow \text{Hg}(l) + \text{O}_2(g)$

(**b**) $2\,\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\,\text{SO}_3(g)$

(**c**) $2\,\text{NO}_2(g) \longrightarrow 2\,\text{NO}(g) + \text{O}_2(g)$

19.92 Consider the reaction $2\,\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\,\text{NO}_2(g)$. (**a**) Using data from Appendix C, calculate $\Delta G°$ at 298 K. (**b**) Calculate ΔG at 298 K if the partial pressures of all gases are 33.4 kPa.

19.93 Use data from Appendix C to calculate the equilibrium constant, K, and $\Delta G°$ at 298 K for each of the following reactions:

(**a**) $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\,\text{HI}(g)$

(**b**) $\text{C}_2\text{H}_5\text{OH}(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g)$

(**c**) $3\,\text{C}_2\text{H}_2(g) \rightleftharpoons \text{C}_6\text{H}_6(g)$

19.94 Consider the decomposition of barium carbonate:

$$\text{BaCO}_3(s) \rightleftharpoons \text{BaO}(s) + \text{CO}_2(g)$$

Using data from Appendix C, calculate the equilibrium pressure of CO_2 at (**a**) 298 K and (**b**) 1100 K.

19.95 The value of K_a for nitrous acid (HNO_2) at 25 °C is given in Appendix D. (**a**) Write the chemical equation for the equilibrium that corresponds to K_a. (**b**) By using the value of K_a, calculate $\Delta G°$ for the dissociation of nitrous acid in aqueous solution. (**c**) What is the value of ΔG at equilibrium? (**d**) What is the value of ΔG when $[\text{H}^+] = 5.0 \times 10^{-2}\,M$, $[\text{NO}_2^-] = 6.0 \times 10^{-4}\,M$, and $[\text{HNO}_2] = 0.20\,M$?

Additional Exercises

19.96 (**a**) Which of the thermodynamic quantities p, H, q, w, and G are state functions? (**b**) Consider a system going from state 1 to state 2 in a reversible and an irreversible way. Compare q_{rev} and q_{irrev}. (**c**) Consider a system going from state 1 to state 2 in a reversible and an irreversible way. Compare w_{rev} and w_{irrev}. (**d**) For a reversible isothermal process, write an expression for ΔH and an expression for ΔG in terms of q, w and T, p and ΔV.

19.97 The crystalline hydrate $Cd(NO_3)_2 \cdot 4H_2O(s)$ loses water when placed in a large, closed, dry vessel at room temperature:

$$Cd(NO_3)_2 \cdot 4H_2O(s) \longrightarrow Cd(NO_3)_2(s) + 4\,H_2O(g)$$

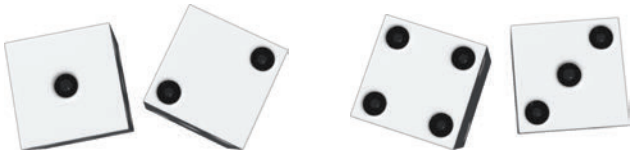
This process is spontaneous and $\Delta H°$ is positive at room temperature. (**a**) What is the sign of $\Delta S°$ at room temperature? (**b**) If the hydrated compound is placed in a large, closed vessel that already contains a large amount of water vapor, does $\Delta S°$ change for this reaction at room temperature?

19.98 Indicate whether each of the following statements is true or false. If it is false, correct it. (**a**) The feasibility of manufacturing NH_3 from N_2 and H_2 depends entirely on the value of ΔH for the process $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$. (**b**) The reaction of Na(*s*) with $Cl_2(g)$ to form NaCl(*s*) is a spontaneous process. (**c**) A spontaneous process can in principle be conducted reversibly. (**d**) Spontaneous processes in general require that work be done to force them to proceed. (**e**) Spontaneous processes are those that are exothermic and that lead to a higher degree of order in the system.

19.99 For each of the following processes, indicate whether the signs of ΔS and ΔH are expected to be positive, negative, or about zero. (**a**) A solid sublimes. (**b**) The temperature of a sample of Co(*s*) is lowered from 60 °C to 25 °C. (**c**) Ethanol evaporates from a beaker. (**d**) A diatomic molecule dissociates into atoms. (**e**) A piece of charcoal is combusted to form $CO_2(g)$ and $H_2O(g)$.

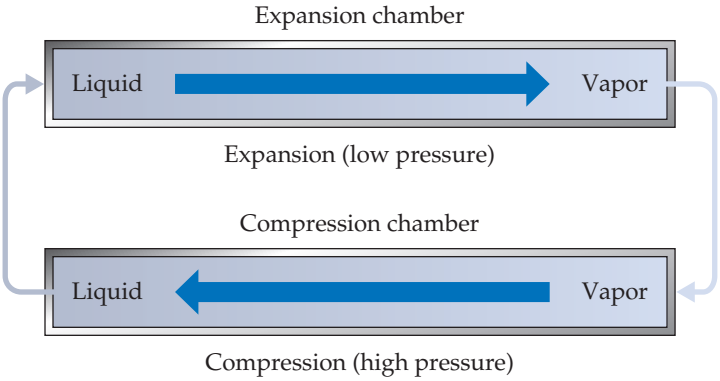
19.100 The reaction $2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$ is highly spontaneous. A classmate calculates the entropy change for this reaction and obtains a large negative value for $\Delta S°$. Did your classmate make a mistake in the calculation? Explain.

19.101 Consider a system that consists of two standard playing dice, with the state of the system defined by the sum of the values shown on the top faces. (**a**) The two arrangements of top faces shown here can be viewed as two possible microstates of the system. Explain. (**b**) To which state does each microstate correspond? (**c**) How many possible states are there for the system? (**d**) Which state or states have the highest entropy? Explain. (**e**) Which state or states have the lowest entropy? Explain. (**f**) Calculate the absolute entropy of the two-dice system.



19.102 Ammonium nitrate dissolves spontaneously and endothermally in water at room temperature. What can you deduce about the sign of ΔS for this solution process?

19.103 A standard air conditioner involves a *refrigerant* that is typically now a fluorinated hydrocarbon, such as CH_2F_2. An air-conditioner refrigerant has the property that it readily vaporizes at atmospheric pressure and is easily compressed to its liquid phase under increased pressure. The operation of an air conditioner can be thought of as a closed system made up of the refrigerant going through the two stages shown here (the air circulation is not shown in this diagram).



During *expansion*, the liquid refrigerant is released into an expansion chamber at low pressure, where it vaporizes. The vapor then undergoes *compression* at high pressure back to its liquid phase in a compression chamber. (**a**) What is the sign of q for the expansion? (**b**) What is the sign of q for the compression? (**c**) In a central air-conditioning system, one chamber is inside the home and the other is outside. Which chamber is where, and why? (**d**) Imagine that a sample of liquid refrigerant undergoes expansion followed by compression, so that it is back to its original state. Would you expect that to be a reversible process? (**e**) Suppose that a house and its exterior are both initially at 31 °C. Some time after the air conditioner is turned on, the house is cooled to 24 °C. Is this process spontaneous or nonspontaneous?

19.104 *Trouton's rule* states that for many liquids at their normal boiling points, the standard molar entropy of vaporization is about 88 J/mol K. (**a**) Estimate the normal boiling point of bromine, Br_2, by determining $\Delta H°_{vap}$ for Br_2 using data from Appendix C. Assume that $\Delta H°_{vap}$ remains constant with temperature and that Trouton's rule holds. (**b**) Look up the normal boiling point of Br_2 in a chemistry handbook or at the WebElements website (www.webelements.com) and compare it to your calculation. What are the possible sources of error, or incorrect assumptions, in the calculation?

19.105 (**a**) Write the chemical equations that correspond to $\Delta G°_f$ for $CH_4(g)$ and for NaCl(*s*). (**b**) For these formation reactions, compare $\Delta G°_f$ and $\Delta H°_f$. (**c**) In general, under which condition is $\Delta G°_f$ more negative (less positive) than $\Delta H°_f$? (i) When the temperature is high, (ii) when $\Delta S°_f$ is positive, (iii) when the reaction is reversible.

19.106 Consider the following three reactions:

(**i**) $Ti(s) + 2\,Cl_2(g) \longrightarrow TiCl_4(g)$

(**ii**) $C_2H_6(g) + 7\,Cl_2(g) \longrightarrow 2\,CCl_4(g) + 6\,HCl(g)$

(**iii**) $BaO(s) + CO_2(g) \longrightarrow BaCO_3(s)$

(**a**) For each of the reactions, use data in Appendix C to calculate $\Delta H°$, $\Delta G°$, K, and $\Delta S°$ at 25 °C. (**b**) Which of these reactions are spontaneous under standard conditions at 25 °C? (**c**) For each of the reactions, predict the manner in which the change in free energy varies with an increase in temperature.

19.107 Using the data in Appendix C and given the pressures listed, calculate K_p and ΔG for each of the following reactions:

(**a**) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$
$P_{N_2} = 263.4$ kPa, $P_{H_2} = 597.8$ kPa, $P_{NH_3} = 101.3$ kPa

(**b**) $2\,N_2H_4(g) + 2\,NO_2(g) \longrightarrow 3\,N_2(g) + 4\,H_2O(g)$
$P_{N_2H_4} = P_{NO_2} = 5.07$ kPa,
$P_{N_2} = 50.7$ kPa, $P_{H_2O} = 30.4$ kPa

(**c**) $N_2H_4(g) \longrightarrow N_2(g) + 2\,H_2(g)$
$P_{N_2H_4} = 101.3$ kPa, $P_{N_2} = 152.0$ kPa, $P_{H_2} = 253.3$ kPa

19.108 (**a**) For each of the following reactions, predict the sign of $\Delta H°$ and $\Delta S°$ without doing any calculations. (**b**) Based on your general chemical knowledge, predict which of these reactions will have $K > 1$ at 25 °C. (**c**) In each case, indicate whether K should increase or decrease with increasing temperature.

(**i**) $2\,Fe(s) + O_2(g) \rightleftharpoons 2\,FeO(s)$

(**ii**) $Cl_2(g) \rightleftharpoons 2\,Cl(g)$

(**iii**) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(**iv**) $CO_2(g) + CaO(s) \rightleftharpoons CaCO_3(s)$

19.109 Acetic acid can be manufactured by combining methanol with carbon monoxide, an example of a *carbonylation* reaction:

$$CH_3OH(l) + CO(g) \longrightarrow CH_3COOH(l)$$

(**a**) Calculate the equilibrium constant for the reaction at 25 °C. (**b**) Industrially, this reaction is run at temperatures above 25 °C. Will an increase in temperature produce an increase or decrease in the mole fraction of acetic acid at equilibrium? Why are elevated temperatures used? (**c**) At what temperature will this reaction have an equilibrium constant equal to 1? (You may assume that $\Delta H°$ and $\Delta S°$ are temperature independent, and you may ignore any phase changes that might occur.)

19.110 The oxidation of glucose ($C_6H_{12}O_6$) in body tissue produces CO_2 and H_2O. In contrast, anaerobic decomposition, which occurs during fermentation, produces ethanol (C_2H_5OH) and CO_2. (**a**) Using data given in Appendix C, compare the equilibrium constants for the following reactions:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(l)$$

$$C_6H_{12}O_6(s) \rightleftharpoons 2\,C_2H_5OH(l) + 2\,CO_2(g)$$

(**b**) Compare the maximum work that can be obtained from these processes under standard conditions.

19.111 The conversion of natural gas, which is mostly methane, into products that contain two or more carbon atoms, such as ethane (C_2H_6), is a very important industrial chemical process. In principle, methane can be converted into ethane and hydrogen:

$$2\,CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

In practice, this reaction is carried out in the presence of oxygen:

$$2\,CH_4(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_6(g) + H_2O(g)$$

(**a**) Using the data in Appendix C, calculate K for these reactions at 25 °C and 500 °C. (**b**) Is the difference in $\Delta G°$ for the two reactions due primarily to the enthalpy term (ΔH) or the entropy term ($-T\Delta S$)? (**c**) Explain how the preceding reactions are an example of driving a nonspontaneous reaction, as discussed in the "Chemistry and Life" box in Section 19.7. (**d**) The reaction of CH_4 and O_2 to form C_2H_6 and H_2O must be carried out carefully to avoid a competing reaction. What is the most likely competing reaction?

19.112 Cells use the hydrolysis of adenosine triphosphate (ATP) as a source of energy (Figure 19.16). The conversion of ATP to ADP has a standard free-energy change of −30.5 kJ/mol. If all the free energy from the metabolism of glucose,

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$

goes into the conversion of ADP to ATP, how many moles of ATP can be produced for each mole of glucose?

19.113 The potassiumion concentration in blood plasma is about $5.0 \times 10^{-3}\ M$, whereas the concentration in muscle cell fluid is much greater (0.15 M). The plasma and intracellular fluid are separated by the cell membrane, which we assume is permeable only to K^+. (**a**) What is ΔG for the transfer of 1 mol of K^+ from blood plasma to the cellular fluid at body temperature 37 °C? (**b**) What is the minimum amount of work that must be used to transfer this K^+?

Integrative Exercises

19.114 Most liquids follow Trouton's rule (see Exercise 19.104), which states that the molar entropy of vaporization is approximately 88 ± 5 J/mol K. The normal boiling points and enthalpies of vaporization of several organic liquids are as follows:

Substance	Normal Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Acetone, $(CH_3)_2CO$	56.1	29.1
Dimethyl ether, $(CH_3)_2O$	−24.8	21.5
Ethanol, C_2H_5OH	78.4	38.6
Octane, C_8H_{18}	125.6	34.4
Pyridine, C_5H_5N	115.3	35.1

(**a**) Calculate ΔS_{vap} for each of the liquids. Do all the liquids obey Trouton's rule? (**b**) With reference to intermolecular forces (Section 11.2), can you explain any exceptions to the rule? (**c**) Would you expect water to obey Trouton's rule? By using data in Appendix B, check the accuracy of your conclusion. (**d**) Chlorobenzene (C_6H_5Cl) boils at 131.8 °C. Use Trouton's rule to estimate ΔH_{vap} for this substance.

19.115 In chemical kinetics, the *entropy of activation* is the entropy change for the process in which the reactants reach the activated complex. Predict whether the entropy of activation for a bimolecular process is usually positive or negative.

19.116 At what temperatures is the following reaction, the reduction of magnetite by graphite to elemental iron, spontaneous?

$$Fe_3O_4(s) + 2\,C(s, \text{graphite}) \longrightarrow 2\,CO_2(g) + 3\,Fe(s)$$

19.117 The following processes were all discussed in Chapter 18, "Chemistry of the Environment." Estimate whether the entropy of the system increases or decreases during each process: (**a**) photodissociation of $O_2(g)$, (**b**) formation of ozone from oxygen molecules and oxygen atoms, (**c**) diffusion of CFCs into the stratosphere, (**d**) desalination of water by reverse osmosis.

19.118 An ice cube with a mass of 25 g at −18 °C (typical freezer temperature) is dropped into a cup that holds 250 mL of hot water, initially at 85 °C. What is the final temperature in the cup? The density of liquid water is 1.00 g/mL; the specific heat capacity of ice is 2.03 J/g °C; the specific heat capacity of liquid water is 4.184 J/g K; the enthalpy of fusion of water is 6.01 kJ/mol.

19.119 Carbon disulfide (CS_2) is a toxic, highly flammable substance. The following thermodynamic data are available for $CS_2(l)$ and $CS_2(g)$ at 298 K:

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
$CS_2(l)$	89.7	65.3
$CS_2(g)$	117.4	67.2

(**a**) Draw the Lewis structure of the molecule. What do you predict for the bond order of the C—S bonds? (**b**) Use the VSEPR method to predict the structure of the CS_2 molecule. (**c**) Liquid CS_2 burns in O_2 with a blue flame, forming $CO_2(g)$ and $SO_2(g)$. Write a balanced equation for this reaction. (**d**) Using the data in the preceding table and in Appendix C, calculate ΔH° and ΔG° for the reaction in part (c). Is the reaction exothermic? Is it spontaneous at 298 K? (**e**) Use the data in the table to calculate ΔS° at 298 K for the vaporization of $CS_2(l)$. Is the sign of ΔS° as you would expect for a vaporization? (**f**) Using data in the table and your answer to part (e), estimate the boiling point of $CS_2(l)$. Do you predict that the substance will be a liquid or a gas at 298 K and 101.3 kPa?

19.120 The following data compare the standard enthalpies and free energies of formation of some crystalline ionic substances and aqueous solutions of the substances:

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
$AgNO_3(s)$	−124.4	−33.4
$AgNO_3(aq)$	−101.7	−34.2
$MgSO_4(s)$	−1283.7	−1169.6
$MgSO_4(aq)$	−1374.8	−1198.4

Write the formation reaction for $AgNO_3(s)$. Based on this reaction, do you expect the entropy of the system to increase or decrease upon the formation of $AgNO_3(s)$? (**b**) Use ΔH_f° and ΔG_f° of $AgNO_3(s)$ to determine the entropy change upon formation of the substance. Is your answer consistent with your reasoning in part (a)? (**c**) Is dissolving $AgNO_3$ in water an exothermic or endothermic process? What about dissolving $MgSO_4$ in water? (**d**) For both $AgNO_3$ and $MgSO_4$, use the data to calculate the entropy change when the solid is dissolved in water. (**e**) Discuss the results from part (d) with reference to material presented in this chapter and in the "A Closer Look" box on page 912.

19.121 Consider the Boudouard reaction:

$$2\,CO(g) \rightleftharpoons C(s) + CO_2(g)$$

Thermodynamic data on these gases are given in Appendix C. You may assume that ΔH° and ΔS° do not vary with temperature. (**a**) At what temperature will an equilibrium mixture of 101.3 kPa total pressure contain 1.00 mol % CO? (**b**) At what temperature will an equilibrium mixture of 5.07 MPa total pressure contain 1.00 mol % CO?

19.122 The reaction

$$SO_2(g) + 2\,H_2S(g) \rightleftharpoons 3\,S(s) + 2\,H_2O(g)$$

is the basis of a suggested method for removal of SO_2 from power-plant stack gases. The standard free energy of each substance is given in Appendix C. (**a**) What is the equilibrium constant for the reaction at 298 K? (**b**) In principle, is this reaction a feasible method of removing SO_2? (**c**) If $P_{SO_2} = P_{H_2S}$ and the vapor pressure of water is 3.33 kPa, calculate the equilibrium SO_2 pressure in the system at 298 K. (**d**) Would you expect the process to be more or less effective at higher temperatures?

19.123 When most elastomeric polymers (e.g., a rubber band) are stretched, the molecules become more ordered, as illustrated here:



Suppose you stretch a rubber band. (**a**) Do you expect the entropy of the system to increase or decrease? (**b**) If the rubber band were stretched isothermally, would heat need to be absorbed or emitted to maintain constant temperature? (**c**) Try this experiment: Stretch a rubber band and wait a moment. Then place the stretched rubber band on your upper lip, and let it return suddenly to its unstretched state (remember to keep holding on!). What do you observe? Are your observations consistent with your answer to part (b)?

Design an Experiment

You are measuring the equilibrium constant for a drug candidate binding to its DNA target over a series of different temperatures. You chose your drug candidate based on computer-aided molecular modeling, which indicates that the drug molecule likely would make many hydrogen bonds and favorable dipole–dipole interactions with the DNA site. You perform a set of experiments in buffer solution for the drug–DNA complex and generate a table of K's at different T's. (**a**) Derive an equation that relates equilibrium constant to standard enthalpy and entropy changes. (*Hint: equilibrium constant, enthalpy and entropy are all related to free energy*). (**b**) Show how you can graph your K and T data to calculate the standard entropy and enthalpy changes for the drug candidate + DNA binding interaction. (**c**) You are surprised to learn that the enthalpy change for the binding reaction is close to zero, and the entropy change is large and positive. Suggest an explanation and design an experiment to test it. (*Hint: Think about water and ions*). (**d**) You try another drug candidate with the DNA target and find that this drug candidate has a large negative enthalpy change upon DNA binding, and the entropy change is small and positive. Suggest an explanation, at the molecular level, and design an experiment to test your hypothesis.

WHAT'S AHEAD

20.1 ▶ Oxidation States and Oxidation–Reduction Reactions

20.2 ▶ Balancing Redox Equations

20.3 ▶ Voltaic Cells

20.4 ▶ Cell Potentials under Standard Conditions

20.5 ▶ Free Energy and Redox Reactions

20.6 ▶ Cell Potentials under Nonstandard Conditions

20.7 ▶ Batteries and Fuel Cells

20.8 ▶ Corrosion

20.9 ▶ Electrolysis

20

ELECTROCHEMISTRY

20.1 | Oxidation States and Oxidation–Reduction Reactions



The electricity that powers much of modern society has many favorable characteristics, but it has a serious shortcoming: it cannot easily be stored. The electricity that flows into power lines is consumed as it is generated, but for many applications, stored electrical energy is needed. In such cases, electrical energy is converted into chemical energy, which can be stored and is portable, and then converted back to electricity when needed.

Oxidation–reduction (redox) reactions occur when electrons are transferred from an atom that is oxidized to an atom that is reduced. Redox reactions are involved not only in the operation of batteries but also in a wide variety of important natural processes,

including the rusting of iron, the browning of foods, and the respiration of animals. Electrochemistry is the study of the relationships between electricity and chemical reactions. It includes the study of both spontaneous and nonspontaneous processes.

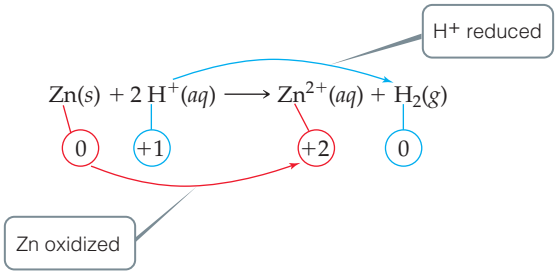
By the end of this section, you should be able to

- Identify the components of a redox reaction

We determine whether a given chemical reaction is an oxidation–reduction reaction by keeping track of the *oxidation numbers* (*oxidation states*) of the elements involved in the reaction. This procedure identifies whether the oxidation number changes for any elements involved in the reaction. For example, consider the net reaction that occurs spontaneously when zinc metal is added to a strong acid (**Figure 20.1**):

$$\mathrm{Zn}(s) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g) \qquad [20.1]$$

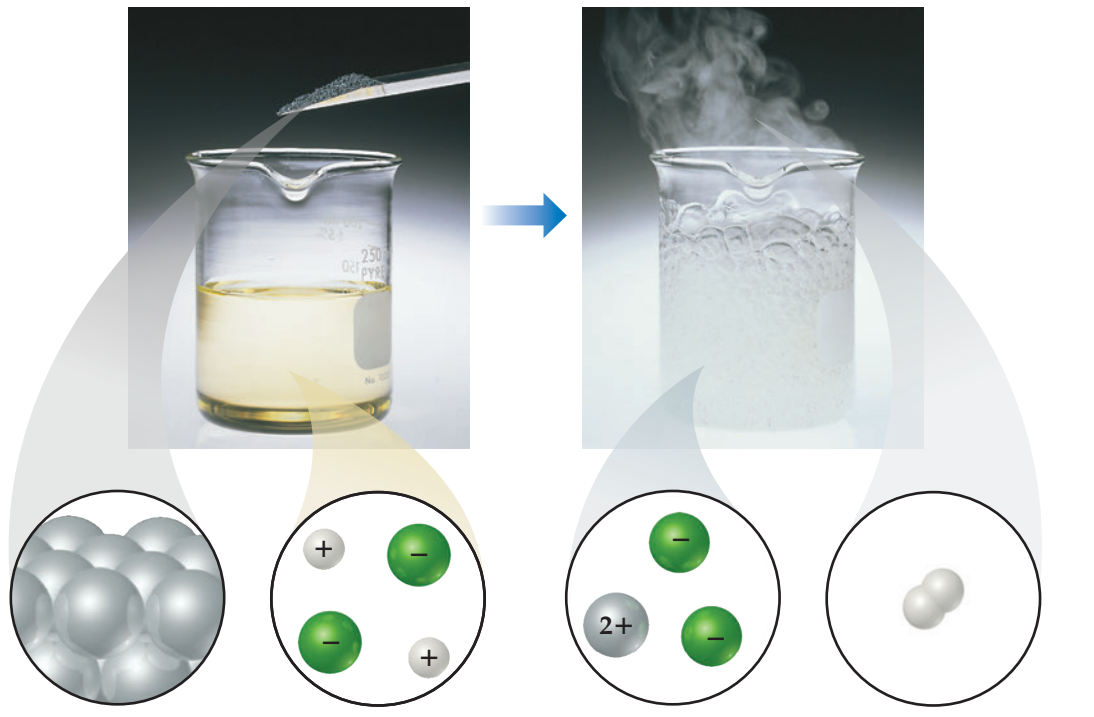
Assigning oxidation numbers to all species in the reaction, we have



[20.2]

The oxidation numbers below the equation show that the oxidation number of Zn changes from 0 to +2, while that of H changes from +1 to 0. Thus, this is an oxidation–reduction

Go Figure Is this reaction exothermic or endothermic?



▲ **Figure 20.1** Oxidation of zinc by hydrochloric acid.

reaction. Electrons are transferred from zinc atoms to hydrogen ions; Zn is oxidized and H^+ is reduced.

In a reaction such as Equation 20.2, a clear transfer of electrons occurs. In some reactions, however, the oxidation numbers change, but we cannot say that any substance literally gains or loses electrons. For example, in the combustion of hydrogen gas,

$$\underset{0}{2\,H_2(g)} + \underset{0}{O_2(g)} \longrightarrow \underset{+1}{2\,H_2O(g)}\ \underset{-2}{} \qquad [20.3]$$

hydrogen is oxidized from the 0 to the +1 oxidation state and oxygen is reduced from the 0 to the −2 oxidation state, indicating that Equation 20.3 is an oxidation–reduction reaction. While keeping track of oxidation states offers a convenient form of "bookkeeping," you should not generally equate the oxidation state of an atom with its actual charge in a chemical compound.

In any redox reaction, both oxidation and reduction must occur. If one substance is oxidized, another must be reduced. The substance that oxidizes another substance is called either the **oxidizing agent** or the **oxidant**. The oxidizing agent acquires electrons from the other substance and so is itself reduced. A **reducing agent**, or **reductant**, is a substance that gives up electrons, thereby causing another substance to be reduced. The reducing agent is therefore oxidized in the process. In Equation 20.2, $H^+(aq)$, the species that is reduced, is the oxidizing agent and $Zn(s)$, the species that is oxidized, is the reducing agent.

Sample Exercise 20.1

Identifying Oxidizing and Reducing Agents

The nickel–cadmium (nicad) battery uses the following redox reaction to generate electricity:

$$Cd(s) + NiO_2(s) + 2\,H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Identify the substances that are oxidized and reduced, and indicate which is the oxidizing agent and which is the reducing agent.

SOLUTION

Analyze We are given a redox equation and asked to identify the substance oxidized and the substance reduced and to label the oxidizing agent and the reducing agent.

Plan First, we use the rules outlined earlier to assign oxidation states, or numbers, to all the atoms and determine which elements change oxidation state. Second, we apply the definitions of oxidation and reduction.

Solve

$$\underset{0}{Cd(s)} + \underset{+4\ -2}{NiO_2(s)} + \underset{+1\ -2}{2\,H_2O(l)} \longrightarrow \underset{+2\ -2\ +1}{Cd(OH)_2(s)} + \underset{+2\ -2\ +1}{Ni(OH)_2(s)}$$

The oxidation state of Cd increases from 0 to +2, and that of Ni decreases from +4 to +2. Thus, the Cd atom is oxidized (loses electrons) and is the reducing agent. The oxidation state of Ni decreases as NiO_2 is converted into $Ni(OH)_2$. Thus, NiO_2 is reduced (gains electrons) and is the oxidizing agent.

Comment A common mnemonic for remembering oxidation and reduction is "LEO the lion says GER": *l*osing *e*lectrons is *o*xidation; *g*aining *e*lectrons is *r*eduction.

Practice Exercise

What is the reducing agent in the following reaction?

$$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l)$$

(**a**) $Br^-(aq)$ (**b**) $H_2O_2(aq)$ (**c**) $H^+(aq)$ (**d**) $Br_2(aq)$

Self-Assessment Exercise

20.1 What are the oxidation number of chlorine in the perchlorate ion, ClO_4^-?

(a) −1

(b) +3

(c) +7

Exercises

20.2 (**a**) What is meant by the term *reduction*? (**b**) On which side of a reduction half-reaction do the electrons appear? (**c**) What is meant by the term *reductant*? (**d**) What is meant by the term *reducing agent*?

20.3 Indicate whether each of the following statements is true or false:

(**a**) If something is reduced, it is formally losing electrons.

(**b**) A reducing agent gets oxidized as it reacts.

(**c**) An oxidizing agent is needed to convert CO into CO_2.

20.4 For each of the following balanced oxidation–reduction reactions, (**i**) identify the oxidation numbers for all the elements in the reactants and products and (**ii**) state the total number of electrons transferred in each reaction.

(**a**) $H_2(g) + F_2(g) \longrightarrow 2\,HF(g)$

(**b**) $2\,Fe^{2+}(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + H_2O(l)$

(**c**) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l)$

20.5 Indicate whether the following balanced equations involve oxidation–reduction. If they do, identify the elements that undergo changes in oxidation number.

(**a**) $2\,AgNO_3(aq) + CoCl_2(aq) \longrightarrow 2\,AgCl(s) + Co(NO_3)_2(aq)$

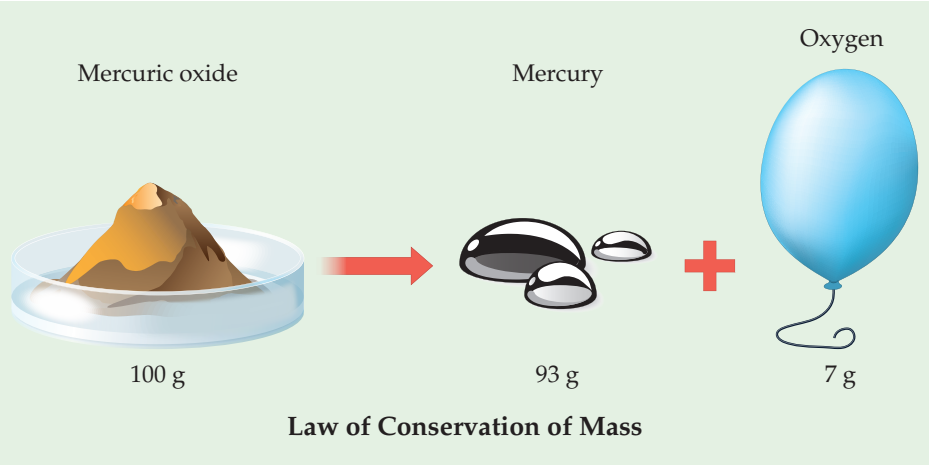
(**b**) $2\,PbO_2(s) \longrightarrow 2\,PbO(s) + O_2(g)$

(**c**) $2\,H_2SO_4(aq) + 2\,NaBr(s) \longrightarrow Br_2(l) + SO_2(g) + Na_2SO_4(aq) + 2\,H_2O(l)$

Answers to Self-Assessment Exercise

20.1 (c)

20.2 | Balancing Redox Equations



Law of Conservation of Mass

Whenever we balance a chemical equation, we must obey the law of conservation of mass: The amount of each element must be the same on both sides of the equation. (Atoms are neither created nor destroyed in any chemical reaction.) As we balance oxidation–reduction reactions, there is an additional requirement: The gains and losses of electrons must be balanced. If a substance loses a certain number of electrons during a reaction, another substance must gain that same number of electrons. (Electrons are neither created nor destroyed in any chemical reaction.)

In many simple chemical equations, such as Equation 20.2, balancing the electrons is handled "automatically"—that is, we balance the equation without explicitly accounting for the transfer of electrons. Many redox equations are more complex than Equation 20.2, however, and cannot be balanced easily without taking into account the number of electrons lost and gained. In this section, we examine the *method of half-reactions*, a systematic procedure for balancing redox equations.

By the end of this section, you should be able to

- Balance redox equations

Half-Reactions

Although oxidation and reduction must take place simultaneously, it is often convenient to consider them as separate processes. For example, the oxidation of Sn^{2+} by Fe^{3+},

$$Sn^{2+}(aq) + 2\,Fe^{3+}(aq) \longrightarrow Sn^{4+}(aq) + 2\,Fe^{2+}(aq)$$

can be considered as consisting of two processes: oxidation of Sn^{2+} and reduction of Fe^{3+}:

$$\textit{Oxidation:}\quad Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2\,e^- \qquad [20.4]$$

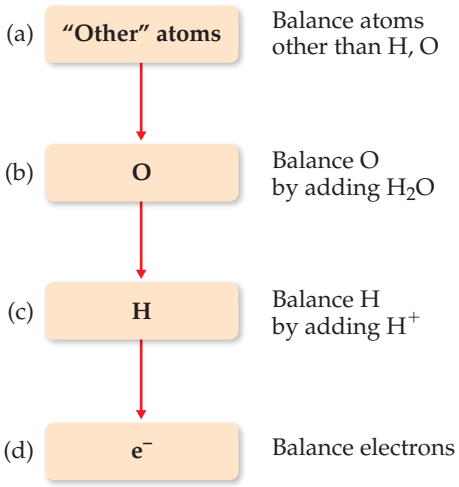
$$\textit{Reduction:}\quad 2\,Fe^{3+}(aq) + 2\,e^- \longrightarrow 2\,Fe^{2+}(aq) \qquad [20.5]$$

Notice that electrons are shown as products in the oxidation process and as reactants in the reduction process.

Equations that show either oxidation or reduction alone, such as Equations 20.4 and 20.5, are called **half-reactions**. In the overall redox reaction, the number of electrons lost in the oxidation half-reaction must equal the number of electrons gained in the reduction half-reaction. When this condition is met and each half-reaction is balanced, the electrons on the two sides cancel when the two half-reactions are added to give the balanced oxidation–reduction equation.

Balancing Equations by the Method of Half-Reactions

In the half-reaction method, we usually begin with a "skeleton" ionic equation showing only the substances undergoing oxidation and reduction. In such cases, we assign oxidation numbers only when we are unsure whether the reaction involves oxidation–reduction. We will find that H^+ (for acidic solutions), OH^- (for basic solutions), and H_2O are often involved as reactants or products in redox reactions. Unless H^+, OH^-, or H_2O is being oxidized or reduced, these species do not appear in the skeleton equation. Their presence, however, can be deduced as we balance the equation.



How to Balance Redox Reactions in Acidic Aqueous Solution

1. Divide the equation into one oxidation half-reaction and one reduction half-reaction.
2. Balance each half-reaction.
   (**a**) First, balance elements other than H and O.
   (**b**) Next, balance O atoms by adding H_2O as needed.
   (**c**) Then balance H atoms by adding H^+ as needed.
   (**d**) Finally, balance charge by adding e^- as needed.

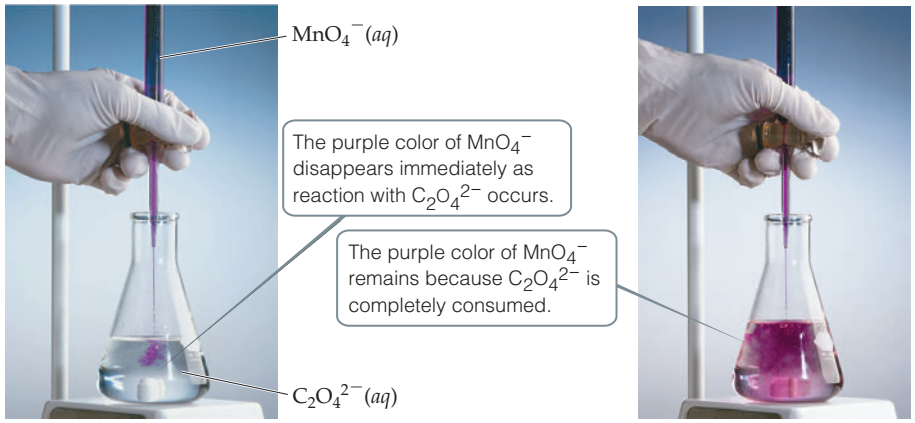
   This specific sequence (a)–(d) is important, and it is summarized in the diagram in the margin. At this point, you can check whether the number of electrons in each half-reaction corresponds to the changes in oxidation state.
3. Multiply half-reactions by integers as needed to make the number of electrons lost in the oxidation half-reaction equal the number of electrons gained in the reduction half-reaction.
4. Add half-reactions and, if possible, simplify by canceling species appearing on both sides of the combined equation.
5. Check to make sure that atoms and charges are balanced.

As an example, let's consider the reaction between permanganate ion (MnO_4^-) and oxalate ion ($C_2O_4^{2-}$) in acidic aqueous solution (**Figure 20.2**). When MnO_4^- is added to an acidified solution of $C_2O_4^{2-}$, the deep purple color of the MnO_4^- ion fades, bubbles of CO_2 form, and the solution takes on the pale pink color of Mn^{2+}. We can write the skeleton equation as

$$MnO_4^-(aq) + C_2O_4^{2-}(aq) \longrightarrow Mn^{2+}(aq) + CO_2(aq) \qquad [20.6]$$

Experiments show that H^+ is consumed and H_2O is produced in the reaction. We will see that their involvement in the reaction is deduced in the course of balancing the equation.

Go Figure Which species is reduced in this reaction? Which species is the reducing agent?



▲ **Figure 20.2** **Titration of an acidic solution of $Na_2C_2O_4$ with $KMnO_4(aq)$.**

To complete and balance Equation 20.6, we first write the two half-reactions (Step 1). One half-reaction must have Mn on both sides of the arrow, and the other must have C on both sides of the arrow:

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$$
$$C_2O_4^{2-}(aq) \longrightarrow CO_2(g)$$

We next complete and balance each half-reaction. First, we balance all the atoms except H and O (Step 2a). In the permanganate half-reaction, we have one manganese atom on each side of the equation and so need to do nothing. In the oxalate half-reaction, we add a coefficient 2 on the right to balance the two carbons on the left:

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$$
$$C_2O_4^{2-}(aq) \longrightarrow 2\,CO_2(g)$$

Next we balance O (Step 2b). The permanganate half-reaction has four oxygens on the left and none on the right; to balance these four oxygen atoms, we add four H_2O molecules on the right:

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

The eight hydrogen atoms now in the products must be balanced by adding 8 H^+ to the reactants (Step 2c):

$$8\,H^+(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

Now there are equal numbers of each type of atom on the two sides of the equation, but the charge still needs to be balanced. The charge of the reactants is $8(1+) + 1(1-) = 7+$, and that of the products is $1(2+) + 4(0) = 2+$. To balance the charge, we add five electrons to the reactant side (Step 2d):

$$5\,e^- + 8\,H^+(aq) + MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$$

We can use oxidation states to check our result. In this half-reaction, Mn goes from the +7 oxidation state in MnO_4^- to the +2 oxidation state of Mn^{2+}. Therefore, each Mn atom gains five electrons, in agreement with our balanced half-reaction.

In the oxalate half-reaction, we have C and O balanced (Step 2a). We balance the charge (Step 2d) by adding two electrons to the products:

$$C_2O_4^{2-}(aq) \longrightarrow 2\,CO_2(g) + 2\,e^-$$

We can check this result using oxidation states. Carbon goes from the +3 oxidation state in $C_2O_4^{2-}$ to the +4 oxidation state in CO_2. Thus, each C atom loses one electron; therefore, the two C atoms in $C_2O_4^{2-}$ lose two electrons, in agreement with our balanced half-reaction.

Now we multiply each half-reaction by an appropriate integer so that the number of electrons gained in one half-reaction equals the number of electrons lost in the other (Step 3). We multiply the MnO_4^- half-reaction by 2 and the $C_2O_4^{2-}$ half-reaction by 5:

$$10\,e^- + 16\,H^+(aq) + 2\,MnO_4^-(aq) \longrightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l)$$
$$5\,C_2O_4^{2-}(aq) \longrightarrow 10\,CO_2(g) + 10\,e^-$$
$$16\,H^+(aq) + 2\,MnO_4^-(aq) + 5\,C_2O_4^{2-}(aq) \longrightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 10\,CO_2(g)$$

The balanced equation is the sum of the balanced half-reactions (Step 4). Note that the electrons on the reactant and product sides of the equation cancel each other.

We check the balanced equation by counting atoms and charges (Step 5). There are 16 H, 2 Mn, 28 O, 10 C, and a net charge of 4+ on each side of the equation, confirming that the equation is correctly balanced.

Sample Exercise 20.2

Balancing Redox Equations in Acidic Solution



Complete and balance this equation by the method of half-reactions:

$$Cr_2O_7^{2-}(aq) + Cl^-(aq) \longrightarrow Cr^{3+}(aq) + Cl_2(g) \quad \text{(acidic solution)}$$

SOLUTION

Analyze We are given an incomplete, unbalanced (skeleton) equation for a redox reaction occurring in acidic solution and asked to complete and balance it.

Plan We use the half-reaction procedure we just learned.

Solve

Step 1: We divide the equation into two half-reactions:

$$Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$$
$$Cl^-(aq) \longrightarrow Cl_2(g)$$

Step 2: We balance each half-reaction. In the first half-reaction the presence of one $Cr_2O_7^{2-}$ among the reactants requires two Cr^{3+} among the products. The seven oxygen atoms in $Cr_2O_7^{2-}$ are balanced by adding seven H_2O to the products. The 14 hydrogen atoms in 7 H_2O are then balanced by adding 14 H^+ to the reactants:

$$14\,H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

We then balance the charge by adding electrons to the left side of the equation so that the total charge is the same on the two sides:

$$6\,e^- + 14\,H^+(aq) + Cr_2O_7^{2-}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

We can check this result by looking at the oxidation state changes. Each chromium atom goes from +6 to +3, gaining three electrons; therefore, the two Cr atoms in $Cr_2O_7^{2-}$ gain six electrons, in agreement with our half-reaction.

In the second half-reaction, two Cl^- are required to balance one Cl_2:

$$2\,Cl^-(aq) \longrightarrow Cl_2(g)$$

We add two electrons to the right side to attain charge balance:

$$2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^-$$

This result agrees with the oxidation state changes. Each chlorine atom goes from −1 to 0, losing one electron; therefore, the two chlorine atoms lose two electrons.

Step 3: We equalize the number of electrons transferred in the two half-reactions. To do so, we multiply the Cl half-reaction by 3 so that the number of electrons gained in the Cr half-reaction (6) equals the number lost in the Cl half-reaction, allowing the electrons to cancel when the half-reactions are added:

$$6\,Cl^-(aq) \longrightarrow 3\,Cl_2(g) + 6\,e^-$$

Step 4: The equations are added to give the balanced equation:

$$14\,H^+(aq) + Cr_2O_7^{2-}(aq) + 6\,Cl^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 3\,Cl_2(g)$$

Step 5: There are equal numbers of atoms of each kind on the two sides of the equation (14 H, 2 Cr, 7 O, 6 Cl). In addition, the charge is the same on the two sides (6+). Thus, the equation is balanced.

Practice Exercise

If you complete and balance the following equation in acidic solution

$$Mn^{2+}(aq) + NaBiO_3(s) \longrightarrow Bi^{3+}(aq) + MnO_4^-(aq) + Na^+(aq)$$

how many water molecules are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)? (**a**) Four on the reactant side (**b**) Three on the product side (**c**) One on the reactant side (**d**) Seven on the product side (**e**) Two on the product side

Balancing Equations for Reactions Occurring in Basic Solution

If a redox reaction occurs in basic solution, the equation must be balanced by using OH^- and H_2O rather than H^+ and H_2O. Because the water molecule and the hydroxide ion both contain hydrogen, this approach can take more moving back and forth from one side of the equation to the other to arrive at the appropriate half-reaction. There is an alternate approach.

How to Balance Redox Reactions in Basic Aqueous Solution

1. Balance the half-reactions as if they occurred in acidic solution.
2. Count the number of H^+ in each half-reaction, and then add the same number of OH^- to each side of the half-reaction.

Using this method, the reaction is mass-balanced because you are adding the same thing to both sides. In essence, what you are doing is "neutralizing" the protons to form water ($H^+ + OH^- \longrightarrow H_2O$) on the side containing H^+, and the other side ends up with the OH^-. The resulting water molecules can be canceled as needed.

Sample Exercise 20.3

Balancing Redox Equations in Basic Solution

Complete and balance this equation for a redox reaction that takes place in basic solution:

$$CN^-(aq) + MnO_4^-(aq) \longrightarrow CNO^-(aq) + MnO_2(s) \quad \text{(basic solution)}$$

SOLUTION

Analyze We are given an incomplete equation for a basic redox reaction and asked to balance it.

Plan We go through the first steps of our procedure as if the reaction were occurring in acidic solution. We then add the appropriate number of OH^- to each side of the equation, combining H^+ and OH^- to form H_2O. We complete the process by simplifying the equation.

Solve

Step 1: We write the incomplete, unbalanced half-reactions:

$$CN^-(aq) \longrightarrow CNO^-(aq)$$
$$MnO_4^-(aq) \longrightarrow MnO_2(s)$$

Continued

Step 2: We balance each half-reaction as if it took place in acidic solution:

$$CN^-(aq) + H_2O(l) \longrightarrow CNO^-(aq) + 2\,H^+(aq) + 2\,e^-$$
$$3\,e^- + 4\,H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l)$$

Now we must take into account that the reaction occurs in basic solution, adding OH^- to both sides of both half-reactions to neutralize H^+:

$$CN^-(aq) + H_2O(l) + 2\,OH^-(aq) \longrightarrow CNO^-(aq) + 2\,H^+(aq) + 2\,e^- + 2\,OH^-(aq)$$
$$3\,e^- + 4\,H^+(aq) + MnO_4^-(aq) + 4\,OH^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)$$

We "neutralize" H^+ and OH^- by forming H_2O when they are on the same side of either half-reaction:

$$CN^-(aq) + H_2O(l) + 2\,OH^-(aq) \longrightarrow CNO^-(aq) + 2\,H_2O(l) + 2\,e^-$$
$$3\,e^- + 4\,H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 2\,H_2O(l) + 4\,OH^-(aq)$$

Next, we cancel water molecules that appear as both reactants and products:

$$CN^-(aq) + 2\,OH^-(aq) \longrightarrow CNO^-(aq) + H_2O(l) + 2\,e^-$$
$$3\,e^- + 2\,H_2O(l) + MnO_4^-(aq) \longrightarrow MnO_2(s) + 4\,OH^-(aq)$$

Both half-reactions are now balanced. You can check the atoms and the overall charge.

Step 3: We multiply the cyanide half-reaction by 3, which gives six electrons on the product side, and multiply the permanganate half-reaction by 2, which gives six electrons on the reactant side:

$$3\,CN^-(aq) + 6\,OH^-(aq) \longrightarrow 3\,CNO^-(aq) + 3\,H_2O(l) + 6\,e^-$$
$$6\,e^- + 4\,H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 2\,MnO_2(s) + 8\,OH^-(aq)$$

Step 4: We add the two half-reactions together and simplify by canceling species that appear as both reactants and products:

$$3\,CN^-(aq) + H_2O(l) + 2\,MnO_4^-(aq) \longrightarrow 3\,CNO^-(aq) + 2\,MnO_2(s) + 2\,OH^-(aq)$$

Step 5: Check that the atoms and charges are balanced.

There are 3 C, 3 N, 2 H, 9 O, 2 Mn, and a charge of 5− on both sides of the equation.

Comment It is important to remember that this procedure does not imply that H^+ ions are involved in the chemical reaction. Recall that in aqueous solutions at 25 °C, $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. Thus, $[H^+]$ is very small in this basic solution.

Practice Exercise

If you complete and balance the following oxidation–reduction reaction in basic solution

$$NO_2^-(aq) + Al(s) \longrightarrow NH_3(aq) + Al(OH)_4^-(aq)$$

how many hydroxide ions are there in the balanced equation (for the reaction balanced with the smallest whole-number coefficients)?
(**a**) One on the reactant side (**b**) One on the product side
(**c**) Four on the reactant side (**d**) Seven on the product side
(**e**) None

Self-Assessment Exercise

20.6 Complete and balance the following redox equation which takes place under acidic conditions:
$Cr(s) + NO_3^-(aq) \longrightarrow Cr^{3+}(aq) + NO(g)$

(a) $Cr(s) + NO_3^-(aq) \longrightarrow Cr^{3+}(aq) + 3NO(g)$
(b) $Cr(s) + NO_3^-(aq)\,2H^+(aq) \longrightarrow Cr^{3+}(aq) + NO(g) + H_2O(l)$
(c) $Cr(s) + NO_3^-(aq)\,4H^+(aq) \longrightarrow Cr^{3+}(aq) + NO(g) + 2H_2O(l)$

Exercises

20.7 Hydrazine (N_2H_4) and dinitrogen tetroxide (N_2O_4) form a self-igniting mixture that has been used as a rocket propellant. The reaction products are N_2 and H_2O. (**a**) Write a balanced chemical equation for this reaction. (**b**) What is being oxidized, and what is being reduced? (**c**) Which substance serves as the reducing agent and which as the oxidizing agent?

20.8 Complete and balance the following half-reactions. In each case indicate whether the half-reaction is an oxidation or a reduction.

(**a**) $Mo^{3+}(aq) \longrightarrow Mo(s)$ (acidic solution)

(**b**) $H_2SO_3(aq) \longrightarrow SO_4^{2-}(aq)$ (acidic solution)

(**c**) $NO_3^-(aq) \longrightarrow NO(g)$ (acidic solution)

(**d**) $O_2(g) \longrightarrow H_2O(l)$ (acidic solution)

(**e**) $O_2(g) \longrightarrow H_2O(l)$ (basic solution)

(**f**) $Mn^{2+}(aq) \longrightarrow MnO_2(s)$ (basic solution)

(**g**) $Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq)$ (basic solution)

20.9 Complete and balance the following equations, and identify the oxidizing and reducing agents. (Recall that the O atoms in hydrogen peroxide, H_2O_2, have an atypical oxidation state.)

(**a**) $NO_2^-(aq) + Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq) + NO_3^-(aq)$ (acidic solution)

(**b**) $S(s) + HNO_3(aq) \longrightarrow H_2SO_3(aq) + N_2O(g)$ (acidic solution)

(**c**) $Cr_2O_7^{2-}(aq) + CH_3OH(aq) \longrightarrow HCOOH(aq) + Cr^{3+}(aq)$ (acidic solution)

(**d**) $BrO_3^-(aq) + N_2H_4(g) \longrightarrow Br^-(aq) + N_2(g)$ (acidic solution)

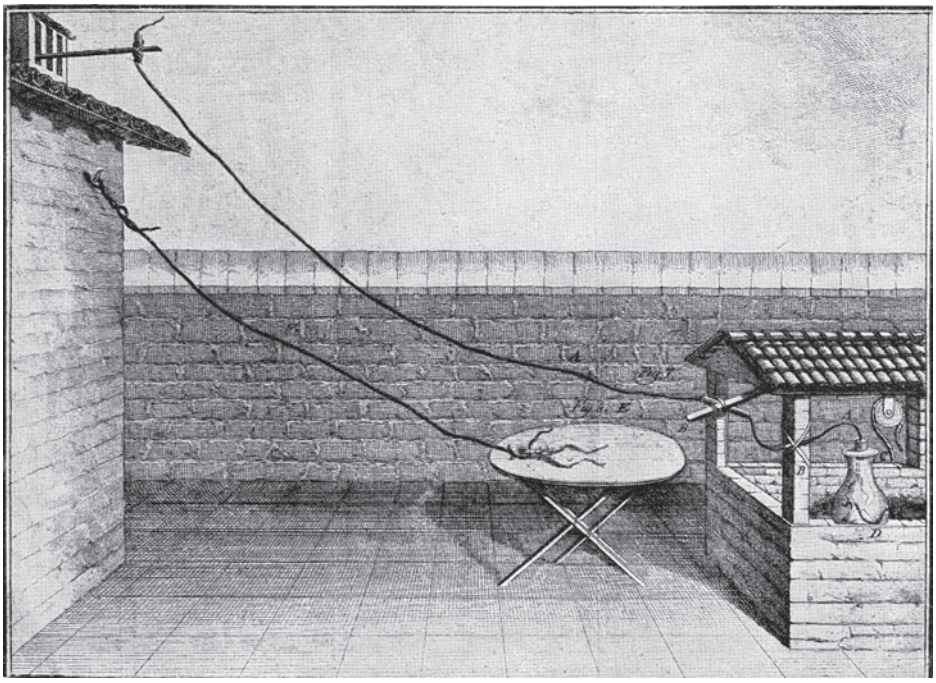
(**e**) $NO_2^-(aq) + Al(s) \longrightarrow NH_4^+(aq) + AlO_2^-(aq)$ (basic solution)

(**f**) $H_2O_2(aq) + ClO_2(aq) \longrightarrow ClO_2^-(aq) + O_2(g)$ (basic solution)

Answers to Self-Assessment Exercise

20.6 (c)

20.3 Voltaic Cells



The story goes that Luigi Galvani and his wife were conducting experiments in static electricity generated by rubbing frog skin. A scalpel touched a nerve in the leg of the frog and they saw a spark and the leg twitched, 'as if it were alive'. They coined the term animal electricity. Alessandro Volta checked these findings after they were published in 1790 and found that the frog was not necessary but instead an electrical current could be generated using two different metals separated by an electrolyte.

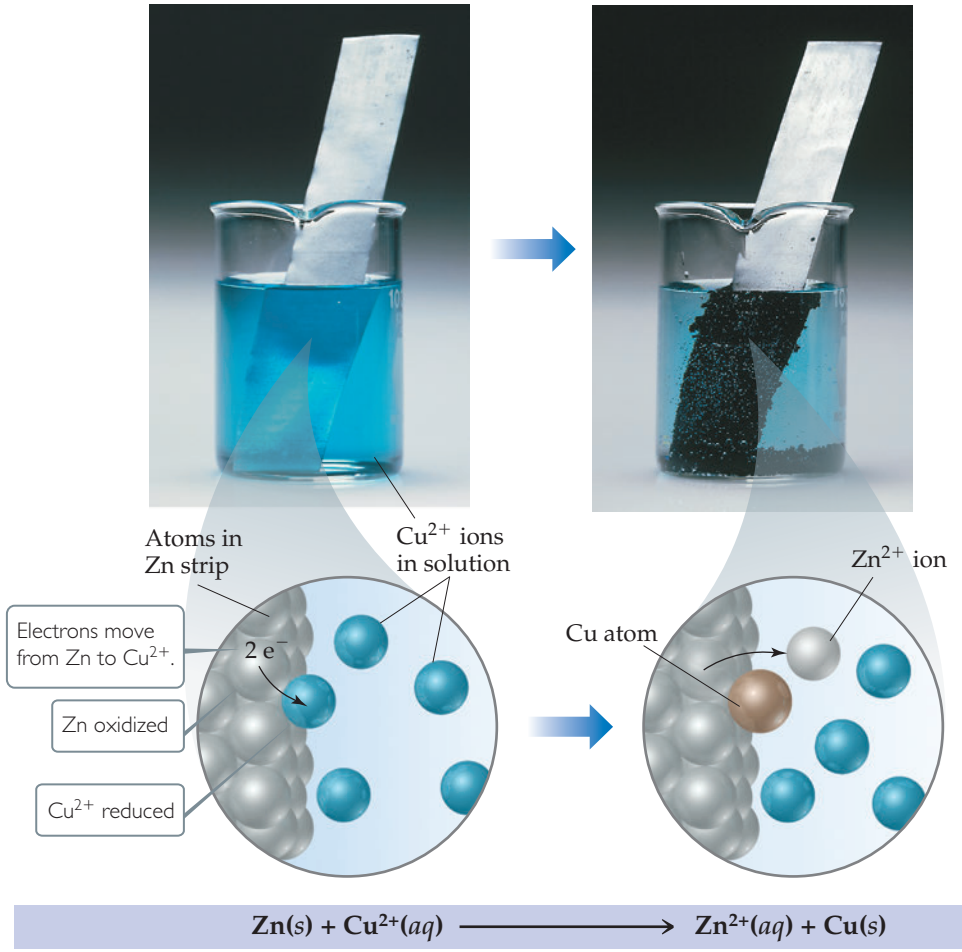
By the end of this section, you should be able to

- Identify the component parts of a voltaic cell

The energy released in a spontaneous redox reaction can be used to perform electrical work. This task is accomplished through a **voltaic** (or **galvanic**) **cell**, a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants present in the same reaction vessel.

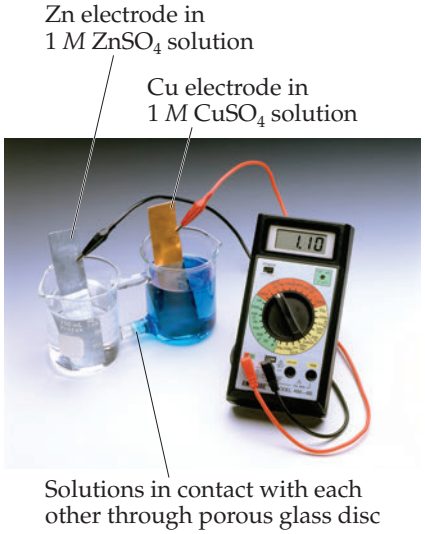
One such spontaneous reaction occurs when a strip of zinc is placed in contact with a solution containing $Cu^{2+}(aq)$. As the reaction proceeds, the blue color of $Cu^{2+}(aq)$ ions fades and copper metal deposits on the zinc. At the same time, the zinc

Go Figure Why does the intensity of the blue solution color lessen as the reaction proceeds?



▲ **Figure 20.3** **A spontaneous oxidation–reduction reaction involving zinc and copper.**

Go Figure Which metal, Cu or Zn, is oxidized in this voltaic cell?



▲ **Figure 20.4** **A Cu–Zn voltaic cell based on the reaction in Equation 20.7.**

begins to dissolve. These transformations, shown in **Figure 20.3**, are summarized by the equation

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad [20.7]$$

Figure 20.4 shows a voltaic cell that uses the redox reaction given in Equation 20.7. Although the setup in Figure 20.4 is more complex than that in Figure 20.3, the reaction is the same in both cases. The significant difference is that in the voltaic cell the Zn metal and $Cu^{2+}(aq)$ are not in direct contact with each other. Instead, Zn metal is in contact with $Zn^{2+}(aq)$ in one compartment, and Cu metal is in contact with $Cu^{2+}(aq)$ in the other compartment. Consequently, $Cu^{2+}(aq)$ reduction can occur only by the flow of electrons through an external circuit, namely, a wire connecting the Zn and Cu strips. Electrons flowing through a wire and ions moving in solution both constitute an *electrical current*. This flow of electrical charge can be used to accomplish electrical work.

The two solid metals connected by the external circuit are called *electrodes*. By definition, the electrode at which oxidation occurs is the **anode** and the electrode at which reduction occurs is the **cathode**.* The electrodes can be made of materials that

*To help remember these definitions, note that *anode* and *oxidation* both begin with a vowel, and *cathode* and *reduction* both begin with a consonant.

Another aid is 'An Ox – Red Cat' linking the Anode with Oxidation and Reduction with the Cathode.

participate in the reaction, as in the present example. Over the course of the reaction, the Zn electrode gradually disappears and the copper electrode gains mass. More typically, the electrodes are made of a conducting material, such as platinum or graphite, that does not gain or lose mass during the reaction but serves as a surface at which electrons are transferred.

Each compartment of a voltaic cell is called a *half-cell*. One half-cell is the site of the oxidation half-reaction, and the other is the site of the reduction half-reaction. In our present example, Zn is oxidized and Cu^{2+} is reduced:

Anode (*oxidation half-reaction*) $\quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$

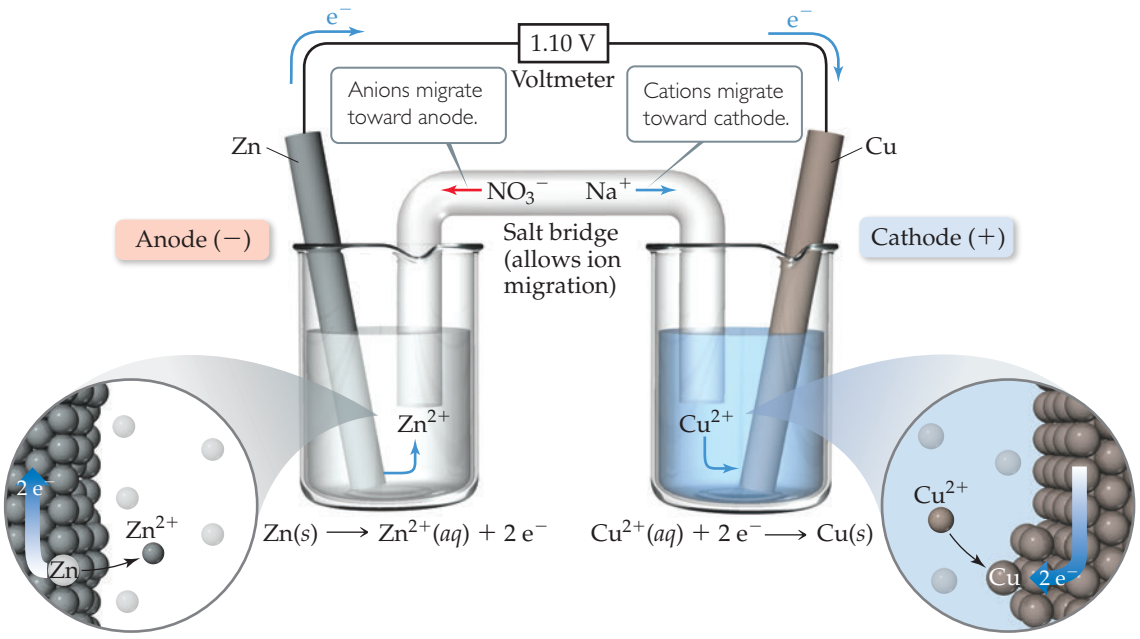
Cathode (*reduction half-reaction*) $\quad Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$

Electrons become available as zinc metal is oxidized at the anode. They flow through the external circuit to the cathode, where they are consumed as $Cu^{2+}(aq)$ is reduced. Because $Zn(s)$ is oxidized in the cell, the zinc electrode loses mass, and the concentration of the $Zn^{2+}(aq)$ solution increases as the cell operates. At the same time, the Cu electrode gains mass, and the $Cu^{2+}(aq)$ solution becomes less concentrated as $Cu^{2+}(aq)$ is reduced to $Cu(s)$.

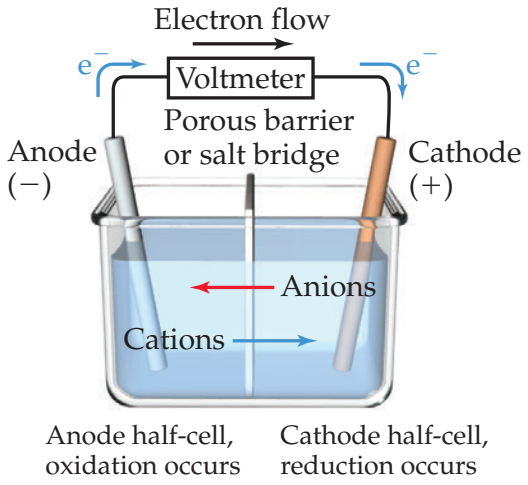
For a voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. As Zn is oxidized in the anode half-cell, $Zn^{2+}(aq)$ ions enter the solution, upsetting the initial Zn^{2+}/SO_4^{2-} charge balance. To keep the solution electrically neutral, there must be some means for $Zn^{2+}(aq)$ cations to migrate out of the anode half-cell and for anions to migrate in. Similarly, the reduction of $Cu^{2+}(aq)$ at the cathode removes these cations from the solution, leaving an excess of SO_4^{2-} anions in that half-cell. To maintain electrical neutrality, some of these anions must migrate out of the cathode half-cell, and positive ions must migrate in. In fact, no measurable electron flow occurs between electrodes unless a means is provided for ions to migrate through the solution from one half-cell to the other, thereby completing the circuit.

In Figure 20.4, a porous glass disc separating the two half-cells allows ions to migrate and maintain the electrical neutrality of the solutions. In **Figure 20.5**, a

Go Figure How is electrical balance maintained in the left beaker as $Zn^{2+}(aq)$ are formed at the anode?



▲ **Figure 20.5** **A voltaic cell that uses a salt bridge to complete the electrical circuit.**



▲ **Figure 20.6 Summary of reactions occurring in a voltaic cell.** The half-cells can be separated by either a porous glass disc (as in Figure 20.4) or by a salt bridge (as in Figure 20.5).

salt bridge serves this purpose. The salt bridge consists of a U-shaped tube containing an electrolyte solution, such as $NaNO_3(aq)$, whose ions will not react with other ions in the voltaic cell or with the electrodes. The electrolyte is often incorporated into a paste or gel so that the electrolyte solution does not pour out when the U-tube is inverted. As oxidation and reduction proceed at the electrodes, ions from the salt bridge migrate into the two half-cells—cations migrating to the cathode half-cell and anions migrating to the anode half-cell—to neutralize charge in the half-cell solutions. Whichever device is used to allow ions to migrate between half-cells, *anions always migrate toward the anode and cations toward the cathode*.

Figure 20.6 summarizes the various relationships in a voltaic cell. Notice in particular that *electrons flow from the anode through the external circuit to the cathode*. Because of this directional flow, the anode in a voltaic cell is labeled with a negative sign and the cathode is labeled with a positive sign. We can envision the electrons as being attracted to the positive cathode from the negative anode through the external circuit.

Sample Exercise 20.4

Describing a Voltaic Cell

The oxidation–reduction reaction

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(s) + 7\,H_2O(l)$$

is spontaneous. A solution containing $K_2Cr_2O_7$ and H_2SO_4 is poured into one beaker, and a solution of KI is poured into another. A salt bridge is used to join the beakers. A metallic conductor that will not react with either solution (such as platinum foil) is suspended in each solution, and the two conductors are connected with wires through a voltmeter or some other device to detect an electric current. The resulting voltaic cell generates an electric current. Indicate the reaction occurring at the anode, the reaction at the cathode, the direction of electron migration, the direction of ion migration, and the signs of the electrodes.

SOLUTION

Analyze We are given the equation for a spontaneous reaction that takes place in a voltaic cell and a description of how the cell is constructed. We are asked to write the half-reactions occurring at the anode and at the cathode, as well as the directions of electron and ion movements and the signs assigned to the electrodes.

Plan Our first step is to divide the chemical equation into half-reactions so that we can identify the oxidation and the reduction processes. We then use the definitions of anode and cathode and the other terminologies summarized in Figure 20.6.

Solve In one half-reaction, $Cr_2O_7^{2-}(aq)$ is converted into $Cr^{3+}(aq)$. Starting with these ions and then completing and balancing the half-reaction, we have

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$

In the other half-reaction, $I^-(aq)$ is converted to $I_2(s)$:

$$6\,I^-(aq) \longrightarrow 3\,I_2(s) + 6\,e^-$$

Now we can use the summary in Figure 20.6 to help us describe the voltaic cell. The first half-reaction is the reduction process (electrons on the reactant side of the equation). By definition, the reduction process occurs at the cathode. The second half-reaction is the oxidation process (electrons on the product side of the equation), which occurs at the anode.

The I^- ions are the source of electrons, and the $Cr_2O_7^{2-}$ ions accept the electrons. Hence, the electrons flow through the external circuit from the electrode immersed in the KI solution (the anode) to the electrode immersed in the $K_2Cr_2O_7$–H_2SO_4 solution (the cathode). The electrodes themselves do not react in any way; they merely provide a means of transferring electrons from or to the solutions. The cations move through the solutions toward the cathode, and the anions move toward the anode. The anode (from which the electrons move) is the negative electrode, and the cathode (toward which the electrons move) is the positive electrode.

▶ Practice Exercise

The following two half-reactions occur in a voltaic cell:

$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \qquad \text{(electrode = Ni)}$$
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad \text{(electrode = Cu)}$$

Which one of the following descriptions most accurately describes what is occurring in the half-cell containing the Cu electrode and $Cu^{2+}(aq)$ solution?

(**a**) The electrode is losing mass and cations from the salt bridge are flowing into the half-cell.
(**b**) The electrode is gaining mass and cations from the salt bridge are flowing into the half-cell.
(**c**) The electrode is losing mass and anions from the salt bridge are flowing into the half-cell.
(**d**) The electrode is gaining mass and anions from the salt bridge are flowing into the half-cell.

Self-Assessment Exercise

20.10 Which statement about the working of a voltaic cell is true?

(a) Electrons flow from the anode to the cathode

(b) Oxidation occurs at the cathode

(c) Anions flow through the salt bridge to the cathode

(d) The cathode is negatively charged

Exercises

20.11 Indicate whether each statement is true or false: (**a**) The anode is the electrode at which oxidation takes place. (**b**) A voltaic cell always has a positive emf. (**c**) A salt bridge or permeable barrier is necessary to allow a voltaic cell to operate.

20.12 A voltaic cell similar to that shown in Figure 20.5 is constructed. One half-cell consists of an iron strip placed in a solution of $FeSO_4$, and the other has an aluminum strip placed in a solution of $Al_2(SO_4)_3$. The overall cell reaction is

$$2\,Al(s) + 3\,Fe^{2+}(aq) \longrightarrow 3\,Fe(s) + 2\,Al^{3+}(aq)$$

(**a**) What is being oxidized, and what is being reduced? (**b**) Write the half-reactions that occur in the two half-cells. (**c**) Which electrode is the anode, and which is the cathode? (**d**) Indicate the signs of the electrodes. (**e**) Do electrons flow from the aluminum electrode to the iron electrode or from the iron to the aluminum? (**f**) In which directions do the cations and anions migrate through the solution? Assume the Al is not coated with its oxide.

Answers to Self-Assessment Exercise

20.10 (a)

20.4 Cell Potentials under Standard Conditions



There are many different combinations of materials that can make up a voltaic cell, and, in this section, we see how they may be quantified. By the end of this section, you should be able to

- Calculate the emf of a cell from standard reduction potentials

Why do electrons transfer spontaneously from a Zn atom to a Cu^{2+} ion, either directly as in Figure 20.3 or through an external circuit as in Figure 20.4? In a simple sense, we can compare the electron flow to the flow of water in a waterfall (**Figure 20.7**). Water flows spontaneously over a waterfall because of a difference in potential energy between the top of the falls and the bottom. In a similar fashion, electrons flow spontaneously through an external circuit from the anode of a voltaic cell to the cathode because of a difference in potential energy. The potential energy of electrons is higher in the anode than in the cathode. Thus, electrons flow spontaneously toward the electrode with the more positive electrical potential.

The difference in potential energy per electrical charge (the *potential difference*) between two electrodes is measured in *volts*. One volt (V) is the potential difference required to impart 1 joule (J) of energy to a charge of 1 coulomb (C):

$$1\,\text{V} = 1\,\frac{\text{J}}{\text{C}}$$

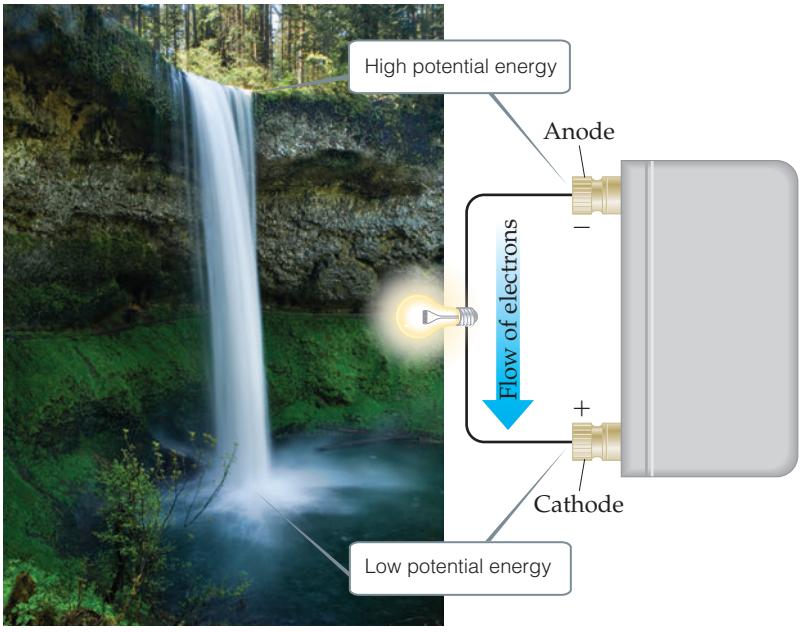
Recall that one electron has a charge of 1.60×10^{-19} C.

The potential difference between the two electrodes of a voltaic cell is called the **cell potential**, denoted E_{cell}. Because the potential difference provides the driving force that pushes electrons through the external circuit, we also call it the **electromotive** ("causing electron motion") **force**, or **emf**. Because E_{cell} is measured in volts, it is also commonly called the *voltage* of the cell.

The cell potential of any voltaic cell is positive. The magnitude of the cell potential depends on the reactions that occur at the cathode and anode, the concentrations of reactants and products, and the temperature, which we will assume to be 25 °C unless otherwise noted. In this section, we focus on cells that are operated at 25 °C under *standard conditions*. Recall from Table 19.2 that standard conditions include 1 *M* concentration for reactants and products in solution and 100.0 kPa pressure for gaseous reactants and products. The cell potential under standard conditions is called either the **standard cell potential** or **standard emf** and is denoted E°_{cell}. For the Zn–Cu voltaic cell in Figure 20.5, for example, the standard cell potential at 25 °C is +1.10 V:

$$\text{Zn}(s) + \text{Cu}^{2+}(aq, 1\,M) \longrightarrow \text{Zn}^{2+}(aq, 1\,M) + \text{Cu}(s) \qquad E^\circ_{\text{cell}} = +1.10\,\text{V}$$

Recall that the superscript ° indicates standard-state conditions.



▲ **Figure 20.7 Water analogy for electron flow.** Just as water spontaneously flows downhill, electrons flow spontaneously from the anode to the cathode in a voltaic cell.

Standard Reduction Potentials

The standard cell potential of a voltaic cell, E°_{cell}, depends on the particular cathode and anode half-cells. We could, in principle, tabulate the standard cell potentials for all possible cathode–anode combinations. However, it is not necessary to undertake this arduous task. Rather, we can assign a standard potential to each half-cell and then use these half-cell potentials to determine E°_{cell}. The cell potential is the difference between two half-cell potentials. By convention, the potential associated with each electrode is chosen to be the potential for *reduction* at that electrode. Thus, standard half-cell potentials are tabulated for reduction reactions, which means they are **standard reduction potentials**, denoted E°_{red}. The standard cell potential, E°_{cell}, is the standard reduction potential of the cathode reaction, E°_{red} (cathode), *minus* the standard reduction potential of the anode reaction, E°_{red} (anode):

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) \qquad [20.8]$$

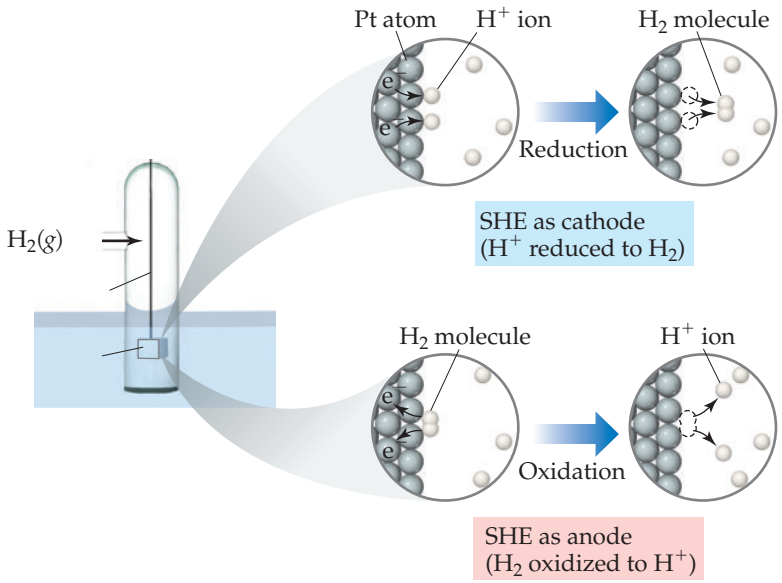
It is not possible to measure the standard reduction potential of a half-reaction directly. If we assign a standard reduction potential to a certain reference half-reaction, however, we can then determine the standard reduction potentials of other half-reactions relative to that reference value. The reference half-reaction is the reduction of $H^+(aq)$ to $H_2(g)$ under standard conditions, which is assigned a standard reduction potential of exactly 0 V:

$$2\,H^+(aq, 1\,M) + 2\,e^- \longrightarrow H_2(g, 100.0\,\text{kPa}) \quad E^\circ_{red} = 0\,\text{V} \qquad [20.9]$$

An electrode designed to produce this half-reaction is called a **standard hydrogen electrode** (SHE). A SHE consists of a platinum wire connected to a piece of platinum foil covered with finely divided platinum that serves as an inert surface for the reaction (**Figure 20.8**). The SHE allows the platinum to be in contact with both 1 M $H^+(aq)$ and a stream of hydrogen gas at 100 kPa. The SHE can operate as either the anode or cathode of a cell, depending on the nature of the other electrode.

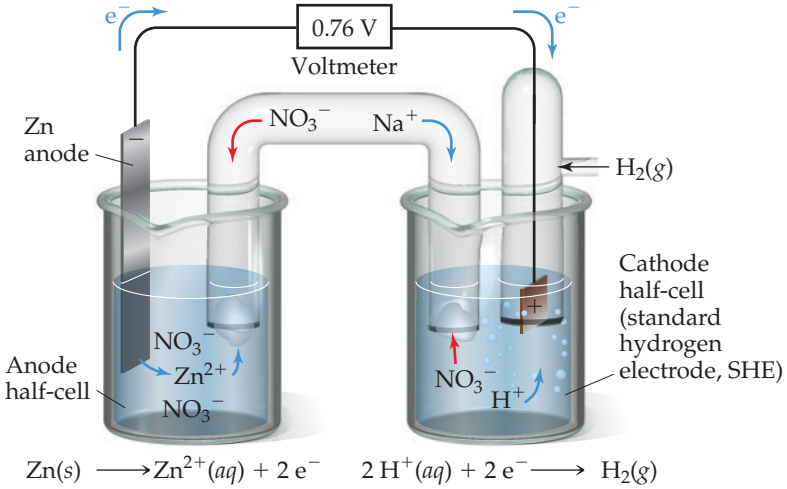
Figure 20.9 shows a voltaic cell using a SHE. The spontaneous reaction is the one shown in Figure 20.1, namely, oxidation of Zn and reduction of H^+:

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$



▲ **Figure 20.8** **The standard hydrogen electrode (SHE) is used as a reference electrode.**

Go Figure Why do Na^+ ions migrate into the cathode half-cell as the cell reaction proceeds?



▲ **Figure 20.9 A voltaic cell using a standard hydrogen electrode (SHE).** The anode half-cell is Zn metal in a $Zn(NO_3)_2(aq)$ solution, and the cathode half-cell is the SHE in a $HNO_3(aq)$ solution.

When the cell is operated under standard conditions, the cell potential is +0.76 V. By using the standard cell potential ($E^\circ_{cell} = 0.76\ V$), the defined standard reduction potential of H^+ ($E^\circ_{red} = 0\ V$) and Equation 20.8, we can determine the standard reduction potential for the Zn^{2+}/Zn half-reaction:

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$$
$$+0.76\ V = 0\ V - E^\circ_{red}\,(\text{anode})$$
$$E^\circ_{red}\,(\text{anode}) = -0.76\ V$$

Thus, a standard reduction potential of −0.76 V can be assigned to the reduction of Zn^{2+} to Zn:

$$Zn^{2+}(aq, 1\ M) + 2\,e^- \longrightarrow Zn(s) \quad E^\circ_{red} = -0.76\ V$$

We write the reaction as a reduction even though the Zn reaction in Figure 20.9 is an oxidation. *Whenever we assign an electrical potential to a half-reaction, we write the reaction as a reduction.* Half-reactions, however, are reversible, being able to operate as either reductions or oxidations. Consequently, half-reactions are sometimes written using two arrows ($\rightleftharpoons$) between reactants and products, as in equilibrium reactions.

The standard reduction potentials for other half-reactions can be determined in a fashion analogous to that used for the Zn^{2+}/Zn half-reaction. **Table 20.1** lists some standard reduction potentials; a more complete list is found in Appendix E. These standard reduction potentials, often called *half-cell potentials*, can be combined to calculate E°_{cell} values for a large variety of voltaic cells.

Because electrical potential measures potential energy per electrical charge, standard reduction potentials are intensive properties. In other words, if we increase the amount of substances in a redox reaction, we increase both the energy and the charges involved, but the ratio of energy (joules) to electrical charge (coulombs) remains constant (V = J/C). Thus, *changing the stoichiometric coefficient in a half-reaction does not affect the value of the standard reduction potential*. For example, E°_{red} for the reduction of 10 mol Zn^{2+} is the same as that for the reduction of 1 mol Zn^{2+}:

$$10\,Zn^{2+}(aq, 1\ M) + 20\,e^- \longrightarrow 10\,Zn(s) \quad E^\circ_{red} = -0.76\ V$$

For each half-cell in a voltaic cell, the standard reduction potential provides a measure of the tendency for reduction to occur: *The more positive the value of* E°_{red}, *the*

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

$E°_{red}$ (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$
+1.51	$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
+1.36	$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
+1.23	$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$
+1.06	$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$
+0.96	$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$
+0.54	$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$
+0.40	$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
0 [defined]	$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$
−0.83	$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Sample Exercise 20.5

Calculating $E°_{red}$ from $E°_{cell}$

For the Zn–Cu voltaic cell shown in Figure 20.5, we have

$$Zn(s) + Cu^{2+}(aq, 1\,M) \longrightarrow Zn^{2+}(aq, 1\,M) + Cu(s) \qquad E°_{cell} = 1.10\,V$$

Given that the standard reduction potential of Zn^{2+} to Zn(s) is −0.76 V, calculate the $E°_{red}$ for the reduction of Cu^{2+} to Cu:

$$Cu^{2+}(aq, 1\,M) + 2\,e^- \longrightarrow Cu(s)$$

SOLUTION

Analyze We are given $E°_{cell}$ and $E°_{red}$ for Zn^{2+} and asked to calculate $E°_{red}$ for Cu^{2+}.

Plan In the voltaic cell, Zn is oxidized and is therefore the anode. Thus, the given $E°_{red}$ for Zn^{2+} is $E°_{red}$ (anode). Because Cu^{2+} is reduced, it is in the cathode half-cell. Thus, the unknown reduction potential for Cu^{2+} is $E°_{red}$ (cathode). Knowing $E°_{cell}$ and $E°_{red}$ (anode), we can use Equation 20.8 to solve for $E°_{red}$ (cathode).

Solve

$$E°_{cell} = E°_{red}\,(\text{cathode}) - E°_{red}\,(\text{anode})$$

$$1.10\,V = E°_{red}\,(\text{cathode}) - (-0.76\,V)$$

$$E°_{red}\,(\text{cathode}) = 1.10\,V - 0.76\,V = 0.34\,V$$

Check This standard reduction potential agrees with the one listed in Table 20.1.

Comment The standard reduction potential for Cu^{2+} can be represented as $E°_{Cu^{2+}} = 0.34$ V and that for Zn^{2+} as $E°_{Zn^{2+}} = -0.76$ V. The subscript identifies the ion that is reduced in the reduction half-reaction.

Practice Exercise

A voltaic cell based on the reaction $2\,Eu^{2+}(aq) + Ni^{2+}(aq) \longrightarrow 2\,Eu^{3+}(aq) + Ni(s)$ generates $E°_{cell} = 0.07$ V. Given the standard reduction potential of Ni^{2+} given in Table 20.1, what is the standard reduction potential for the reaction $Eu^{3+}(aq) + e^- \longrightarrow Eu^{2+}(aq)$?
(**a**) −0.35 V (**b**) 0.35 V (**c**) −0.21 V (**d**) 0.21 V (**e**) 0.07 V

Sample Exercise 20.6

Calculating E°_{cell} from E°_{red}

Use Table 20.1 to calculate E°_{cell} for the voltaic cell described in Sample Exercise 20.4, which is based on the reaction

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,I_2(s) + 7\,H_2O(l)$$

SOLUTION

Analyze We are given the equation for a redox reaction and asked to use data in Table 20.1 to calculate the standard cell potential for the associated voltaic cell.

Plan Our first step is to identify the half-reactions that occur at the cathode and anode, which we did in Sample Exercise 20.4. Then we use Table 20.1 and Equation 20.8 to calculate the standard cell potential.

Solve

The half-reactions are:

Cathode: $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$

Anode: $6\,I^-(aq) \longrightarrow 3\,I_2(s) + 6\,e^-$

According to Table 20.1, the standard reduction potential for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+} is +1.33 V and the standard reduction potential for the reduction of I_2 to I^- (the reverse of the oxidation half-reaction) is +0.54 V. We use these values in Equation 20.8:

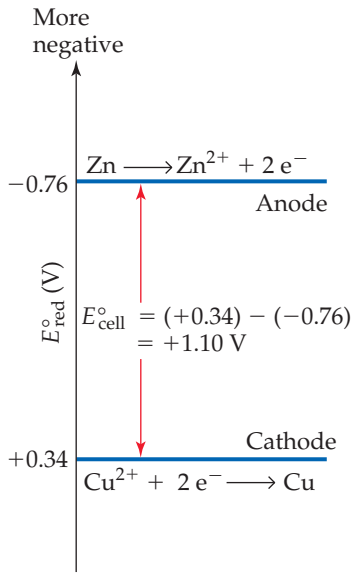
$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) = 1.33\,V - 0.54\,V = 0.79\,V$$

Although we must multiply the iodide half-reaction by 3 to obtain a balanced equation, we do *not* multiply the E°_{red} value by 3. As we have noted, the standard reduction potential is an intensive property and so is independent of the stoichiometric coefficients.

Check The cell potential, 0.79 V, is a positive number. As noted earlier, a voltaic cell must have a positive potential.

Practice Exercise

Using the data in Table 20.1, what value would you calculate for the standard emf (E°_{cell}) for a voltaic cell that employs the overall cell reaction $2\,Ag^+(aq) + Ni(s) \longrightarrow 2\,Ag(s) + Ni^{2+}(aq)$?
(**a**) +0.52 V (**b**) −0.52 V (**c**) +1.08 V (**d**) −1.08 V (**e**) +0.80 V



▲ **Figure 20.10** Half-cell potentials and standard cell potential for the Zn–Cu voltaic cell.

greater the tendency for reduction under standard conditions. In any voltaic cell operating under standard conditions, the E°_{red} value for the reaction at the cathode is more positive than the E°_{red} value for the reaction at the anode. Thus, electrons flow spontaneously through the external circuit from the electrode with the more negative value of E°_{red} to the electrode with the more positive value of E°_{red}. **Figure 20.10** graphically illustrates the relationship between the standard reduction potentials for the two half-reactions in the Zn–Cu voltaic cell of Figure 20.5.

Strengths of Oxidizing and Reducing Agents

Table 20.1 lists half-reactions in the order of decreasing tendency to undergo reduction. For example, F_2 is located at the top of the table, having the most positive value for E°_{red}. Thus, F_2 is the most easily reduced species in Table 20.1 and therefore the strongest oxidizing agent listed.

Sample Exercise 20.7

Determining Half-Reactions at Electrodes and Calculating Cell Potentials

A voltaic cell is based on the two standard half-reactions

$$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$$
$$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$$

Use data in Appendix E to determine (**a**) which half-reaction occurs at the cathode and which occurs at the anode and (**b**) the standard cell potential.

SOLUTION

Analyze We have to look up E°_{red} for two half-reactions. We then use these values first to determine the cathode and the anode and then to calculate the standard cell potential, E°_{cell}.

Plan The cathode will have the reduction with the more positive E°_{red} value, and the anode will have the less positive E°_{red}. To write the half-reaction at the anode, we reverse the half-reaction written for the reduction, so that the half-reaction is written as an oxidation.

Solve

(**a**) According to Appendix E, $E^\circ_{red}(Cd^{2+}/Cd) = -0.40$ V and $E^\circ_{red}(Sn^{2+}/Sn) = -0.14$ V. The standard reduction potential for Sn^{2+} is more positive (less negative) than that for Cd^{2+}. Hence, the reduction of Sn^{2+} is the reaction that occurs at the cathode:

Cathode: $Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$

The anode reaction, therefore, is the loss of electrons by Cd:

Anode: $Cd(s) \longrightarrow Cd^{2+}(aq) + 2\,e^-$

(**b**) The cell potential is given by the difference in the standard reduction potentials at the cathode and anode (Equation 20.8):

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$$
$$= (-0.14\text{ V}) - (-0.40\text{ V}) = 0.26\text{ V}$$

Notice that it is unimportant that the E°_{red} values of both half-reactions are negative; the negative values merely indicate how these reductions compare to the reference reaction, the reduction of $H^+(aq)$.

Check The cell potential is positive, as it must be for a voltaic cell.

Practice Exercise

Consider three voltaic cells, each similar to the one shown in Figure 20.5. In each voltaic cell, one half-cell contains a 1.0 *M* $Fe(NO_3)_2(aq)$ solution with an Fe electrode. The contents of the other half-cells are as follows:

Cell 1: a 1.0 *M* $CuCl_2(aq)$ solution with a Cu electrode

Cell 2: a 1.0 *M* $NiCl_2(aq)$ solution with a Ni electrode

Cell 3: a 1.0 *M* $ZnCl_2(aq)$ solution with a Zn electrode

In which voltaic cell(s) does iron act as the anode?
(**a**) Cell 1
(**b**) Cell 2
(**c**) Cell 3
(**d**) Cells 1 and 2
(**e**) All three cells

Among the most frequently used oxidizing agents are the halogens, O_2, and oxyanions such as MnO_4^-, $Cr_2O_7^{2-}$, and NO_3^-, whose central atoms have high positive oxidation states. As seen in Table 20.1, all these species have large positive values of E°_{red} and therefore easily undergo reduction.

The lower the tendency for a half-reaction to occur in one direction, the greater the tendency for it to occur in the opposite direction. Thus, *the half-reaction with the most negative reduction potential in Table 20.1 is the one most easily reversed and run as an oxidation*. Being at the bottom of Table 20.1, $Li^+(aq)$ is the most difficult species in the list to reduce and is therefore the poorest oxidizing agent listed. Although $Li^+(aq)$ has little tendency to gain electrons, the reverse reaction, oxidation of Li(*s*) to $Li^+(aq)$, is highly favorable. Thus, Li is the strongest reducing agent among the substances listed in Table 20.1. (Note that, because Table 20.1 lists half-reactions as reductions, only the substances on the

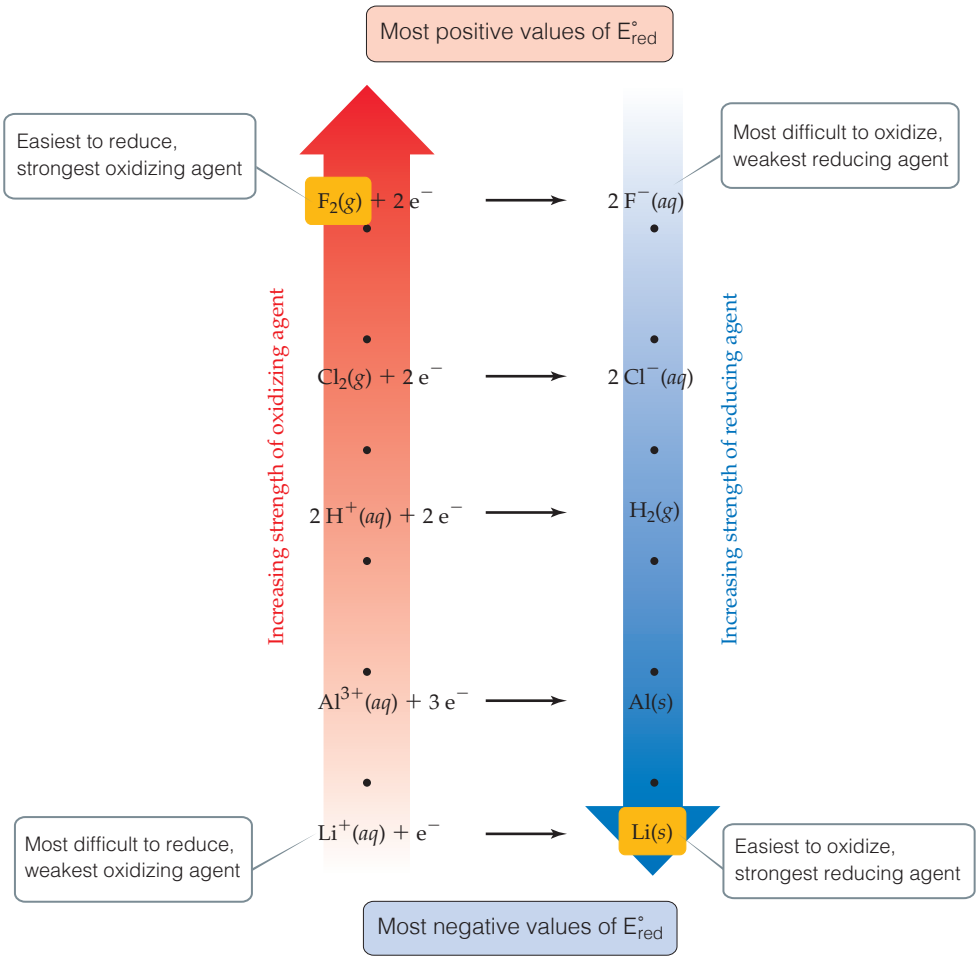
reactant side of these equations can serve as oxidizing agents; only those on the product side can serve as reducing agents.)

Commonly used reducing agents include H_2 and the active metals, such as the alkali metals and the alkaline earth metals. Other metals whose cations have negative E°_{red} values—Zn and Fe, for example—are also used as reducing agents. Solutions of reducing agents are difficult to store for extended periods because of the ubiquitous presence of O_2, a good oxidizing agent.

The information contained in Table 20.1 is summarized graphically in **Figure 20.11**. For the half-reactions at the top of Table 20.1 the substances on the reactant side of the equation are the most readily reduced species in the table and are therefore the strongest oxidizing agents. Substances on the product side of these reactions are the most difficult to oxidize and so are the weakest reducing agents in the table. Thus, Figure 20.11 shows $F_2(g)$ as the strongest oxidizing agent and $F^-(aq)$ as the weakest reducing agent. Conversely, the reactants in half-reactions at the bottom of Table 20.1, such as $Li^+(aq)$ are the most difficult to reduce and so are the weakest oxidizing agents, while the products of these reactions, such as Li(*s*), are the most readily oxidized species in the table and so are the strongest reducing agents.

This inverse relationship between oxidizing and reducing strength is similar to the inverse relationship between the strengths of conjugate acids and bases.

Go Figure Can an acidic solution oxidize a piece of aluminum?



▲ **Figure 20.11** **Relative strengths of oxidizing and reducing agents.**

Sample Exercise 20.8

Determining Relative Strengths of Oxidizing Agents

Using Table 20.1, rank the following ions in the order of increasing strength as oxidizing agents: $NO_3^-(aq)$, $Ag^+(aq)$, $Cr_2O_7^{2-}(aq)$.

SOLUTION

Analyze We are asked to rank the abilities of several ions to act as oxidizing agents.

Plan The more readily an ion is reduced (the more positive its $E°_{red}$ value), the stronger it is as an oxidizing agent.

Solve

From Table 20.1, we have:

$$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l) \qquad E°_{red} = +0.96\ V$$

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E°_{red} = +0.80\ V$$

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) \qquad E°_{red} = +1.33\ V$$

Because the standard reduction potential of $Cr_2O_7^{2-}$ is the most positive, $Cr_2O_7^{2-}$ is the strongest oxidizing agent of the three. The rank order is:

$$Ag^+ < NO_3^- < Cr_2O_7^{2-}$$

Practice Exercise

Based on the data in Table 20.1, which of the following species would you expect to be the strongest oxidizing agent?

(a) $Cl^-(aq)$ **(b)** $Cl_2(g)$ **(c)** $O_2(g)$ **(d)** $H^+(aq)$ **(e)** $Na^+(aq)$

Self-Assessment Exercise

20.13 The standard reduction potential of $Ni^{2+}(aq)$ is $E°_{red} = -0.28$ V, and that of $Fe^{2+}(aq)$ is $E°_{red} = -0.44$ V. In a Ni–Fe voltaic cell, which electrode is the cathode, Ni or Fe?

(a) Fe

(b) Ni

Exercises

20.14 (**a**) Which electrode of a voltaic cell, the cathode or the anode, corresponds to the higher potential energy for the electrons? (**b**) What are the units for electrical potential? How does this unit relate to energy expressed in joules?

20.15 A voltaic cell that uses the reaction

$$PdCl_4^{2-}(aq) + Cd(s) \longrightarrow Pd(s) + 4\,Cl^-(aq) + Cd^{2+}(aq)$$

has a measured standard cell potential of +1.03 V. (**a**) Write the two half-cell reactions. (**b**) By using data from Appendix E, determine $E°_{red}$ for the reaction involving Pd. (**c**) Sketch the voltaic cell, label the anode and cathode, and indicate the direction of electron flow.

20.16 Using data in Appendix E, calculate the standard emf for each of the following reactions:

(**a**) $H_2(g) + F_2(g) \longrightarrow 2\,H^+(aq) + 2\,F^-(aq)$

(**b**) $Cu^{2+}(aq) + Ca(s) \longrightarrow Cu(s) + Ca^{2+}(aq)$

(**c**) $3\,Fe^{2+}(aq) \longrightarrow Fe(s) + 2\,Fe^{3+}(aq)$

(**d**) $2\,ClO_3^-(aq) + 10\,Br^-(aq) + 12\,H^+(aq) \longrightarrow Cl_2(g) + 5\,Br_2(l) + 6\,H_2O(l)$

20.17 Given the following half-reactions and associated standard reduction potentials:

$$AuBr_4^-(aq) + 3\,e^- \longrightarrow Au(s) + 4\,Br^-(aq) \qquad E°_{red} = -0.86\ V$$

$$Eu^{3+}(aq) + e^- \longrightarrow Eu^{2+}(aq) \qquad E°_{red} = -0.43\ V$$

$$IO^-(aq) + H_2O(l) + 2\,e^- \longrightarrow I^-(aq) + 2\,OH^-(aq) \qquad E°_{red} = +0.49\ V$$

(**a**) Write the equation for the combination of these half-cell reactions that leads to the largest positive emf and calculate the value. (**b**) Write the equation for the combination of half-cell reactions that leads to the smallest positive emf and calculate that value.

20.18 A voltaic cell consists of a strip of cadmium metal in a solution of $Cd(NO_3)_2$ in one beaker, and in the other beaker a platinum electrode is immersed in a NaCl solution, with Cl_2 gas bubbled around the electrode. A salt bridge connects the two beakers. (**a**) Which electrode serves as the anode, and which as the cathode? (**b**) Does the Cd

electrode gain or lose mass as the cell reaction proceeds? (**c**) Write the equation for the overall cell reaction. (**d**) What is the emf generated by the cell under standard conditions?

20.19 From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger oxidizing agent:

(**a**) $Cl_2(g)$ or $Br_2(l)$

(**b**) $Zn^{2+}(aq)$ or $Cd^{2+}(aq)$

(**c**) $Cl^-(aq)$ or $ClO_3^-(aq)$

(**d**) $H_2O_2(aq)$ or $O_3(g)$

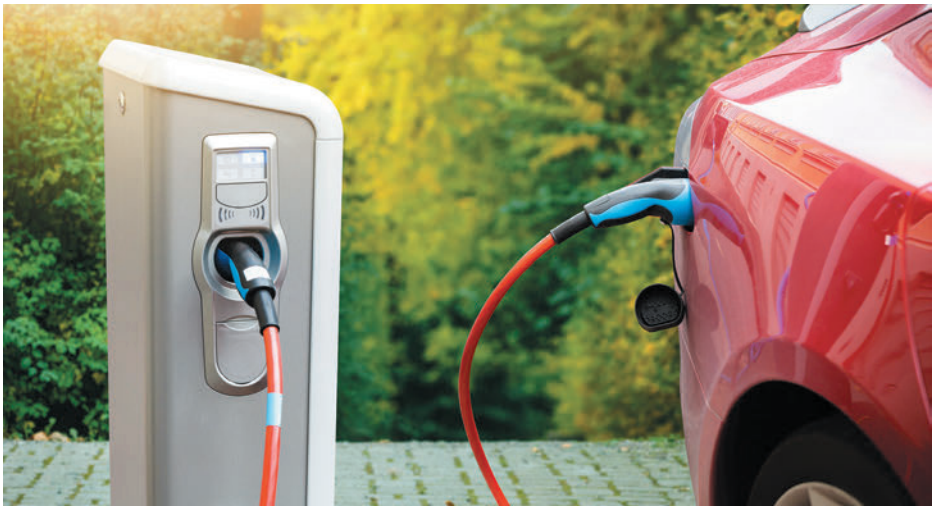
20.20 Is each of the following substances likely to serve as an oxidant or a reductant: (**a**) $Ce^{3+}(aq)$, (**b**) $Ca(s)$, (**c**) $ClO_3^-(aq)$, (**d**) $N_2O_5(g)$?

20.21 The standard reduction potential for the reduction of $RuO_4^-(aq)$ to $RuO_4^{2-}(aq)$ is +0.59 V. By using Appendix E, which of the following substances can oxidize $RuO_4^{2-}(aq)$ to $RuO_4^-(aq)$ under standard conditions: $Br_2(l)$, $BrO_3^-(aq)$, $Mn^{2+}(aq)$, $O_2(g)$, $Sn^{2+}(aq)$?

Answers to Self-Assessment Exercise

20.13 (b)

20.5 | Free Energy and Redox Reactions



Surprisingly, electric cars have been around since the end of the nineteenth century, however with a limited range and high battery cost they could not compete with the internal combustion engine. Recently, the development of new lithium ion battery technology and the falling cost of lithium has meant that electric vehicles are now edging into the domestic car market. The cost of the batteries remains a significant factor but in the decade since 2010 this has dropped by 600%. Electric vehicles have engine efficiencies of around 70%, significantly higher than either petrol or diesel engines which use only around 15-20% of the fuel energy content to move the vehicle. You can read more on electric vehicles in the Chemistry Put to Work box on page 987.

In this section, we examine the relationship between redox potentials and ΔG, and by the end you should be able to

- Relate E° to ΔG° and K.

We have observed that voltaic cells use spontaneous redox reactions to produce a positive cell potential. Given half-cell potentials, we can determine whether a given redox reaction is spontaneous. In this endeavor, we can use a form of Equation 20.8 that describes redox reactions in general, not just reactions in voltaic cells:

$$E^\circ = E^\circ_{red}\,(\text{reduction process}) - E^\circ_{red}\,(\text{oxidation process}) \qquad [20.10]$$

In writing the equation this way, we have dropped the subscript "cell" to indicate that the calculated emf does not necessarily refer to a voltaic cell. Also, we have generalized the standard reduction potentials by using the general terms *reduction* and *oxidation* rather than the terms specific to voltaic cells, *cathode* and *anode*. We can now make a general statement about the spontaneity of a reaction and its associated emf, E: *A positive value of* E *indicates a spontaneous process; a negative value of* E *indicates a nonspontaneous process*. We use E to represent the emf under nonstandard conditions and $E°$ to indicate the standard emf.

We can use standard reduction potentials to understand the activity series of metals. Recall that any metal in the activity series (Table 4.5) is oxidized by the ions of any metal below it. We can now recognize the origin of this rule based on standard reduction potentials. The activity series is based on the oxidation reactions of the metals, ordered from strongest reducing agent at the top to weakest reducing agent at the bottom. (Thus, the ordering is inverted relative to that in Table 20.1.) For example, nickel lies above silver in the activity series, making nickel the stronger reducing agent. Because a reducing agent is oxidized in any redox reaction, nickel is more easily oxidized than

Sample Exercise 20.9

Determining Spontaneity

Use Table 20.1 to determine whether the following reactions are spontaneous under standard conditions.

(**a**) $Cu(s) + 2\,H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g)$

(**b**) $Cl_2(g) + 2\,I^-(aq) \longrightarrow 2\,Cl^-(aq) + I_2(s)$

SOLUTION

Analyze We are given two reactions and must determine whether each is spontaneous.

Plan To determine whether a redox reaction is spontaneous under standard conditions, we first need to write its reduction and oxidation half-reactions. We can then use the standard reduction potentials and Equation 20.10 to calculate the standard emf, $E°$, for the reaction. If a reaction is spontaneous, its standard emf must be a positive number.

Solve

(**a**) We first must identify the oxidation and reduction half-reactions that when combined give the overall reaction.

Reduction: $2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$

Oxidation: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$

We look up standard reduction potentials for both half-reactions and use them to calculate $E°$ using Equation 20.10:

$$E° = E°_{red}\,(\text{reduction process}) - E°_{red}\,(\text{oxidation process})$$
$$= (0\,V) - (0.34\,V) = -0.34\,V$$

Because $E°$ is negative, the reaction is not spontaneous in the direction written. Copper metal does not react with acids as written in Equation (a). The reverse reaction, however, *is* spontaneous and has a positive $E°$ value:

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2\,H^+(aq) \quad E° = +0.34\,V$$

Thus, Cu^{2+} can be reduced by H_2.

(**b**) We follow a procedure analogous to that in (a):

Reduction: $Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$

Oxidation: $2\,I^-(aq) \longrightarrow I_2(s) + 2\,e^-$

In this case:

$$E° = (1.36\,V) - (0.54\,V) = +0.82\,V$$

Because the value of $E°$ is positive, this reaction is spontaneous and could be used to build a voltaic cell.

Practice Exercise

Which of the following elements is capable of oxidizing $Fe^{2+}(aq)$ ions to $Fe^{3+}(aq)$ ions: chlorine, bromine, iodine?

(**a**) I_2 (**b**) Cl_2 (**c**) Cl_2 and I_2 (**d**) Cl_2 and Br_2 (**e**) all three elements

silver. In a mixture of nickel metal and silver cations, therefore, we expect a displacement reaction in which the silver ions are displaced in the solution by nickel ions:

$$Ni(s) + 2\,Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2\,Ag(s)$$

In this reaction, Ni is oxidized and Ag^+ is reduced. Therefore, the standard emf for the reaction is

$$\begin{aligned} E^\circ &= E^\circ_{red}\,(Ag^+/Ag) - E^\circ_{red}(Ni^{2+}/Ni) \\ &= (+0.80\,V) - (-0.28\,V) = +1.08\,V \end{aligned}$$

The positive value of E° indicates that the displacement of silver by nickel resulting from oxidation of Ni metal and reduction of Ag^+ is a spontaneous process. Remember that although we multiply the silver half-reaction by 2, the reduction potential is not multiplied.

Emf, Free Energy, and the Equilibrium Constant

The change in the Gibbs free energy, ΔG, is a measure of the spontaneity of a process that occurs at constant temperature and pressure. The emf, E, of a redox reaction also indicates whether the reaction is spontaneous. The relationship between emf and the free-energy change is

$$\Delta G = -nFE \qquad [20.11]$$

In this equation, n is a positive number without units that represents the number of moles of electrons transferred according to the balanced equation for the reaction, and F is the **Faraday constant**, named after Michael Faraday (Figure 20.12):

$$F = 96{,}485\,C/mol = 96{,}485\,J/V\,mol$$

The Faraday constant is the quantity of electrical charge on 1 mol of electrons.

The units of ΔG calculated with Equation 20.11 are J/mol. As in Equation 19.19, we use "per mole" to mean per mole of reaction as indicated by the coefficients in the balanced equation.

Because both n and F are positive numbers, a positive value of E in Equation 20.11 leads to a negative value of ΔG. Remember: *A positive value of* E *and a negative value of* ΔG *both indicate a spontaneous reaction*. When the reactants and products are all in their standard states, Equation 20.11 can be modified to relate ΔG° and E°.

$$\Delta G^\circ = -nFE^\circ \qquad [20.12]$$

Because ΔG° is related to the equilibrium constant, K, for a reaction by the expression $\Delta G^\circ = -RT \ln K$ (Equation 19.20), we can relate E° to K by solving Equation 20.12 for E° and then substituting the Equation 19.20 expression for ΔG°.

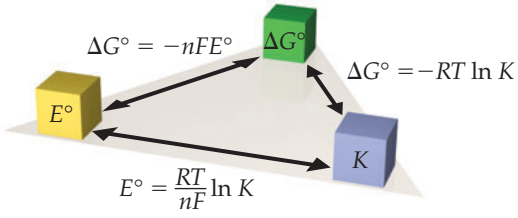
$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RT \ln K}{-nF} = \frac{RT}{nF} \ln K \qquad [20.13]$$

Figure 20.13 summarizes the relationships among E°, ΔG°, and K.



▲ **Figure 20.12 Michael Faraday.** Faraday (1791–1867) was born in England, a child of a poor blacksmith. At the age of 14 he was apprenticed to a bookbinder who gave him time to read and to attend lectures. In 1812 he became an assistant in Humphry Davy's laboratory at the Royal Institution. He succeeded Davy as the most famous and influential scientist in England, making an amazing number of important discoveries, including his formulation of the quantitative relationships between electrical current and the extent of chemical reaction in electrochemical cells.

Go Figure What does the variable ***n*** represent in the ΔG° and E° equations?



▲ **Figure 20.13 Relationships of *E*°, Δ*G*°, and *K*.** Any one of these important parameters can be used to calculate the other two. The signs of E° and ΔG° determine the direction in which the reaction proceeds under standard conditions. The magnitude of K determines the relative amounts of reactants and products in an equilibrium mixture.

Sample Exercise 20.10

Using Standard Reduction Potentials to Calculate $\Delta G°$ and K

(**a**) Use the standard reduction potentials in Table 20.1 to calculate the standard free energy change, $\Delta G°$, and the equilibrium constant, K, at 298 K for the reaction

$$4\,Ag(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 4\,Ag^+(aq) + 2\,H_2O(l)$$

(**b**) Suppose the reaction in part (a) is written

$$2\,Ag(s) + \frac{1}{2}\,O_2(g) + 2\,H^+(aq) \longrightarrow 2\,Ag^+(aq) + H_2O(l)$$

What are the values of $E°$, $\Delta G°$, and K when the reaction is written in this way?

SOLUTION

Analyze We are asked to determine $\Delta G°$ and K for a redox reaction, using standard reduction potentials.

Plan We use the data in Table 20.1 and Equation 20.10 to determine $E°$ for the reaction and then use $E°$ in Equation 20.12 to calculate $\Delta G°$. We can then use either Equation 19.20 or Equation 20.13 to calculate K.

Solve

(**a**) We first calculate $E°$ by breaking the equation into two half-reactions and obtaining $E°_{red}$ values from Table 20.1 (or Appendix E):

Reduction: $O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$ $\quad E°_{red} = +1.23\ V$

Oxidation: $4\,Ag(s) \longrightarrow 4\,Ag^+(aq) + 4\,e^-$ $\quad E°_{red} = +0.80\ V$

Even though the second half-reaction has 4 Ag, we use the $E°_{red}$ value directly from Table 20.1 because emf is an intensive property. Using Equation 20.10, we have:

$$E° = (1.23\ V) - (0.80\ V) = 0.43\ V$$

The half-reactions show the transfer of four electrons. Thus, for this reaction $n = 4$. We now use Equation 20.12 to calculate $\Delta G°$:

$$\begin{aligned}\Delta G° &= -nFE° \\ &= -(4)(96{,}485\ J/\cancel{V}\,mol)(+0.43\ \cancel{V}) \\ &= -1.7 \times 10^5\ J/mol = -170\ kJ/mol\end{aligned}$$

Now we need to calculate the equilibrium constant, K, using $\Delta G° = RT \ln K$. Because $\Delta G°$ is a large negative number, which means the reaction is thermodynamically very favorable, we expect K to be large.

$$\begin{aligned}\Delta G° &= -RT \ln K \\ -1.7 \times 10^5\ J/mol &= -(8.314\ J/K\,mol)\,(298\ K) \ln K \\ \ln K &= \frac{-1.7 \times 10^5\ \cancel{J}/\cancel{mol}}{-(8.314\ J/\cancel{K}\,\cancel{mol})(298\ \cancel{K})} \\ \ln K &= 69 \\ K &= 9 \times 10^{29}\end{aligned}$$

(**b**) The overall equation is the same as that in part (a), multiplied by $\frac{1}{2}$. The half-reactions are:

Reduction: $\frac{1}{2}\,O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O(l)$ $\quad E°_{red} = +1.23\ V$

Oxidation: $2\,Ag(s) \longrightarrow 2\,Ag^+(aq) + 2\,e^-$ $\quad E°_{red} = +0.80\ V$

The values of $E°_{red}$ are the same as they were in part (a); they are not changed by multiplying the half-reactions by $\frac{1}{2}$. Thus, $E°$ has the same value as in part (a): $E° = +0.43$ V. Notice, though, that the value of n has changed to $n = 2$, which is one-half the value in part (a). Thus, $\Delta G°$ is half as large as in part (a):

$$\Delta G° = -(2)(96{,}485\ J/\cancel{V}\text{-}mol)(+0.43\ \cancel{V}) = -83\ kJ/mol$$

The value of $\Delta G°$ is half that in part (a) because the coefficients in the chemical equation are half those in (a).

Now we can calculate K as before:

$$\begin{aligned}-8.3 \times 10^4\ J/mol &= -(8.314\ J/K\,mol)(298\ K) \ln K \\ K &= 4 \times 10^{14}\end{aligned}$$

Continued

Comment $E°$ is an *intensive* quantity, so multiplying a chemical equation by a certain factor will not affect the value of $E°$. Multiplying an equation will change the value of n, however, and hence the value of $\Delta G°$. The change in free energy, in units of J/mol of reaction as written, is an *extensive* quantity. The equilibrium constant is also an extensive quantity.

Practice Exercise

For the reaction

$$3\,Ni^{2+}(aq) + 2\,Cr(OH)_3(s) + 10\,OH^-(aq) \longrightarrow 3\,Ni(s) + 2\,CrO_4^{2-}(aq) + 8\,H_2O(l)$$

$\Delta G° = +87$ kJ/mol. Given the standard reduction potential of $Ni^{2+}(aq)$ in Table 20.1, what value do you calculate for the standard reduction potential of the half-reaction

$$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3\,e^- \longrightarrow Cr(OH)_3(s) + 5\,OH^-(aq)?$$

(a) −0.43 V **(b)** −0.28 V **(c)** 0.02 V **(d)** −0.13 V **(e)** −0.15 V

A CLOSER LOOK Electrical Work

For any spontaneous process, ΔG is a measure of the maximum useful work, w_{max}, that can be extracted from the process: $\Delta G = w_{max}$. Because $\Delta G = -nFE$, the maximum useful electrical work obtainable from a voltaic cell is

$$w_{max} = -nFE_{cell} \qquad [20.14]$$

Because cell emf, E_{cell}, is always positive for a voltaic cell, w_{max} is negative, indicating that work is done *by* a system *on* its surroundings, as we expect for a voltaic cell.

As Equation 20.14 shows, the more charge a voltaic cell moves through a circuit (that is, the larger nF is) and the larger the emf pushing the electrons through the circuit (that is, the larger $E°_{cell}$ is), the more work the cell can accomplish. In Sample Exercise 20.10, we calculated $\Delta G° = -170$ kJ/mol for the reaction $4\,Ag(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 4\,Ag^+(aq) + 2\,H_2O(l)$. Thus, a voltaic cell utilizing this reaction could perform a maximum of 170 kJ of work in consuming 4 mol Ag, 1 mol O_2, and 4 mol H^+.

If a reaction is not spontaneous, ΔG is positive and E is negative. To force a nonspontaneous reaction to occur in an electrochemical cell, we need to apply an external potential, E_{ext}, that exceeds $|E_{cell}|$. For example, if a nonspontaneous process has $E = -0.9$ V, then the external potential E_{ext} must be greater than +0.9 V in order for the process to occur. We will examine such nonspontaneous processes in Section 20.9.

Electrical work can be expressed in energy units of watts times time. The *watt* (W) is a unit of electrical power (that is, rate of energy expenditure):

$$1\ W = 1\ J/s$$

Thus, a watt-second is a joule. The unit employed by electric utilities is the kilowatt-hour (kWh), which equals 3.6×10^6 J:

$$1\ kWh = (1000\ \cancel{W})(1\ \cancel{h})\left(\frac{3600\ \cancel{s}}{1\ \cancel{h}}\right)\left(\frac{1\ J/\cancel{s}}{1\ \cancel{W}}\right) = 3.6 \times 10^6\ J$$

Related Exercises: 20.27, 20.87

Self-Assessment Exercise

20.22 For a cell in which E° > 0 V, which statement is true?

(a) $\Delta G°$ > 0 and K is > 1

(b) $\Delta G°$ < 0 and K is > 1

(c) $\Delta G°$ > 0 and 0 < K < 1

(d) $\Delta G°$ < 0 and 0 < K < 1

Exercises

20.23 For each of the following reactions, write a balanced equation, calculate the standard emf, calculate $\Delta G°$ at 298 K, and calculate the equilibrium constant K at 298 K. (**a**) Aqueous iodide ion is oxidized to $I_2(s)$ by $Hg_2^{2+}(aq)$. (**b**) In acidic solution, copper(I) ion is oxidized to copper(II) ion by nitrate ion. (**c**) In basic solution, $Cr(OH)_3(s)$ is oxidized to $CrO_4^{2-}(aq)$ by $ClO^-(aq)$.

20.24 If the equilibrium constant for a two-electron redox reaction at 298 K is 2.2×10^5, calculate the corresponding $\Delta G°$ and $E°$.

20.25 Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:

(**a**) $Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$

(**b**) $3\,Ce^{4+}(aq) + Bi(s) + H_2O(l) \longrightarrow 3\,Ce^{3+}(aq) + BiO^+(aq) + 2\,H^+(aq)$

(**c**) $N_2H_5^+(aq) + 4\,Fe(CN)_6^{3-}(aq) \longrightarrow N_2(g) + 5\,H^+(aq) + 4\,Fe(CN)_6^{4-}(aq)$

20.26 At 298 K a cell reaction has a standard cell potential of +0.63 V. The equilibrium constant for the reaction is 3.8×10^{10}. What is the value of n for the reaction?

20.27 Consider the voltaic cell illustrated in Figure 20.5, which is based on the cell reaction

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 50.0 g of copper is formed?

Answers to Self-Assessment Exercise

20.22 (b)

20.6 | Cell Potentials under Nonstandard Conditions



Many metabolic processes involve redox reactions, which not only store energy but allow its release in a controlled and efficient manner. One such example is photosynthesis, in which absorption of a photon by chlorophyll triggers release of an electron in photosystem I. This electron cascades down an electron transport chain, ultimately reducing nicotinamide adenine dinucleotide phosphate (NADP) to NADPH, used by all cells as a reducing agent. The electron lost by photosystem I is replaced by photosystem II on oxidation of water to oxygen and hydrogen ions. Of course, the process is much more complex than suggested here, but is based on redox reactions and concentration gradients, which we can understand.

By the end of this section, you should be able to

- Calculate emf under nonstandard conditions.

We have seen how to calculate the emf of a cell when the reactants and products are under standard conditions. As a voltaic cell is discharged, however, reactants are consumed and products are generated, so concentrations change. The emf progressively drops until $E = 0$, at which point we say the cell is "dead." In this section, we examine how the emf generated under nonstandard conditions can be calculated by using an equation first derived by Walther Nernst (1864–1941), a German chemist who established many of the theoretical foundations of electrochemistry.

The Nernst Equation

The effect of concentration on cell emf can be obtained from the effect of concentration on free-energy change. Recall that the free-energy change for any chemical reaction, ΔG, is related to the standard free-energy change for the reaction, $\Delta G°$:

$$\Delta G = \Delta G° + RT \ln Q \qquad [20.15]$$

The quantity Q is the reaction quotient, which has the form of the equilibrium expression except that the concentrations are those that exist in the reaction mixture at a given moment.

Substituting $\Delta G = -nFE$ (Equation 20.11) into Equation 20.15 gives

$$-nFE = -nFE° + RT \ln Q$$

Solving this equation for E gives the **Nernst equation**:

$$E = E° - \frac{RT}{nF} \ln Q \qquad [20.16]$$

This equation is customarily expressed in terms of the base-10 logarithm:

$$E = E^\circ - \frac{2.303\,RT}{nF}\log Q \qquad [20.17]$$

At $T = 298$ K, the quantity $2.303\,RT/F$ equals 0.0592, with units of volts, and so the Nernst equation simplifies to

$$E = E^\circ - \frac{0.0592\text{ V}}{n}\log Q \qquad (T = 298\text{ K}) \qquad [20.18]$$

We can use this equation to find the emf E produced by a cell under nonstandard conditions or to determine the concentration of a reactant or product by measuring E for the cell. For example, consider the following reaction:

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$$

In this case $n = 2$ (two electrons are transferred from Zn to Cu^{2+}), and the standard emf is +1.10 V. Thus, at 298 K the Nernst equation gives

$$E = 1.10\text{ V} - \frac{0.0592\text{ V}}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \qquad [20.19]$$

Recall that pure solids are excluded from the expression for Q. According to Equation 20.19, the emf increases as $[Cu^{2+}]$ increases and as $[Zn^{2+}]$ decreases. For example, when $[Cu^{2+}]$ is 5.0 M and $[Zn^{2+}]$ is 0.050 M, we have

$$E = 1.10\text{ V} - \frac{0.0592\text{ V}}{2}\log\left(\frac{0.050}{5.0}\right)$$

$$= 1.10\text{ V} - \frac{0.0592\text{ V}}{2}(-2.00) = 1.16\text{ V}$$

Thus, increasing the concentration of reactant Cu^{2+} and decreasing the concentration of product Zn^{2+} relative to standard conditions increases the emf of the cell relative to standard conditions ($E^\circ = +1.10$ V).

The Nernst equation helps us understand why the emf of a voltaic cell drops as the cell discharges. As reactants are converted to products, the value of Q increases, so the value of E decreases, eventually reaching $E = 0$. Because $\Delta G = -nFE$ (Equation 20.11), it follows that $\Delta G = 0$ when $E = 0$. Recall that a system is at equilibrium when $\Delta G = 0$. Thus, when $E = 0$, the cell reaction has reached equilibrium, and no net reaction occurs.

In general, increasing the concentration of reactants or decreasing the concentration of products increases the driving force for the reaction, resulting in a higher emf. Conversely, decreasing the concentration of reactants or increasing the concentration of products causes the emf to decrease from its value under standard conditions.

Sample Exercise 20.11

Cell Potential under Nonstandard Conditions

Calculate the emf at 298 K generated by a voltaic cell in which the reaction is

$$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\,\text{H}^+(aq) + 6\,\text{I}^-(aq) \longrightarrow 2\,\text{Cr}^{3+}(aq) + 3\,\text{I}_2(s) + 7\,\text{H}_2\text{O}(l)$$

when

$$[\text{Cr}_2\text{O}_7^{2-}] = 2.0\ M,\ [\text{H}^+] = 1.0\ M,\ [\text{I}^-] = 1.0\ M,\ \text{and}\ [\text{Cr}^{3+}] = 1.0 \times 10^{-5}\ M$$

SOLUTION

Analyze We are given a chemical equation for a voltaic cell and the concentrations of reactants and products under which it operates. We are asked to calculate the emf of the cell under these nonstandard conditions.

Plan To calculate the emf of a cell under nonstandard conditions, we use the Nernst equation in the form of Equation 20.18.

Solve

We calculate $E°$ for the cell from standard reduction potentials (Table 20.1 or Appendix E). The standard emf for this reaction was calculated in Sample Exercise 20.6: $E° = 0.79$ V. As that exercise shows, six electrons are transferred from reducing agent to oxidizing agent, so $n = 6$. The reaction quotient, Q, is:

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}[I^-]^6}$$

$$= \frac{(1.0 \times 10^{-5})^2}{(2.0)(1.0)^{14}(1.0)^6} = 5.0 \times 10^{-11}$$

Using Equation 20.18, we have:

$$E = 0.79\ \text{V} - \left(\frac{0.0592\ \text{V}}{6}\right)\log(5.0 \times 10^{-11})$$

$$= 0.79\ \text{V} - \left(\frac{0.0592\ \text{V}}{6}\right)(-10.30)$$

$$= 0.79\ \text{V} + 0.10\ \text{V} = 0.89\ \text{V}$$

Check This result is qualitatively what we expect: Because the concentration of $Cr_2O_7^{2-}$ (a reactant) is greater than 1 M and the concentration of Cr^{3+} (a product) is less than 1 M, the emf is greater than $E°$. Because Q is about 10^{-10}, log Q is about -10. Thus, the correction to $E°$ is about $0.06 \times 10/6$, which is 0.1, in agreement with the more detailed calculation.

Practice Exercise

Consider a voltaic cell whose overall reaction is $Pb^{2+}(aq) + Zn(s) \longrightarrow Pb(s) + Zn^{2+}(aq)$. What is the emf generated by this voltaic cell when the ion concentrations are $[Pb^{2+}] = 1.5 \times 10^{-3}\ M$ and $[Zn^{2+}] = 0.55\ M$?
(**a**) 0.71 V (**b**) 0.56 V (**c**) 0.49 V (**d**) 0.79 V (**e**) 0.64 V

Sample Exercise 20.12

Calculating Concentrations in a Voltaic Cell

If the potential of a Zn–H_2 cell (like that in Figure 20.9) is 0.45 V at 25 °C when $[Zn^{2+}] = 1.0\ M$ and $P_{H_2} = 100.0$ kPa, what is the pH of the cathode solution?

SOLUTION

Analyze We are given a description of a voltaic cell, its emf, the concentration of Zn^{2+}, and the partial pressure of H_2 (both products in the cell reaction). We are asked to calculate the pH of the cathode solution, which we can calculate from the concentration of H^+, a reactant.

Plan We write the equation for the cell reaction and use standard reduction potentials to calculate $E°$ for the reaction. After determining the value of n from our reaction equation, we solve the Nernst equation, Equation 20.18, for Q. We use the equation for the cell reaction to write an expression for Q that contains $[H^+]$ to determine $[H^+]$. Finally, we use $[H^+]$ to calculate pH.

Solve

The cell reaction is:

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

The standard emf is:

$$E° = E°_{red}\,(\text{reduction}) - E°_{red}\,(\text{oxidation})$$

$$= 0\ \text{V} - (-0.76\ \text{V}) = +0.76\ \text{V}$$

Because each Zn atom loses two electrons,

$$n = 2$$

Using Equation 20.18, we can solve for Q:

$$0.45\ \text{V} = 0.76\ \text{V} - \frac{0.0592\ \text{V}}{2}\log Q$$

$$Q = 10^{10.5} = 3 \times 10^{10}$$

Q has the form of the equilibrium constant for the reaction:

$$Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = \frac{(1.0)100.0}{[H^+]^2} = 3 \times 10^{10}$$

Solving for $[H^+]$, we have:

$$[H^+]^2 = \frac{101.3}{3 \times 10^{10}} = 3.4 \times 10^{-9}$$

$$[H^+] = \sqrt{3.4 \times 10^{-9}} = 6 \times 10^{-5}\ M$$

Finally, we use $[H^+]$ to calculate the pH of the cathode solution.

$$pH = \log[H^+] = -\log(6 \times 10^{-5}) = 4.2$$

Continued

Comment A voltaic cell whose cell reaction involves H^+ can be used to measure $[H^+]$ or pH. A pH meter is a specially designed voltaic cell with a voltmeter calibrated to read pH directly.

Practice Exercise

Consider a voltaic cell where the anode half-reaction is $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ and the cathode half-reaction is $Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$. What is the concentration of Sn^{2+} if Zn^{2+} is $2.5 \times 10^{-3}\,M$ and the cell emf is 0.660 V? Use the reduction potentials in Appendix E that are reported to three significant figures. (**a**) $3.3 \times 10^{-2}\,M$ (**b**) $1.9 \times 10^{-4}\,M$ (**c**) $9.0 \times 10^{-3}\,M$ (**d**) $6.9 \times 10^{-4}\,M$ (**e**) $7.6 \times 10^{-3}\,M$

Concentration Cells

In the voltaic cells we have looked at thus far, the reactive species at the anode has been different from the reactive species at the cathode. Cell emf depends on concentration, however, so a voltaic cell can be constructed using the *same* species in both half-cells as long as the concentrations are different. A cell based solely on the emf generated because of a difference in a concentration is called a **concentration cell**.

An example of a concentration cell is diagrammed in Figure 20.14(**a**). One half-cell consists of a strip of nickel metal immersed in a $1.00 \times 10^{-3}\,M$ solution of $Ni^{2+}(aq)$. The other half-cell also has an Ni(s) electrode, but it is immersed in a 1.00 M solution of $Ni^{2+}(aq)$. The two half-cells are connected by a salt bridge and by an external wire running through a voltmeter. The half-cell reactions are the reverse of each other:

$$\textit{Anode:} \quad Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \qquad E^\circ_{red} = -0.28\ V$$

$$\textit{Cathode:} \quad Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s) \qquad E^\circ_{red} = -0.28\ V$$

Although the *standard* emf for this cell is zero,

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) = (-0.28\ V) - (-0.28\ V) = 0\ V$$

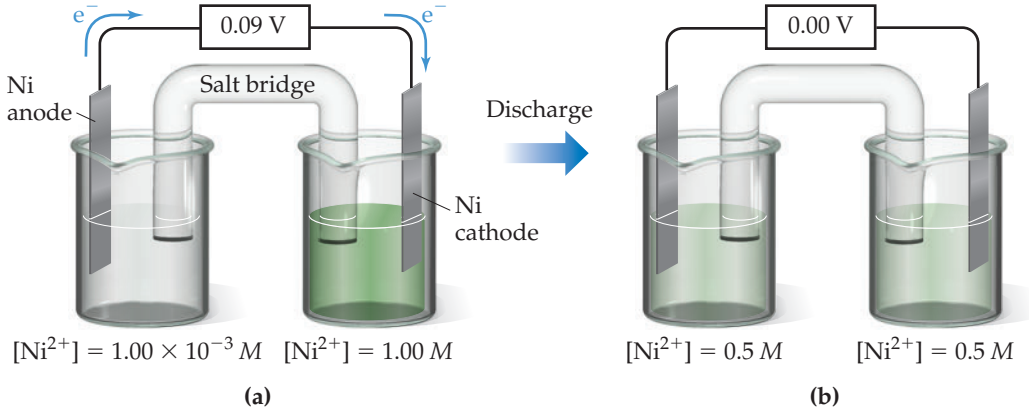
the cell operates under *nonstandard* conditions because the concentration of $Ni^{2+}(aq)$ is not 1 M in both half-cells. In fact, the cell operates until $[Ni^{2+}]_{anode} = [Ni^{2+}]_{cathode}$. Oxidation of Ni($s$) occurs in the half-cell containing the more dilute solution, which means this is the anode of the cell. Reduction of $Ni^{2+}(aq)$ occurs in the half-cell containing the more concentrated solution, making it the cathode. The *overall* cell reaction is therefore

$$\textit{Anode:} \quad Ni(s) \longrightarrow Ni^{2+}(aq, \text{dilute}) + 2\,e^-$$

$$\textit{Cathode:} \quad Ni^{2+}(aq, \text{concentrated}) + 2\,e^- \longrightarrow Ni(s)$$

$$\textit{Overall:} \quad Ni^{2+}(aq, \text{concentrated}) \longrightarrow Ni^{2+}(aq, \text{dilute})$$

Go Figure Which electrode, if any, gains mass as the reaction proceeds?



▲ **Figure 20.14 Concentration cell based on Ni^{2+}–Ni cell reaction. (a)** Concentrations of $Ni^{2+}(aq)$ in the two half-cells are unequal, and the cell generates an electrical current and a voltage. **(b)** The cell operates until $[Ni^{2+}]$ is the same in the two half-cells, at which point the cell has reached equilibrium and the emf goes to zero.



◀ **Figure 20.15 An electric eel.** Differences in ion concentrations, mainly Na^+ and K^+, in special cells called electrocytes produce an emf on the order of 0.1 V. By connecting thousands of these cells in series, these South American fish are able to generate short electric pulses as high as 500 V.

We can calculate the emf of a concentration cell by using the Nernst equation. For this particular cell, we see that $n = 2$. The expression for the reaction quotient for the overall reaction is $Q = [Ni^{2+}]_{dilute}/[Ni^{2+}]_{concentrated}$. Thus, the emf at 298 K is

$$\begin{aligned} E &= E^\circ - \frac{0.0592\ \text{V}}{n}\log Q \\ &= 0 - \frac{0.0592\ \text{V}}{2}\log\frac{[Ni^{2+}]_{dilute}}{[Ni^{2+}]_{concentrated}} = -\frac{0.0592\ \text{V}}{2}\log\frac{1.00\times10^{-3}\,M}{1.00\,M} \\ &= +0.089\ \text{V} \end{aligned}$$

This concentration cell generates an emf of nearly 0.09 V, even though $E^\circ = 0$. The difference in concentration provides the driving force for the cell. When the concentrations in the two half-cells become the same, $Q = 1$ and $E = 0$.

The idea of generating a potential by a concentration difference is the basis for the operation of pH meters. It is also a critical aspect in biology. For example, nerve cells in the brain generate a potential across the cell membrane by having different concentrations of ions on the two sides of the membrane. Electric eels use cells called electrocytes that are based on a similar principle to generate short, but intense, pulses of electricity to stun prey and dissuade predators (**Figure 20.15**). The regulation of the heartbeat in mammals, as discussed in the following Chemistry and Life box, is another example of the importance of electrochemistry to living organisms.

CHEMISTRY AND LIFE Heartbeats and Electrocardiography

The human heart is a marvel of efficiency and dependability. In a typical day, an adult's heart pumps more than 7000 L of blood through the circulatory system, usually with no maintenance required beyond a sensible diet and lifestyle. We generally think of the heart as a mechanical device, a muscle that circulates blood via regularly spaced muscular contractions. However, more than two centuries ago, two pioneers in electricity, Luigi Galvani (1729–1787) and Alessandro Volta (1745–1827), discovered that the contractions of the heart are controlled by electrical phenomena, as are nerve impulses throughout the body. The pulses of electricity that cause the heart to beat result from a remarkable combination of electrochemistry and the properties of semipermeable membranes.

Cell walls are membranes with variable permeability with respect to a number of physiologically important ions (especially Na^+, K^+, and Ca^{2+}). The concentrations of these ions are different for the fluids inside the cells (the *intracellular fluid*, or ICF) and outside the cells (the *extracellular fluid*, or ECF). In cardiac muscle cells, for example, the concentrations of K^+ in the ICF and ECF are typically about 135 millimolar (m*M*) and 4 m*M*, respectively. For Na^+, however, the concentration difference between the ICF and ECF is opposite to that for K^+; typically, $[Na^+]_{ICF} = 10$ m*M* and $[Na^+]_{ECF} = 145$ m*M*.

The cell membrane is initially permeable to K^+ ions but is much less so to Na^+ and Ca^{2+}. The difference in concentration of K^+ ions between the ICF and ECF generates a concentration cell. Even though the same ions are present on both sides of the membrane, there is a potential difference between the two fluids that we can calculate using the Nernst equation with $E^\circ = 0$. At physiological temperature (37 °C) the potential in millivolts for moving K^+ from the ECF to the ICF is

Continued

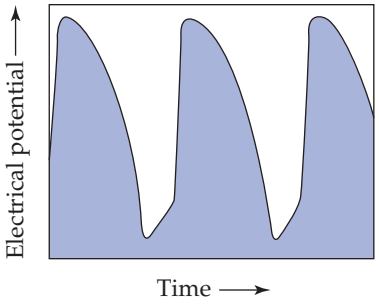
$$E = E^\circ - \frac{2.30\,RT}{nF}\log\frac{[K^+]_{ICF}}{[K^+]_{ECF}}$$

$$= 0 - (61.5\text{ mV})\log\left(\frac{135\text{ m}\cancel{M}}{4\text{ m}\cancel{M}}\right) = -94\text{ mV}$$

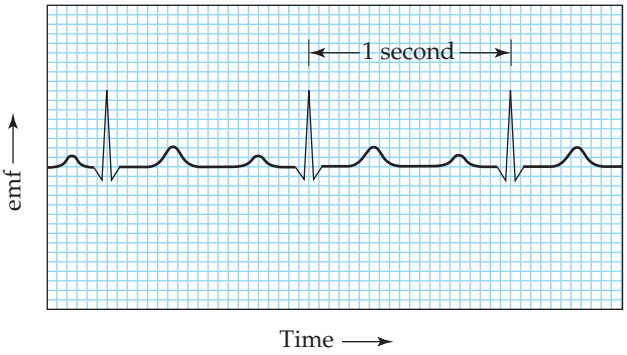
In essence, the interior of the cell and the ECF together serve as a voltaic cell. The negative sign for the potential indicates that work is required to move K^+ into the ICF.

Changes in the relative concentrations of the ions in the ECF and ICF lead to changes in the emf of the voltaic cell. The cells of the heart that govern the rate of heart contraction are called the *pacemaker cells*. The membranes of the cells regulate the concentrations of ions in the ICF, allowing them to change in a systematic way. The concentration changes cause the emf to change in a cyclic fashion, as shown in **Figure 20.16**. The emf cycle determines the rate at which the heart beats. If the pacemaker cells malfunction because of disease or injury, an artificial pacemaker can be surgically implanted. The artificial pacemaker contains a small battery that generates the electrical pulses needed to trigger the contractions of the heart.

During the late 1800s, scientists discovered that the electrical impulses that cause the contraction of the heart muscle are strong enough to be detected at the surface of the body. This observation formed the basis for *electrocardiography*, noninvasive monitoring of the heart by using a complex array of electrodes on the skin to measure voltage changes during heartbeats. A typical electrocardiogram is shown in **Figure 20.17**. It is quite striking that, although the heart's major function is the *mechanical* pumping of blood, it is most easily monitored by using the *electrical* impulses generated by tiny voltaic cells.



▲ **Figure 20.16 Changes in electrical potential in the human heart.** Variation of the electrical potential caused by changes of ion concentrations in the pacemaker cells of the heart.



▲ **Figure 20.17 A typical electrocardiogram.** The printout records the electrical events monitored by electrodes attached to the body surface.

Sample Exercise 20.13

Determining pH Using a Concentration Cell

A voltaic cell is constructed with two hydrogen electrodes. Electrode 1 has $P_{H_2} = 100.0$ kPa and an unknown concentration of $H^+(aq)$. Electrode 2 is a standard hydrogen electrode ($P_{H_2} = 100.0$ kPa, $[H^+] = 1.00\ M$). At 298 K the measured cell potential is 0.211 V, and the electrical current is observed to flow from electrode 1 through the external circuit to electrode 2. What is the pH of the solution at electrode 1?

SOLUTION

Analyze We are given the potential of a concentration cell and the direction in which the current flows. We also have the concentrations or partial pressures of all reactants and products except for $[H^+]$ in half-cell 1, which is our unknown.

Plan We can use the Nernst equation to determine Q and then use Q to calculate the unknown concentration. Because this is a concentration cell, $E^\circ_{cell} = 0$ V.

Solve

Using the Nernst equation, we have:

$$0.211\text{ V} = 0 - \frac{0.0592\text{ V}}{2}\log Q$$

$$\log Q = -(0.211\text{ V})\left(\frac{2}{0.0592\text{ V}}\right) = -7.13$$

$$Q = 10^{-7.13} = 7.4 \times 10^{-8}$$

Because electrons flow from electrode 1 to electrode 2, electrode 1 is the anode of the cell and electrode 2 is the cathode. The electrode reactions are therefore as follows, with the concentration of $H^+(aq)$ in electrode 1 represented with the unknown x:

$$\textit{Electrode 1:}\quad H_2(g, 100.0\text{ kPa}) \longrightarrow 2\,H^+(aq, x\,M) + 2\,e^- \qquad E^\circ_{red} = 0$$

$$\textit{Electrode 2:}\quad 2\,H^+(aq, 1.00\,M) + 2\,e^- \longrightarrow H_2(g, 100.0\text{ kPa}) \qquad E^\circ_{red} = 0$$

$$\textit{Overall:}\quad 2\,H^+(aq, 1.00\,M) \longrightarrow 2\,H^+(aq, x\,M)$$

Thus,

$$Q = \frac{[H^+(aq, x\,M)]^2}{[H^+(aq, 1.00\,M)]^2}$$

$$= \frac{x^2}{(1.00)^2} = x^2 = 7.4 \times 10^{-8}$$

$$x = [H^+] = \sqrt{7.4 \times 10^{-8}} = 2.7 \times 10^{-4}$$

At electrode 1, therefore, the pH of the solution is:

$$pH = -\log[H^+] = -\log(2.7 \times 10^{-4}) = 3.57$$

Comment The concentration of H^+ at electrode 1 is lower than that in electrode 2, which is why electrode 1 is the anode of the cell: The oxidation of H_2 to $H^+(aq)$ increases $[H^+]$ at electrode 1.

Practice Exercise
A concentration cell is constructed with two $Zn(s)-Zn^{2+}(aq)$ half-cells. In one half-cell $[Zn^{2+}] = 1.35\,M$, and in the other $[Zn^{2+}] = 3.75 \times 10^{-4}\,M$. (**a**) Which half-cell is the anode? (**b**) What is the emf of the cell?

Self-Assessment Exercise

20.28 A voltaic cell consisting of a Ni/Ni^{2+} half–cell and Sn/Sn^{2+} half-cell is constructed with the following initial concentrations: $[Ni^{2+}] = 1.0\,M$; $[Sn^{2+}] = 1.0\,M$. What is the concentration of ions in each half cell when the potential = 0.12 V?

(a) $[Ni^{2+}] = 1.7\,M$ and $[Sn^{2+}] = 0.27\,M$
(b) $[Ni^{2+}] = 1.4\,M$ and $[Sn^{2+}] = 0.57\,M$

Exercises

20.29 A voltaic cell is constructed with all reactants and products in their standard states. Will the concentration of the reactants increase, decrease, or remain the same as the cell operates?

20.30 A voltaic cell utilizes the following reaction:

$$Al(s) + 3\,Ag^+(aq) \longrightarrow Al^{3+}(aq) + 3\,Ag(s)$$

What is the effect on the cell emf of each of the following changes? (**a**) Water is added to the anode half-cell, diluting the solution. (**b**) The size of the aluminum electrode is increased. (**c**) A solution of $AgNO_3$ is added to the cathode half-cell, increasing the quantity of Ag^+ but not changing its concentration. (**d**) HCl is added to the $AgNO_3$ solution, precipitating some of the Ag^+ as AgCl.

20.31 A voltaic cell utilizes the following reaction and operates at 298 K:

$$3\,Ce^{4+}(aq) + Cr(s) \longrightarrow 3\,Ce^{3+}(aq) + Cr^{3+}(aq)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Ce^{4+}] = 3.0\,M$, $[Ce^{3+}] = 0.10\,M$, and $[Cr^{3+}] = 0.010\,M$? (**c**) What is the emf of the cell when $[Ce^{4+}] = 0.010\,M$, $[Ce^{3+}] = 2.0\,M$, and $[Cr^{3+}] = 1.5\,M$?

20.32 A voltaic cell utilizes the following reaction:

$$2\,Fe^{3+}(aq) + H_2(g) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H^+(aq)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf for this cell when $[Fe^{3+}] = 3.50\,M$, $P_{H_2} = 96.3$ kPa, $[Fe^{2+}] = 0.0010\,M$, and the pH in both half-cells is 4.00?

20.33 A voltaic cell is constructed with two silver–silver chloride electrodes, each of which is based on the following half-reaction:

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$$

The two half-cells have $[Cl^-] = 0.0150\,M$ and $[Cl^-] = 2.55\,M$, respectively. (**a**) Which electrode is the cathode of the cell? (**b**) What is the standard emf of the cell? (**c**) What is the cell emf for the concentrations given? (**d**) For each electrode, predict whether $[Cl^-]$ will increase, decrease, or stay the same as the cell operates.

20.34 A voltaic cell is constructed that is based on the following reaction:

$$Sn^{2+}(aq) + Pb(s) \longrightarrow Sn(s) + Pb^{2+}(aq)$$

(**a**) If the concentration of Sn^{2+} in the cathode half-cell is 1.00 M and the cell generates an emf of +0.22 V, what is the concentration of Pb^{2+} in the anode half-cell? (**b**) If the anode half-cell contains $[SO_4^{2-}] = 1.00\,M$ in equilibrium with $PbSO_4(s)$, what is the K_{sp} of $PbSO_4$?

Answers to Self-Assessment Exercise

20.28 (a)

20.7 | Batteries and Fuel Cells



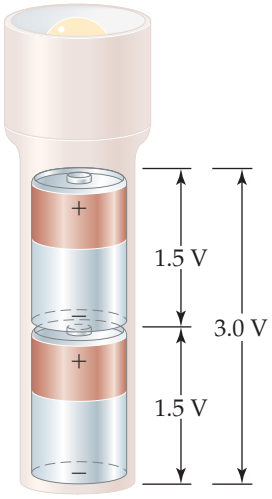
Batteries are the most familiar devices for converting between electrical and chemical energies. Objects like laptop computers, cell phones, pacemakers, and countless other devices rely on batteries to provide the electricity needed for operation.

A considerable amount of effort is currently focused on research and development of new batteries, particularly for powering electric vehicles, for storage of solar energy and power tools. New batteries are needed that are lighter, can charge faster, deliver more power, and have longer lifetimes. At the heart of such developments are the oxidation–reduction reactions that power batteries.

By the end of this section, you should be able to

- Identify the components of common batteries

A **battery** is a portable, self-contained electrochemical power source that consists of one or more voltaic cells. For example, the 1.5 V batteries used to power torches and many consumer electronic devices are single voltaic cells. Greater voltages can be achieved by using multiple cells, as in 12 V vehicle batteries. When cells are connected in series (which means the cathode of one attached to the anode of another), the battery produces a voltage that is the sum of the voltages of the individual cells. (Figure 20.18). Battery electrodes are marked following the convention of Figure 20.6—plus for cathode and minus for anode.



▲ **Figure 20.18 Combining batteries.** When batteries are connected in series, as in most flashlights, the total voltage is the sum of the individual voltages.

Although any spontaneous redox reaction can serve as the basis for a voltaic cell, making a commercial battery that has specific performance characteristics requires considerable ingenuity. The substances oxidized at the anode and reduced by the cathode determine the voltage, and the usable life of the battery depends on the quantities of these substances packaged in the battery. Usually, a barrier analogous to the porous barrier of Figure 20.6 separates the anode and cathode half-cells.

Different applications require batteries with different properties. The battery required to start a car, for example, must be capable of delivering a large electrical current for a short time period, whereas the battery that powers a heart pacemaker must be very small and capable of delivering a small but steady current over an extended time period. Some batteries are **primary cells**, meaning they cannot be recharged and must be either discarded or recycled after the voltage drops to zero. A **secondary cell** can be recharged from an external power source after its voltage has dropped.

As we consider some common batteries, notice how the principles we have discussed so far help us understand these important sources of portable electrical energy.

Lead–Acid Battery

A 12 V lead–acid automotive battery consists of six voltaic cells in series, each producing 2 V. The cathode of each cell is lead dioxide (PbO_2) packed on a lead grid (**Figure 20.19**). The anode of each cell is lead. Both electrodes are immersed in sulfuric acid.

The reactions that occur during discharge are

$$\textit{Cathode:}\quad PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$$

$$\textit{Anode:}\quad Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$$

$$\textit{Overall:}\ PbO_2(s) + Pb(s) + 2\,HSO_4^-(aq) + 2\,H^+(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l) \quad [20.20]$$

The standard cell potential can be obtained from the standard reduction potentials in Appendix E:

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) = (+1.69\ \text{V}) - (-0.36\ \text{V}) = +2.05\ \text{V}$$

The reactants Pb and PbO_2 are the electrodes. Because these reactants are solids, there is no need to separate the cell into half-cells; the Pb and PbO_2 cannot come into contact with each other unless one electrode touches another. To keep the electrodes from touching, wood or glass-fiber spacers are placed between them (Figure 20.19). Using a reaction whose reactants and products are solids has another benefit. Because solids are excluded from the reaction quotient Q, the relative amounts of $Pb(s)$, $PbO_2(s)$, and $PbSO_4(s)$ have no effect on the voltage of the lead storage battery, helping the battery maintain a relatively constant voltage during discharge. The voltage does vary somewhat with use because the concentration of H_2SO_4 varies with the extent of discharge. As Equation 20.20 indicates, H_2SO_4 is consumed during the discharge.

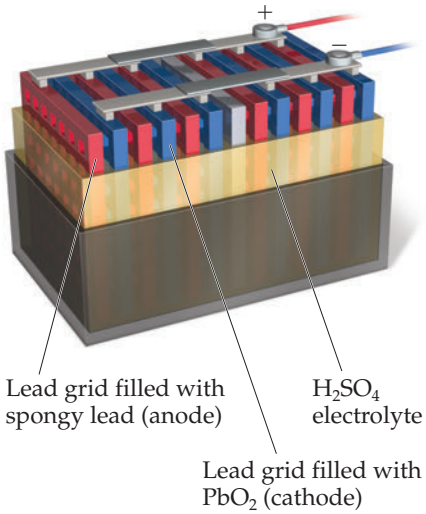
A major advantage of the lead–acid battery is that it can be recharged. During recharging, an external source of energy is used to reverse the direction of the cell reaction, regenerating $Pb(s)$ and $PbO_2(s)$:

$$2\,PbSO_4(s) + 2\,H_2O(l) \longrightarrow PbO_2(s) + Pb(s) + 2\,HSO_4^-(aq) + 2\,H^+(aq)$$

In a vehicle, the alternator provides the energy necessary for recharging the battery. Recharging is possible because $PbSO_4$ formed during discharge adheres to the electrodes. As the external source forces electrons from one electrode to the other, the $PbSO_4$ is converted to Pb at one electrode and to PbO_2 at the other.

Go Figure

What is the oxidation state of lead in the cathode of this battery?



▲ **Figure 20.19 A 12 V automotive lead–acid battery.** Each anode/cathode pair in this schematic cutaway produces a voltage of about 2 V. Six pairs of electrodes are connected in series, producing 12 V.

Alkaline Battery

The most common primary (nonrechargeable) battery is the alkaline battery (**Figure 20.20**). The anode is powdered zinc metal immobilized in a gel in contact with a concentrated solution of KOH (hence, the name *alkaline* battery). The cathode is a mixture of $MnO_2(s)$ and graphite, separated from the anode by a porous fabric. The battery is sealed in a steel can to reduce the risk of any of the concentrated KOH escaping.

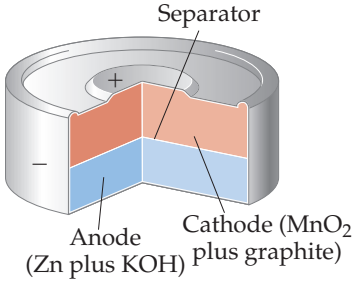
The cell reactions are complex but can be approximately represented as follows:

$$\textit{Cathode:}\quad 2\,MnO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow 2\,MnO(OH)(s) + 2\,OH^-(aq)$$

$$\textit{Anode:}\quad Zn(s) + 2\,OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2\,e^-$$

Go Figure

What substance is oxidized as the battery discharges?



▲ **Figure 20.20 Cutaway view of a miniature alkaline battery.**

Nickel–Cadmium and Nickel–Metal Hydride Batteries

The tremendous growth in high-power-demand portable electronic devices in the last decade has increased the demand for lightweight, readily rechargable batteries.

One relatively common rechargeable battery is the nickel–cadmium (nicad) battery. During discharge, cadmium metal is oxidized at the anode while nickel oxyhydroxide [NiO(OH)(*s*)] is reduced at the cathode:

$$\textit{Cathode}: \quad 2\,NiO(OH)(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq)$$

$$\textit{Anode}: \quad Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-$$

As in the lead–acid battery, the solid reaction products adhere to the electrodes, which permits the electrode reactions to be reversed during charging. A single nicad voltaic cell has a voltage of 1.30 V. Nicad battery packs typically contain three or more cells in series to produce the higher voltages needed by most electronic devices.

Although nickel–cadmium batteries have a number of attractive characteristics, the use of cadmium as the anode introduces significant limitations. Because cadmium is toxic, these batteries must be recycled. The toxicity of cadmium has led to a decline in their popularity from a peak annual production level of approximately 1.5 billion batteries in the early 2000s. Cadmium also has a relatively high density, which increases battery weight, an undesirable characteristic for use in portable devices and electric vehicles. These shortcomings have fueled the development of the nickel–metal hydride (NiMH) battery. The cathode reaction is the same as that for nickel–cadmium batteries, but the anode reaction is very different. The anode consists of a metal alloy, typically with AM_5 stoichiometry, where A is lanthanum (La) or a mixture of metals from the lanthanide series, and M is mostly nickel alloyed with smaller amounts of other transition metals. On charging, water is reduced at the anode to form hydroxide ions and hydrogen atoms that are absorbed into the AM_5 alloy. When the battery is operating (discharging), the hydrogen atoms are oxidized and the resulting H^+ ions react with OH^- ions to form H_2O.

Lithium-Ion Batteries

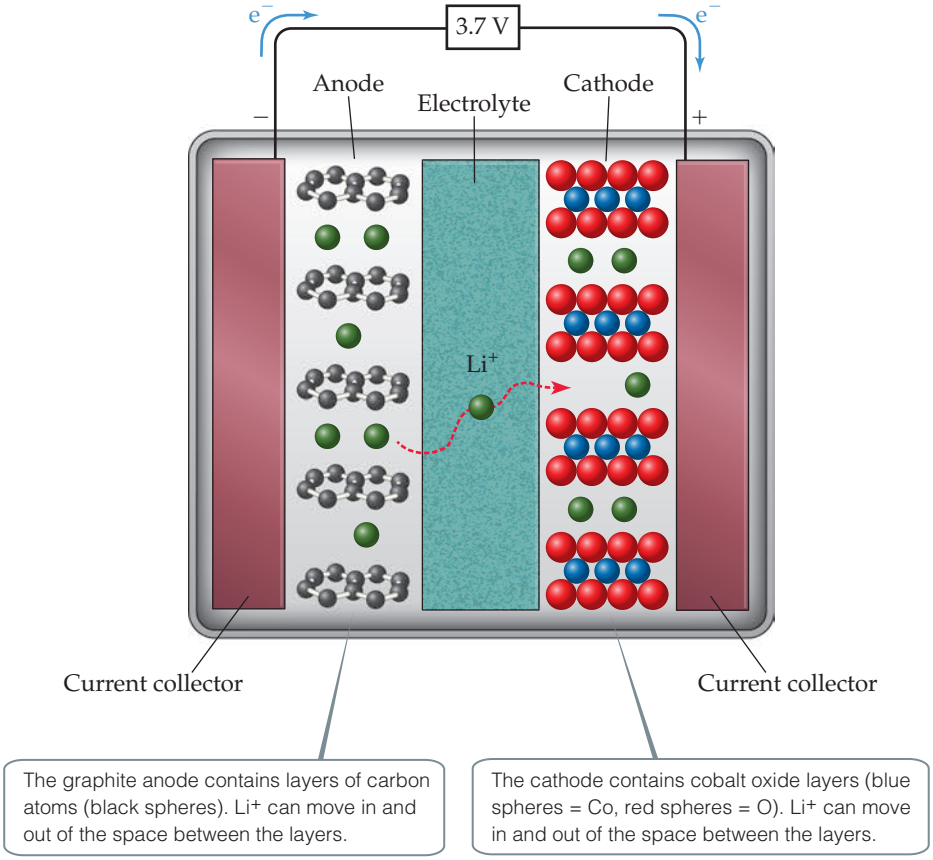
Currently, most portable electronic devices, including cell phones and laptop computers, are powered by rechargeable lithium-ion (Li-ion) batteries. Because lithium is a very light element, Li-ion batteries achieve a greater *specific energy density*—the amount of energy stored per unit mass—than nickel-based batteries. Because Li^+ has a very large negative standard reduction potential (Table 20.1), Li-ion batteries produce a higher voltage per cell than other batteries. A Li-ion battery based on ($LiCoO_2$) cathode produces a maximum voltage of 3.7 V per cell, nearly three times higher than the 1.3 V per cell that nickel–cadmium and nickel–metal hydride batteries generate. As a result, a Li-ion battery can deliver more power than other batteries of comparable size, which leads to a higher *volumetric energy density*—the amount of energy stored per unit volume.

The technology of Li-ion batteries is based on the ability of Li^+ ions to be inserted into and removed from certain layered solids. In most commercial cells, the anode is made of graphite, which contains layers of sp^2 bonded carbon atoms [Figure 12.29(b)]. The cathode is made of a transition metal oxide that also has a layered structure, typically lithium cobalt oxide ($LiCoO_2$). The two electrodes are separated by an electrolyte, which functions like a salt bridge by allowing Li^+ ions to pass through it. When the cell is being charged, cobalt ions are oxidized and Li^+ ions migrate out of $LiCoO_2$ and into the graphite. During discharge, when the battery is producing electricity for use, the Li^+ ions spontaneously migrate from the graphite anode through the electrolyte to the cathode, enabling electrons to flow through the external circuit (**Figure 20.21**).

Hydrogen Fuel Cells

The thermal energy released by burning fuels can be converted to electrical energy. The thermal energy may convert water to steam, for instance, which drives a turbine that in turn drives an electrical generator. Typically, a maximum of only 40% of the energy from combustion is converted to electricity in this manner; the remainder is lost as heat. The direct production of electricity from fuels by a voltaic cell could, in principle, yield

Go Figure When a Li-ion battery is fully discharged, the cathode has an empirical formula of $LiCoO_2$. What is the oxidation number of cobalt in this state? Does the oxidation number of the cobalt increase or decrease as the battery charges?



▲ **Figure 20.21 Schematic of a Li-ion battery.** When the battery is discharging (operating), Li^+ ions move out of the anode and migrate through the electrolyte where they enter the spaces between the cobalt oxide layers, reducing the cobalt ions. To recharge the battery, electrical energy is used to drive the Li^+ back to the anode, oxidizing the cobalt ions in the cathode.

CHEMISTRY PUT TO WORK Batteries for Hybrid and Electric Vehicles

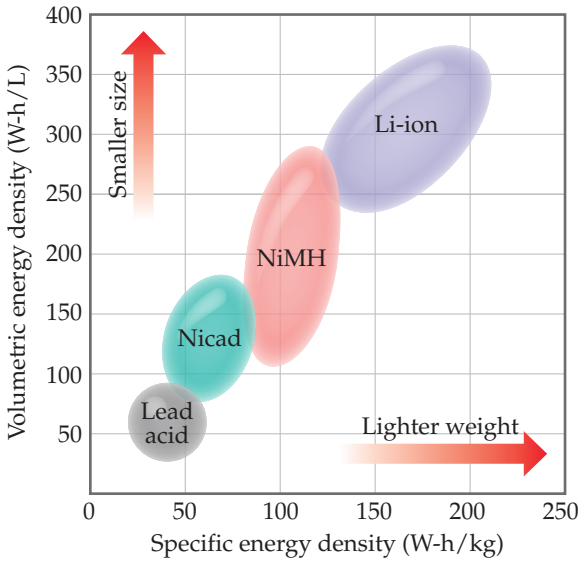
There has been a tremendous growth over the last two decades in the development of electric vehicles. This growth has been driven by a desire to reduce the use of fossil fuels and lower emissions. Today both hybrid electric vehicles and fully electric vehicles are commercially available. Hybrid electric vehicles can be powered either by electricity from batteries or by a conventional combustion engine, while fully electric vehicles are powered exclusively by the batteries (**Figure 20.22**). Hybrid electric vehicles can be further divided into plug-in hybrids, which require the owner to charge the battery by plugging it into a conventional outlet, or regular hybrids, which use regenerative braking and power from the combustion engine to charge the batteries.

Among the many technological advances needed to make electric vehicles practical, none is more important than advances in battery technology. Batteries for electric vehicles must have a high specific energy density, to reduce the weight of the car, as well as a high volumetric energy density, to minimize the space needed for the battery pack. A plot of energy densities for various types of rechargeable batteries is shown in **Figure 20.23**. The lead–acid batteries used in petrol- and diesel-powered automobiles are reliable and inexpensive, but their energy densities are far too low for



▲ **Figure 20.22 Electric car.** This Tesla electric automobile can go about 320 kilometers after 30 minutes of charging at this station.

Continued



▲ **Figure 20.23 Energy densities of various types of batteries.** The higher the volumetric energy density, the smaller the amount of space needed for the batteries. The higher the specific energy density, the smaller the mass of the batteries. A Watt-hour (W-h) is equivalent to 3.6×10^3 Joules.

practical use in an electric vehicle. Nickel–metal hydride batteries offer roughly three times higher energy density and until recently were the batteries of choice for commercial hybrid vehicles, such as the Toyota Prius.

Fully electric vehicles and plug-in hybrids use Li-ion batteries because they offer the highest energy density of all commercially available batteries. As Li-ion battery technology has advanced, these batteries have started to displace the nickel–metal hydride batteries used in hybrid electric cars. Concern over safety is one factor that has delayed implementation of Li-ion batteries in commercial automobiles. In rare cases overheating and/or overcharging can cause Li-ion batteries to combust. Most electric vehicles now use Li-ion batteries where the $LiCoO_2$ cathode has been replaced by a cathode made from lithium manganese spinel ($LiMn_2O_4$). Batteries made with $LiMn_2O_4$ cathodes have several advantages. They are not prone to thermal runaway events that can lead to combustion, they tend to have longer lifetimes, and manganese is less expensive and more environmentally friendly than cobalt. However, they do have one important shortcoming—the capacity of batteries made from $LiMn_2O_4$ is only about two-thirds that of batteries with $LiCoO_2$ cathodes. Scientists and engineers are intensively looking for new materials that will lead to further improvements in the energy density, cost, lifetime, and safety of batteries.

Related Exercises: 20.39, 20.59, 20.97

a higher rate of conversion of chemical energy to electrical energy. Voltaic cells that perform this conversion using conventional fuels, such as H_2 and CH_4, are called **fuel cells**. Fuel cells are *not* batteries because they are not self-contained systems—the fuel must be continuously supplied to generate electricity.

The most common fuel cell systems involve the reaction of $H_2(g)$ and $O_2(g)$ to form $H_2O(l)$. These cells can generate electricity twice as efficiently as the best internal combustion engine. Under acidic conditions, the reactions are

$$\begin{array}{lr} \textit{Cathode:} & O_2(g) + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O(l) \\ \textit{Anode:} & 2\,H_2(g) \longrightarrow 4\,H^+ + 4\,e^- \\ \hline \textit{Overall:} & 2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \end{array}$$

These cells employ hydrogen gas as the fuel and oxygen gas from air as the oxidant and generate about 1 V.

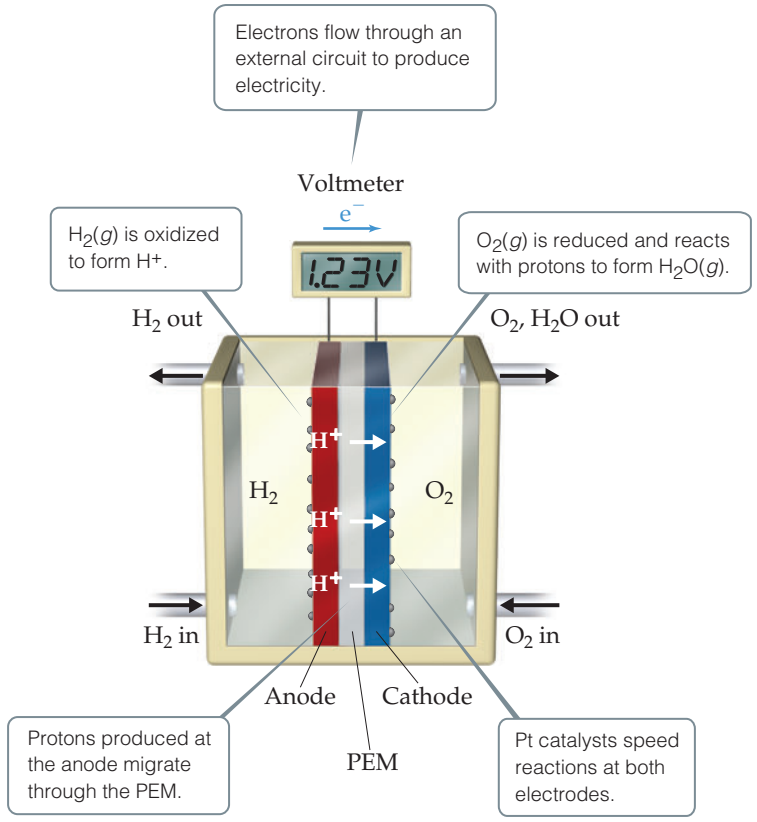
Fuel cells are often named for either the fuel or the electrolyte used. In the hydrogen-PEM fuel cell (the acronym PEM stands for either proton-exchange membrane or polymer-electrolyte membrane), the anode and cathode are separated by a membrane that is permeable to protons but not to electrons (**Figure 20.24**). The membrane therefore acts as the salt bridge. The electrodes are typically made from graphite.

The hydrogen-PEM cell operates at around 80 °C. At this temperature, the electrochemical reactions would normally occur very slowly, and so small islands of platinum are deposited on each electrode to catalyze the reactions. The high cost and relative scarcity of platinum are two factors that limit wider use of hydrogen-PEM fuel cells.

In order to power a vehicle, multiple cells must be assembled into a fuel cell *stack*. The amount of power generated by a stack depends on the number and size of the fuel cells in the stack and on the surface area of the PEM.

Much fuel cell research today is directed toward improving electrolytes and catalysts and developing cells that use fuels such as hydrocarbons and alcohols, which are less difficult to handle and distribute than hydrogen gas.

Go Figure What half-reaction occurs at the cathode?



▲ **Figure 20.24 A hydrogen-PEM fuel cell.** The proton-exchange membrane (PEM) allows H^+ ions generated by H_2 oxidation at the anode to migrate to the cathode, where H_2O is formed.

Self-Assessment Exercise

20.35 Which statement is true?

(a) Primary batteries can be recharged.

(b) The terminal of a battery marked with a plus is where the oxidation reaction occurs.

(c) Batteries containing solid reactants have a constant voltage during discharge.

Exercises

20.36 During the discharge of an alkaline battery, 4.50 g of Zn is consumed at the anode of the battery. (**a**) What mass of MnO_2 is reduced at the cathode during this discharge? (**b**) How many coulombs of electrical charge are transferred from Zn to MnO_2?

20.37 Mercuric oxide dry-cell batteries are often used where a flat discharge voltage and long life are required, such as in watches and cameras. The two half-cell reactions that occur in the battery are

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$
$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

(**a**) Write the overall cell reaction. (**b**) The value of E°_{red} for the cathode reaction is +0.098 V. The overall cell potential is +1.35 V. Assuming that both half-cells operate under standard conditions, what is the standard reduction potential for the anode reaction? (**c**) Why is the potential of the anode reaction different than would be expected if the reaction occurred in an acidic medium?

20.38 In some applications nickel–cadmium batteries have been replaced by nickel–zinc batteries. The overall cell reaction for this relatively new battery is:

$$2\,H_2O(l) + 2\,NiO(OH)(s) + Zn(s) \longrightarrow 2\,Ni(OH)_2(s) + Zn(OH)_2(s)$$

(**a**)What is the cathode half-reaction? (**b**)What is the anode half-reaction? (**c**) A single nickel–cadmium cell has a voltage of 1.30 V. Based on the difference in the standard reduction potentials of Cd^{2+} and Zn^{2+}, what voltage would you estimate a nickel–zinc battery will produce? (**d**) Would you expect the specific energy density of a nickel–zinc battery to be higher or lower than that of a nickel–cadmium battery?

20.39 Li-ion batteries used in automobiles typically use a $LiMn_2O_4$ cathode in place of the $LiCoO_2$ cathode found in most Li-ion batteries. (**a**) Calculate the mass percent lithium in each electrode material. (**b**) Which material has a higher percentage of lithium? Does this help to explain why batteries made with $LiMn_2O_4$ cathodes deliver less power on discharging? (**c**) In a battery that uses a $LiCoO_2$ cathode, approximately 50% of the lithium migrates from the cathode to the anode on charging. In a battery that uses a $LiMn_2O_4$ cathode, what fraction of the lithium in $LiMn_2O_4$ would need to migrate out of the cathode to deliver the same amount of lithium to the graphite anode?

20.40 (**a**) What is the difference between a battery and a fuel cell? (**b**) Can the "fuel" of a fuel cell be a solid?

Answers to Self-Assessment Exercise

20.35 (c)

20.8 Corrosion



The rusting of iron is a familiar corrosion process that carries a significant economic impact. Rust has a higher volume then iron, and this can destroy the structural integrity of iron-reinforced constructions if appropriate corrosion protection is not in place. One estimate suggests that up to 20% of the iron produced annually in the United States is used to replace iron objects that have been discarded because of rust damage. This can be particularly problematic in iron boats, where sea water acts as a good electrolyte and the site of corrosion is often hidden from view by the water. One method of protecting the iron is to attach a more active metal, usually zinc, to the hull, which will corrode preferentially, and may be easier to inspect for electrochemical corrosion than the entire hull of a ship.

In this section, we examine the undesirable redox reactions that lead to **corrosion** of metals. Corrosion reactions are spontaneous redox reactions in which a metal is attacked by some substance in its environment and converted to an unwanted compound.

By the end of this section, you should be able to

- Appreciate the factors affecting corrosion and how to prevent corrosion

For nearly all metals, oxidation is thermodynamically favorable in air at room temperature. When oxidation of a metal object is not inhibited, it can destroy the object. Oxidation can form an insulating protective oxide layer, however, that prevents further

reaction of the underlying metal. Based on the standard reduction potential for Al^{3+}, for example, we expect aluminum metal to be readily oxidized. The many aluminum soft-drink and beer cans that litter the environment are ample evidence, however, that aluminum undergoes only very slow chemical corrosion. The exceptional stability of this active metal in air is due to the formation of a thin protective coat of oxide—a hydrated form of Al_2O_3—on the metal surface. The oxide coat is impermeable to O_2 or H_2O and so protects the underlying metal from further corrosion.

Magnesium metal is similarly protected, and some metal alloys, such as stainless steel, likewise form protective impervious oxide coats.

Corrosion of Iron (Rusting)

Rusting of iron requires both oxygen and water, and the process can be accelerated by other factors such as pH, presence of salts, contact with metals more difficult to oxidize than iron, and stress on the iron. The corrosion process involves oxidation and reduction, and the metal conducts electricity. Thus, electrons can move through the metal from a region where oxidation occurs to a region where reduction occurs, as in voltaic cells. Because the standard reduction potential for reduction of $Fe^{2+}(aq)$ is less positive than that for reduction of O_2, $Fe(s)$ can be oxidized by $O_2(g)$:

$$\textit{Cathode:}\quad O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E^\circ_{red} = 1.23\ V$$

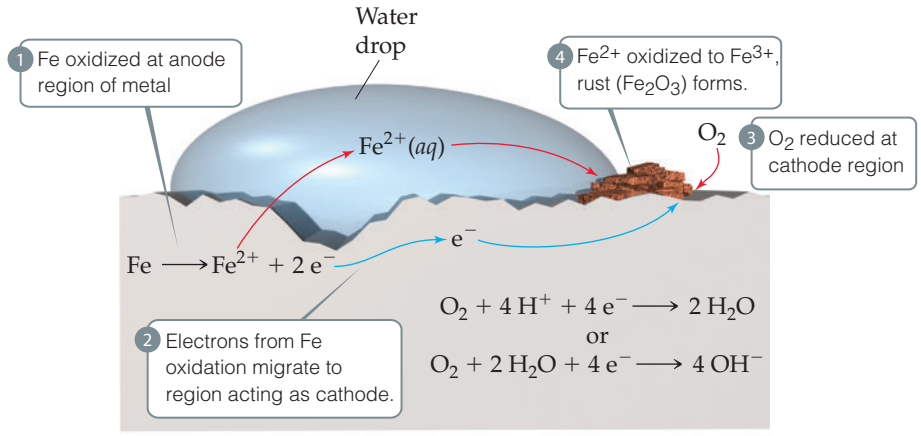
$$\textit{Anode:}\quad Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^- \qquad E^\circ_{red} = -0.44\ V$$

A portion of the iron, often associated with a dent or region of strain, can serve as an anode at which Fe is oxidized to Fe^{2+} (**Figure 20.25**). The electrons produced in the oxidation migrate through the metal from this anodic region to another portion of the surface, which serves as the cathode where O_2 is reduced. The reduction of O_2 requires H^+, so lowering the concentration of H^+ (increasing the pH) makes O_2 reduction less favorable. Iron in contact with a solution whose pH is greater than 9 does not corrode.

The Fe^{2+} formed at the anode is eventually oxidized to Fe^{3+}, which forms the hydrated iron(III) oxide known as rust:*

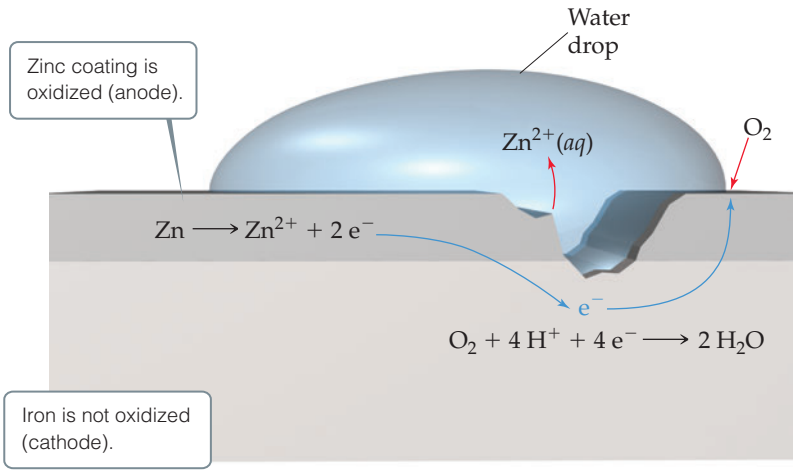
$$4\,Fe^{2+}(aq) + O_2(g) + 4\,H_2O(l) + x\,H_2O(l) \longrightarrow 2\,Fe_2O_3 \cdot x\,H_2O(s) + 8\,H^+(aq)$$

Go Figure What is the oxidizing agent in this corrosion reaction?



▲ **Figure 20.25 Corrosion of iron in contact with water.** One region of the iron acts as the cathode, and another region acts as the anode.

*Frequently, metal compounds obtained from aqueous solution have water associated with them. For example, copper(II) sulfate crystallizes from water with 5 mol of water per mole of $CuSO_4$. We represent this substance by the formula $CuSO_4 \cdot 5H_2O$. Such compounds are called hydrates. Rust is a hydrate of iron(III) oxide with a variable amount of water of hydration. We represent this variable water content by writing the formula $Fe_2O_3 \cdot xH_2O$.



▲ **Figure 20.26 Cathodic protection of iron in contact with zinc.** The standard reduction potentials are $E^\circ_{red,\,Fe^{2+}} = -0.44$ V, $E^\circ_{red,\,Zn^{2+}} = -0.76$ V, making the zinc more readily oxidized.

Because the cathode is generally the area having the largest supply of O_2, rust often deposits there. If you look closely at a shovel after it has stood outside in the moist air with wet dirt adhered to its blade, you may notice that pitting has occurred under the dirt but that rust has formed elsewhere, where O_2 is more readily available. The enhanced corrosion caused by the presence of salts is usually evident on cars in areas where roads are heavily salted during winter. Like a salt bridge in a voltaic cell, the ions of the salt provide the electrolyte necessary to complete the electrical circuit.

Preventing Corrosion of Iron

Objects made of iron are often covered with a coat of paint or another metal to protect against corrosion. Covering the surface with paint prevents oxygen and water from reaching the iron surface. If the coating is broken, however, and the iron is exposed to oxygen and water, corrosion begins as the iron is oxidized.

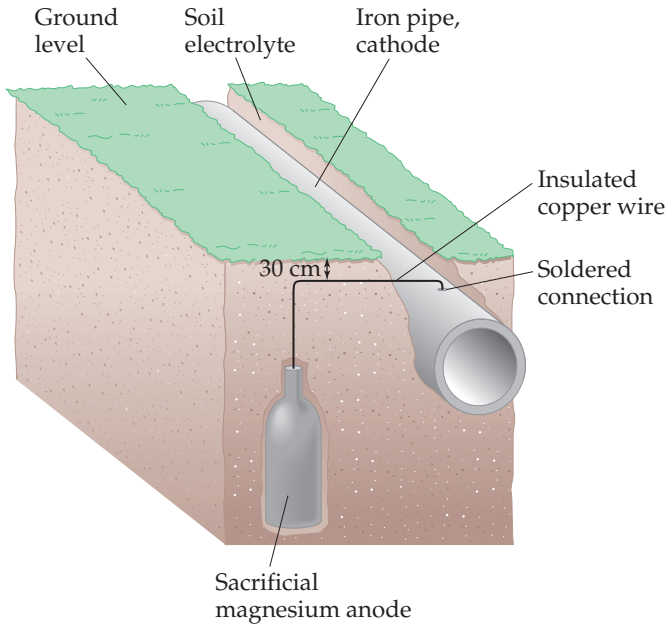
With *galvanized iron*, which is iron coated with a thin layer of zinc, the iron is protected from corrosion even after the surface coat is broken. The standard reduction potentials are

$$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s) \quad E^\circ_{red} = -0.44\,V$$

$$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) \quad E^\circ_{red} = -0.76\,V$$

Because E°_{red} for Fe^{2+} is less negative (more positive) than E°_{red} for Zn^{2+}, $Zn(s)$ is more readily oxidized than $Fe(s)$. Thus, even if the zinc coating is broken and the galvanized iron is exposed to oxygen and water, as in **Figure 20.26**, the zinc serves as the anode and is corroded (oxidized) instead of the iron. The iron serves as the cathode at which O_2 is reduced.

Protecting a metal from corrosion by making it the cathode in an electrochemical cell is known as **cathodic protection**. The metal that is oxidized while protecting the cathode is called the *sacrificial anode*. Underground pipelines and storage tanks made of iron are often protected against corrosion by making the iron the cathode of a voltaic cell. For example, pieces of a metal that is more easily oxidized than iron, such as magnesium ($E^\circ_{red} = -2.37$ V), are buried near the pipe or storage tank and connected to it by wire (**Figure 20.27**). In moist soil, where corrosion can occur, the sacrificial metal serves as the anode, and the pipe or tank experiences cathodic protection.



▲ **Figure 20.27 Cathodic protection of an iron pipe.** A mixture of gypsum, sodium sulfate, and clay surrounds the sacrificial magnesium anode to promote conductivity of ions.

Self-Assessment Exercise

20.41 Based on the values in Table 20.1, which of these metals could provide cathodic protection to iron: Ag, Zn, Cu, Ni?

(a) Ag

(b) Zn

(c) Cu

(d) Ni

Exercises

20.42 (**a**) Write the anode and cathode reactions that cause the corrosion of iron metal to aqueous iron(II). (**b**) Write the balanced half-reactions involved in the air oxidation of $Fe^{2+}(aq)$ to $Fe_2O_3 \cdot 3\,H_2O(s)$.

20.43 An iron object is plated with a coating of tin (Sn) to protect against corrosion. Does the tin protect iron by cathodic protection?

20.44 Copper corrodes to cuprous oxide, Cu_2O, or cupric oxide, CuO, depending on environmental conditions. (**a**) What is the oxidation state of copper in cuprous oxide? (**b**) What is the oxidation state of copper in cupric oxide? (**c**) Copper peroxide is another oxidation product of elemental copper. Suggest a formula for copper peroxide based on its name. (**d**) Copper(III) oxide is another unusual oxidation product of elemental copper. Suggest a chemical formula for copper(III) oxide.

Answers to Self-Assessment Exercise

20.41 (d)

20.9 Electrolysis

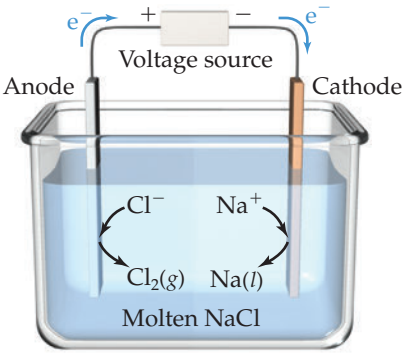


There are many materials around us that combine the structural or economic properties of one material with the decorative or corrosion-resistive properties of another. For example, a chrome plating on iron to give a highly resistant, shiny surface or the plating of gold onto copper for connectors used in the electronics industry and the silver plating onto a copper-nickel-zinc alloy for decorative purposes. These examples use an electrical current to drive a nonspontaneous process. The same principle is used for the extraction of some metals from their ore.

By the end of this section, you should be able to

- Describe, quantitatively, the reactions occurring in an electrolytic cell

Voltaic cells are based on spontaneous redox reactions. It is also possible for *nonspontaneous* redox reactions to occur, however, by using electrical energy to drive them.



$$2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^-$$

$$2\,Na^+(l) + 2\,e^- \longrightarrow 2\,Na(l)$$

▲ **Figure 20.28 Electrolysis of molten sodium chloride.** Pure NaCl melts at 801 °C.

For example, electricity can be used to decompose molten sodium chloride into its component elements Na and Cl_2. Such processes driven by an outside source of electrical energy are called **electrolysis reactions** and take place in **electrolytic cells**.

An electrolytic cell consists of two electrodes immersed either in a molten salt or in a solution. A battery or some other source of electrical energy acts as an electron pump, pushing electrons into one electrode and pulling them from the other. Just as in voltaic cells, the electrode at which reduction occurs is called the cathode, and the electrode at which oxidation occurs is called the anode.

In the electrolysis of molten NaCl, Na^+ ions gain electrons and are reduced to Na at the cathode, **Figure 20.28**. As Na^+ ions near the cathode are depleted, additional Na^+ ions migrate in. Similarly, there is net movement of Cl^- ions to the anode where they are oxidized. The electrode reactions for the electrolysis are

$$\textit{Cathode:} \quad 2\,Na^+(l) + 2\,e^- \longrightarrow 2\,Na(l)$$

$$\textit{Anode:} \quad 2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^-$$

$$\textit{Overall:} \quad 2\,Na^+(l) + 2\,Cl^-(l) \longrightarrow 2\,Na(l) + Cl_2(g)$$

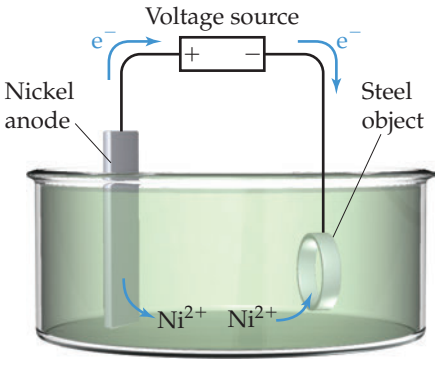
Notice how the energy source is connected to the electrodes in Figure 20.28. The positive terminal is connected to the anode and the negative terminal is connected to the cathode, which forces electrons to move from the anode to the cathode.

Because of the high melting points of ionic substances, the electrolysis of molten salts requires very high temperatures. Do we obtain the same products if we electrolyze the aqueous solution of a salt instead of the molten salt? Frequently, the answer is no because water itself might be oxidized to form O_2 or reduced to form H_2 rather than the ions of the salt.

In our examples of the electrolysis of NaCl, the electrodes are *inert*; they do not react but merely serve as the surface where oxidation and reduction occur. Several practical applications of electrochemistry, however, are based on *active* electrodes—electrodes that participate in the electrolysis process. *Electroplating*, for example, uses electrolysis to deposit a thin layer of one metal on another metal to improve beauty or resistance to corrosion. Examples include electroplating nickel or chromium onto steel and electroplating a precious metal like silver onto a less expensive one.

Figure 20.29 illustrates an electrolytic cell for electroplating nickel onto a piece of steel. The anode is a strip of nickel metal, and the cathode is the steel. The electrodes are immersed in a solution of $NiSO_4(aq)$. When an external voltage is applied, reduction occurs at the cathode. The standard reduction potential of Ni^{2+} ($E^\circ_{red} = -0.28$ V) is less negative than that of H_2O ($E^\circ_{red} = -0.83$ V), so Ni^{2+} is preferentially reduced, depositing a layer of nickel metal on the steel cathode.

Go Figure What is E° for this cell?



Anode
$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^-$

Cathode
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$

▲ **Figure 20.29 Electrolytic cell with an active metal electrode.** Nickel dissolves from the anode to form $Ni^{2+}(aq)$. At the cathode, $Ni^{2+}(aq)$ is reduced and forms a nickel "plate" on the steel cathode.

At the anode, the nickel metal is oxidized. To explain this behavior, we need to compare the substances in contact with the anode, H_2O and $NiSO_4(aq)$, with the anode material, Ni. For the $NiSO_4(aq)$ solution, neither Ni^{2+} nor SO_4^{2-} can be oxidized (because both already have their elements in their highest common oxidation state). Both the H_2O solvent and the Ni atoms in the anode, however, can undergo oxidation:

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \qquad E^\circ_{red} = +1.23\ V$$

$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \qquad E^\circ_{red} = -0.28\ V$$

We saw in Section 20.4 that the half-reaction with the more negative E°_{red} undergoes oxidation more readily. (Remember Figure 20.11: The strongest reducing agents, which are the substances oxidized most readily, have the most negative E°_{red} values.) Thus, it is the Ni(*s*), with its $E^\circ_{red} = -0.28$ V, that is oxidized at the anode rather than the H_2O. If we look at the overall reaction, it appears as if nothing has been accomplished. However, this is not true because Ni atoms are transferred from the Ni anode to the steel cathode, plating the steel with a thin layer of nickel atoms.

The standard emf for the overall reaction is

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}) = (-0.28\ V) - (-0.28\ V) = 0$$

Because the standard emf is zero, only a small emf is needed to cause the transfer of nickel atoms from one electrode to the other.

Quantitative Aspects of Electrolysis

The stoichiometry of a half-reaction shows how many electrons are needed to achieve an electrolytic process. For example, the reduction of Na^+ to Na is a one-electron process:

$$Na^+ + e^- \longrightarrow Na$$

Thus, 1 mol of electrons plates out 1 mol of Na metal, 2 mol of electrons plate out 2 mol of Na metal, and so forth. Similarly, 2 mol of electrons are required to produce 1 mol of Cu from Cu^{2+}, and 3 mol of electrons are required to produce 1 mol of Al from Al^{3+}:

$$Cu^{2+} + 2\,e^- \longrightarrow Cu$$

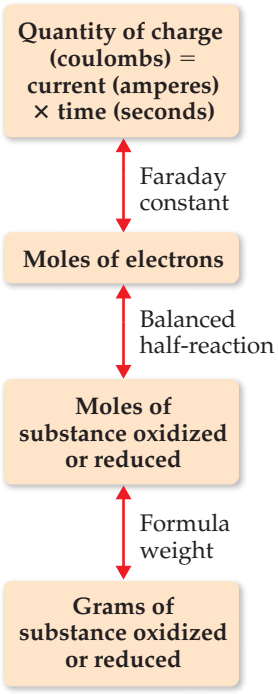
$$Al^{3+} + 3\,e^- \longrightarrow Al$$

For any half-reaction, the amount of substance reduced or oxidized in an electrolytic cell is directly proportional to the number of electrons passed into the cell.

The quantity of charge passing through an electrical circuit, such as that in an electrolytic cell, is generally measured in *coulombs*. As noted in Section 20.5, the charge on 1 mol of electrons is 96,485 C. A coulomb is the quantity of charge passing a point in a circuit in 1 s when the current is 1 ampere (A). Therefore, the number of coulombs passing through a cell can be obtained by multiplying the current in amperes by the elapsed time in seconds.

$$\text{coulombs} = \text{amperes} \times \text{seconds} \qquad [20.21]$$

Figure 20.30 shows how the quantities of substances produced or consumed in electrolysis are related to the quantity of electrical charge used. The same relationships can also be applied to voltaic cells. In other words, electrons can be thought of as "reagents" in electrolysis reactions.



▲ **Figure 20.30** Relationship between charge and amount of reactant and product in electrolysis reactions.

Sample Exercise 20.14

Relating Electrical Charge and Quantity of Electrolysis

Calculate the number of grams of aluminum produced in 1.00 h by the electrolysis of molten $AlCl_3$ if the electrical current is 10.0 A.

SOLUTION

Analyze We are told that $AlCl_3$ is electrolyzed to form Al and asked to calculate the number of grams of Al produced in 1.00 h with 10.0 A.

Plan Figure 20.30 provides a roadmap for this problem. Using the current, time, a balanced half-reaction, and the atomic weight of aluminum we can calculate the mass of Al produced.

Continued

Solve

First, we calculate the coulombs of electrical charge passed into the electrolytic cell (note that 10.0 A = 10.0 C/s):

$$\text{Coulombs} = \text{amperes} \times \text{seconds} = (10.0\ \text{C/}\cancel{\text{s}})(1.00\ \cancel{\text{h}})\left(\frac{3600\ \cancel{\text{s}}}{\cancel{\text{h}}}\right) = 3.60 \times 10^4\ \text{C}$$

Second, we calculate the number of moles of electrons that pass into the cell:

$$\text{Moles e}^- = (3.60 \times 10^4\ \cancel{\text{C}})\left(\frac{1\ \text{mol e}^-}{96{,}485\ \cancel{\text{C}}}\right) = 0.373\ \text{mol e}^-$$

Third, we relate number of moles of electrons to number of moles of aluminum formed, using the half-reaction for the reduction of Al^{3+}:

$$Al^{3+} + 3\,e^- \longrightarrow Al$$

Thus, 3 mol of electrons are required to form 1 mol of Al:

$$\text{Moles Al} = (0.373\ \cancel{\text{mol e}^-})\left(\frac{1\ \text{mol Al}}{3\ \cancel{\text{mol e}^-}}\right) = 0.124\ \text{mol Al}$$

Finally, we convert moles to grams:

$$\text{Grams Al} = (0.124\ \cancel{\text{mol Al}})\left(\frac{27.0\ \text{g Al}}{1\ \cancel{\text{mol Al}}}\right) = 3.36\ \text{g Al}$$

Or, we could have combined all of the above steps:

$$\text{Grams Al} = (3.60 \times 10^4\ \cancel{\text{C}})\left(\frac{1\ \cancel{\text{mol e}^-}}{96{,}485\ \cancel{\text{C}}}\right)\left(\frac{1\ \cancel{\text{mol Al}}}{3\ \cancel{\text{mol e}^-}}\right)\left(\frac{27.0\ \text{g Al}}{1\ \cancel{\text{mol Al}}}\right) = 3.36\ \text{g Al}$$

▶ Practice Exercise

How much time is needed to deposit 1.0 g of chromium metal from an aqueous solution of $CrCl_3$ using a current of 1.5 A?

(**a**) 3.8×10^{-2} s (**b**) 21 min (**c**) 62 min (**d**) 139 min (**e**) 3.2×10^3 min

CHEMISTRY PUT TO WORK Electrometallurgy of Aluminum

Many processes used to produce or refine metals are based on electrolysis. Collectively, these processes are referred to as *electrometallurgy*. Electrometallurgical procedures can be broadly differentiated according to whether they involve electrolysis of a molten salt or of an aqueous solution.

Electrolytic methods using molten salts are important for obtaining the more active metals, such as sodium, magnesium, and aluminum. These metals cannot be obtained from aqueous solution because water is more easily reduced than the metal ions. The standard reduction potentials of water under both acidic ($E^\circ_{red} = 0.00$ V) and basic ($E^\circ_{red} = -0.83$ V) conditions are more positive than those of Na^+ ($E^\circ_{red} = -2.71$ V), Mg^{2+} ($E^\circ_{red} = -2.37$ V), and Al^{3+} ($E^\circ_{red} = -1.66$ V).

Historically, obtaining aluminum metal has been a challenge. It is obtained from bauxite ore, which is chemically treated to concentrate aluminum oxide (Al_2O_3). The melting point of aluminum oxide is above 2000 °C, which is too high to permit its use as a molten medium for electrolysis.

The electrolytic process used commercially to produce aluminum is the *Hall–Héroult process*, named after its inventors, Charles M. Hall and Paul Héroult. Hall (1863–1914) (**Figure 20.31**) began working on the problem of reducing aluminum in about 1885 after he had learned from a professor of the difficulty of reducing ores of very active metals. Before the development of an electrolytic process, aluminum was obtained by a chemical reduction using sodium or potassium as the reducing agent, a costly procedure that made aluminum metal expensive. As late as 1852, the cost of aluminum was $545 per pound, far greater than the cost of gold. During the Paris Exposition in 1855, aluminum was exhibited as a rare metal, even though it is the third most abundant element in Earth's crust.



▲ **Figure 20.31** Charles M. Hall as a young man.

Hall, who was 21 years old when he began his research, utilized handmade and borrowed equipment in his studies and used a woodshed near his Ohio home as his laboratory. In about a year's time, he developed an electrolytic procedure using an ionic compound that melts to form a conducting medium that dissolves Al_2O_3 but does not interfere with the electrolysis reactions. The ionic compound he selected was the relatively rare mineral cryolite (Na_3AlF_6). Héroult, who was the same age as Hall, independently made the same

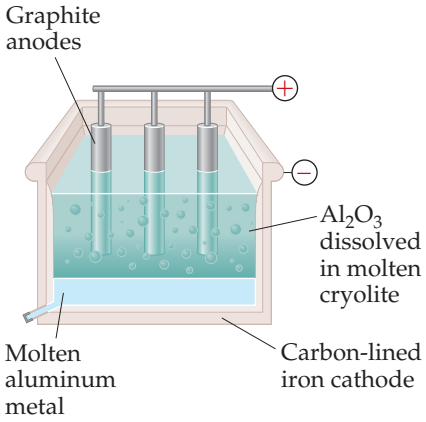
discovery in France at about the same time. Because of the research of these two unknown young scientists, large-scale production of aluminum became commercially feasible, and aluminum became a common and familiar metal. Indeed, the factory that Hall subsequently built to produce aluminum evolved into Alcoa Corporation.

In the Hall–Héroult process, Al_2O_3 is dissolved in molten cryolite, which melts at 1012 °C and is an effective electrical conductor (Figure 20.32). Graphite rods are employed as anodes and are consumed in the electrolysis:

$$\textit{Anode:} \quad C(s) + 2\,O^{2-}(l) \longrightarrow CO_2(g) + 4\,e^-$$

$$\textit{Cathode:} \quad 3\,e^- + Al^{3+}(l) \longrightarrow Al(l)$$

A large amount of electrical energy is needed in the Hall–Héroult process, with the result that many aluminum plants are close to cheap sources of electricity, such as hydroelectric power plants. Because recycled aluminum requires only 5% of the energy needed to produce "new" aluminum, considerable energy savings can be realized by increasing the amount of aluminum recycled. Approximately 65% of aluminum beverage containers are recycled in the United States.



▲ **Figure 20.32 The Hall–Héroult process.** Because molten aluminum is denser than the mixture of cryolite (Na_3AlF_6) and Al_2O_3, the metal collects at the bottom of the cell.

Self-Assessment Exercise

20.45 An electrolytic cell contains a solution of MCl_3. A total charge of 3610 C is passed through the cell, depositing 0.648 g of the metal, M, at the cathode. What is the identity of the metal, M?

(a) V
(b) Cr
(c) Mn
(d) Co

Exercises

20.46 (**a**) What is an *electrolytic cell*? (**b**) The negative terminal of a voltage source is connected to an electrode of an electrolytic cell. Is the electrode the anode or the cathode of the cell? Explain. (**c**) The electrolysis of water is often done with a small amount of sulfuric acid added to the water. What is the role of the sulfuric acid? (**d**) Why are active metals such as Al obtained by electrolysis using molten salts rather than aqueous solutions?

20.47 Metallic magnesium can be made by the electrolysis of molten $MgCl_2$. (**a**) What mass of Mg is formed by passing a current of 4.55 A through molten $MgCl_2$, for 4.50 days? (**b**) How many minutes are needed to plate out 25.00 g Mg from molten $MgCl_2$ using 3.50 A of current?

20.48 Elemental calcium is produced by the electrolysis of molten $CaCl_2$. (**a**) What mass of calcium can be produced by this process if a current of 7.5×10^3 A is applied for 48 h? Assume that the electrolytic cell is 68% efficient. (**b**) What is the minimum voltage needed to cause the electrolysis?

20.49 A mixture of copper and gold metals that is subjected to electrorefining contains tellurium as an impurity. The standard reduction potential between tellurium and its lowest common oxidation state, Te^{4+}, is

$$Te^{4+}(aq) + 4\,e^- \longrightarrow Te(s) \quad E^\circ_{red} = 0.57\ V$$

Given this information, describe the probable fate of tellurium impurities during electrorefining. Do the impurities fall to the bottom of the refining bath, unchanged, as copper is oxidized, or do they go into solution as ions? If they go into solution, do they plate out on the cathode?

Answers to Self-Assessment Exercises

20.45 (b)

Sample Integrative Exercise

Putting Concepts Together

The K_{sp} at 298 K for iron(II) fluoride is 2.4×10^{-6}. (**a**) Write a half-reaction that gives the likely products of the two-electron reduction of $FeF_2(s)$ in water. (**b**) Use the K_{sp} value and the standard reduction potential of $Fe^{2+}(aq)$ to calculate the standard reduction potential for the half-reaction in part (a). (**c**) Rationalize the difference between the reduction potential in part (a) and the reduction potential for $Fe^{2+}(aq)$.

Continued

SOLUTION

Analyze We are going to combine what we know about equilibrium constants and electrochemistry to obtain reduction potentials.

Plan For (a) we need to determine which ion, Fe^{2+} or F^-, is more likely to be reduced by two electrons and complete the overall reaction $FeF_2 + 2\,e^- \longrightarrow ?$. For (b) we need to write the chemical equation associated with the K_{sp} and see how it relates to $E°$ for the reduction half-reaction in (a). For (c) we need to compare $E°$ from (b) with the value for the reduction of Fe^{2+}.

Solve

(a) Iron(II) fluoride is an ionic substance that consists of Fe^{2+} and F^- ions. We are asked to predict where two electrons could be added to FeF_2. We cannot envision adding the electrons to the F^- ions to form F^{2-}, so it seems likely that we could reduce the Fe^{2+} ions to $Fe(s)$. We therefore predict the half-reaction:

$$FeF_2(s) + 2\,e^- \longrightarrow Fe(s) + 2\,F^-(aq)$$

(b) The K_{sp} for FeF_2 refers to the following equilibrium:

$$FeF_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\,F^-(aq) \qquad K_{sp} = [Fe^{2+}][F^-]^2 = 2.4 \times 10^{-6}$$

We were also asked to use the standard reduction potential of Fe^{2+}, whose half-reaction and standard reduction potentials are listed in Appendix E:

$$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s) \qquad E = -0.440\ V$$

According to Hess's law, if we can add chemical equations to get a desired equation, then we can add their associated thermodynamic state functions, like ΔH or ΔG, to determine the thermodynamic quantity for the desired reaction. So we need to consider whether the three equations we are working with can be combined in a similar fashion. Notice that if we add the K_{sp} reaction to the standard reduction half-reaction for Fe^{2+}, we get the half-reaction we want:

1. $FeF_2(s) \longrightarrow Fe^{2+}(aq) + 2\,F^-(aq)$
2. $Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$

Overall:

3. $FeF_2(s) + 2\,e^- \longrightarrow Fe(s) + 2\,F^-(aq)$

Reaction 3 is still a half-reaction, so we do see the free electrons.

If we knew $\Delta G°$ for reactions 1 and 2, we could add them to get $\Delta G°$ for reaction 3. We can relate $\Delta G°$ to $E°$ by $\Delta G° = -nFE°$ (Equation 20.12) and to K by $\Delta G° = -RT \ln K$ (Equation 19.20; see also Figure 20.13). Furthermore, we know that K for reaction 1 is the K_{sp} of FeF_2, and we know $E°$ for reaction 2. Therefore, we can calculate $\Delta G°$ for reactions 1 and 2:

(Recall that 1 volt is 1 joule per coulomb.)

Reaction 1:

$$\Delta G° = -RT \ln K = -(8.314\ J/\cancel{K}\,mol)(298\ \cancel{K}) \ln(2.4 \times 10^{-6}) = 3.21 \times 10^4\ J/mol$$

Reaction 2:

$$\Delta G° = -nFE° = -(2)(96{,}485\ \cancel{C}/mol)(-0.440\ J/\cancel{C}) = 8.49 \times 10^4\ J/mol$$

Then $\Delta G°$ for reaction 3, the one we want, is the sum of the $\Delta G°$ values for reactions 1 and 2:

$$3.21 \times 10^4\ J/mol + 8.49 \times 10^4\ J/mol = 1.17 \times 10^5\ J/mol$$

We can convert this to $E°$ from the relationship $\Delta G° = -nFE°$:

$$1.17 \times 10^5\ J/mol = -(2)(96{,}485\ C/mol)E°$$

$$E° = \frac{1.17 \times 10^5\ J/\cancel{mol}}{-(2)(96{,}485\ C/\cancel{mol})} = -0.606\ J/C = -0.606\ V$$

(c) The standard reduction potential for FeF_2 (-0.606 V) is more negative than that for Fe^{2+} (-0.440 V), telling us that the reduction of FeF_2 is the less favorable process. When FeF_2 is reduced, we not only reduce the Fe^{2+} but also break up the ionic solid. Because this additional energy must be overcome, the reduction of FeF_2 is less favorable than the reduction of Fe^{2+}.

Chapter Summary and Key Terms

OXIDATION STATES AND OXIDATION–REDUCTION REACTIONS (INTRODUCTION AND SECTION 20.1) In this chapter, we have focused on **electrochemistry**, the branch of chemistry that relates electricity and chemical reactions. Electrochemistry involves oxidation–reduction reactions, also called redox reactions. These reactions involve a change in the oxidation state of one or more elements. In every oxidation–reduction reaction one substance is oxidized (its oxidation state, or number, increases) and one substance is reduced (its oxidation state, or number, decreases). The substance that is oxidized is referred to as a **reducing agent**, or **reductant**, because it causes the reduction of some other substance. Similarly, the substance that is reduced is referred to as an **oxidizing agent**, or **oxidant**, because it causes the oxidation of some other substance.

BALANCING REDOX EQUATIONS (SECTION 20.2) An oxidization–reduction reaction can be balanced by dividing the reaction into two **half-reactions**, one for oxidation and one for reduction. A half-reaction is a balanced chemical equation that includes electrons. In oxidation half-reactions, the electrons are on the product (right) side of the equation. In reduction half-reactions, the electrons are on the reactant (left) side of the equation. Each half-reaction is balanced separately, and the two are brought together with proper coefficients to balance the electrons on each side of the equation, so the electrons cancel when the half-reactions are added.

VOLTAIC CELLS (SECTION 20.3) A **voltaic** (or **galvanic**) **cell** uses a spontaneous oxidation–reduction reaction to generate electricity. In a voltaic cell the oxidation and reduction half-reactions often occur in separate half-cells. Each half-cell has a solid surface called an electrode, where the half-reaction occurs. The electrode where oxidation occurs is called the **anode**, and the electrode where reduction occurs is called the **cathode**. The electrons released at the anode flow through an external circuit (where they do electrical work) to the cathode. Electrical neutrality in the solution is maintained by the migration of ions between the two half-cells through a device such as a salt bridge.

CELL POTENTIALS UNDER STANDARD CONDITIONS (SECTION 20.4) A voltaic cell generates an **electromotive force (emf)** that moves the electrons from the anode to the cathode through the external circuit. The origin of emf is a difference in the electrical potential energy of the two electrodes in the cell. The emf of a cell is called its **cell potential**, E_{cell} and is measured in volts ($1\,V = 1\,J/C$). The cell potential under standard conditions is called the **standard emf**, or the **standard cell potential**, and is denoted E°_{cell}.

A **standard reduction potential**, E°_{red}, can be assigned for an individual half-reaction. This is achieved by comparing the potential of the half-reaction to that of the **standard hydrogen electrode** (SHE), which is defined to have $E^\circ_{red} = 0\,V$.

The standard cell potential of a voltaic cell is the difference between the standard reduction potentials of the half-reactions that occur at the cathode and the anode:

$$E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode}).$$

The value of E°_{cell} is positive for a voltaic cell.

For a reduction half-reaction, E°_{red} is a measure of the tendency of the reduction to occur; the more positive the value for E°_{red}, the greater the tendency of the substance to be reduced. Substances that are easily reduced act as strong oxidizing agents; thus, E°_{red} provides a measure of the oxidizing strength of a substance. Substances that are strong oxidizing agents produce products that are weak reducing agents and vice versa.

FREE ENERGY AND REDOX REACTIONS (SECTION 20.5) The emf, E, is related to the change in the Gibbs free energy, $\Delta G = -nFE$, where n is the number of moles of electrons transferred during the redox process and F is the **Faraday constant**, defined as the quantity of electrical charge on one mole of electrons: $F = 96{,}485\,C/mol$. Because E is related to ΔG, the sign of E indicates whether a redox process is spontaneous: $E > 0$ indicates a spontaneous process, and $E < 0$ indicates a nonspontaneous one. Because ΔG is also related to the equilibrium constant for a reaction ($\Delta G^\circ = -RT\ln K$), we can relate E to K as well.

CELL POTENTIALS UNDER NONSTANDARD CONDITIONS (SECTION 20.6) The emf of a redox reaction varies with temperature and with the concentrations of reactants and products. The **Nernst equation** relates the emf under nonstandard conditions to the standard emf and the reaction quotient Q:

$$E = E^\circ - (RT/nF)\ln Q = E^\circ - (0.0592/n)\log Q$$

The factor 0.0592 is valid when $T = 298\,K$. A **concentration cell** is a voltaic cell in which the same half-reaction occurs at both the anode and the cathode but with different concentrations of reactants in each half-cell. At equilibrium, $Q = K$ and $E = 0$.

BATTERIES AND FUEL CELLS (SECTION 20.7) A **battery** is a self-contained electrochemical power source that contains one or more voltaic cells. Batteries are based on a variety of different redox reactions. Batteries that cannot be recharged are called **primary cells**, while those that can be recharged are called **secondary cells**. The common alkaline dry cell battery is an example of a primary cell battery. Lead–acid, nickel–cadmium, nickel–metal hydride, and lithium-ion batteries are examples of secondary cells. **Fuel cells** are voltaic cells that utilize redox reactions in which reactants such as H_2 have to be continuously supplied to the cell to generate voltage.

CORROSION (SECTION 20.8) Electrochemical principles help us understand **corrosion**, undesirable redox reactions in which a metal is attacked by some substance in its environment. The corrosion of iron into rust is caused by the presence of water and oxygen, and it is accelerated by the presence of electrolytes, such as road salt. The protection of a metal by putting it in contact with another metal that more readily undergoes oxidation is called **cathodic protection**. Galvanized iron, for example, is coated with a thin layer of zinc; because zinc is oxidized more readily than iron, the zinc serves as a sacrificial anode in the redox reaction.

ELECTROLYSIS (SECTION 20.9) An **electrolysis reaction**, which is carried out in an **electrolytic cell**, employs an external source of electricity to drive a nonspontaneous electrochemical reaction. The current-carrying medium within an electrolytic cell may be either a molten salt or an electrolyte solution. The electrodes in an electrolytic cell can be inert or active, meaning that the electrode can be involved in the electrolysis reaction. Active electrodes are important in electroplating and in metallurgical processes.

The quantity of substances formed during electrolysis can be calculated by considering the number of electrons involved in the redox reaction and the amount of electrical charge that passes into the cell. The amount of electrical charge is measured in coulombs and is related to the magnitude of the current and the time it flows ($1\,C = 1\,A\text{-}s$).

Learning Outcomes After studying this chapter, you should be able to:

- Identify oxidation, reduction, oxidizing agent, and reducing agent in a chemical equation. (Section 20.1) *Related Exercises: 20.2, 20.62, 20.65*
- Complete and balance redox equations using the method of half-reactions. (Section 20.2) *Related Exercises: 20.9, 20.68*
- Sketch a voltaic cell and identify its cathode, anode, and the directions in which electrons and ions move. (Section 20.3) *Related Exercises: 20.12, 20.70*
- Calculate standard emfs (cell potentials), E°_{cell}, from standard reduction potentials. (Section 20.4) *Related Exercises: 20.15, 20.16, 20.17, 20.75, 20.76*
- Use reduction potentials to predict whether a redox reaction is spontaneous. (Section 20.4) *Related Exercises: 20.21, 20.82*
- Relate E°_{cell} to ΔG° and equilibrium constants. (Section 20.5) *Related Exercises: 20.23, 20.83*
- Calculate emf under nonstandard conditions. (Section 20.6) *Related Exercises: 20.32, 20.91*
- Identify the components of common batteries. (Section 20.7) *Related Exercises: 20.36, 20.94*
- Describe the construction of a lithium-ion battery and explain how it works (Section 20.7) *Related Exercises: 20.39, 20.97*
- Describe the construction of a fuel cell and explain how it generates electrical energy. (Section 20.7) *Related Exercises: 20.40, 20.98*
- Explain how corrosion occurs and how it is prevented by cathodic protection. (Section 20.8) *Related Exercises: 20.42, 20.99*
- Describe the reactions in electrolytic cells. (Section 20.9) *Related Exercises: 20.46, 20.102*
- Relate amounts of products and reactants in redox reactions to electrical charge. (Section 20.9) *Related Exercises: 20.48, 20.104*

Key Equations

- $E^\circ_{cell} = E^\circ_{red}\,(\text{cathode}) - E^\circ_{red}\,(\text{anode})$ [20.8] Relating standard emf to standard reduction potentials of the reduction (cathode) and oxidation (anode) half-reactions
- $\Delta G = -nFE$ [20.11] Relating free-energy change and emf
- $E = E^\circ - \dfrac{0.0592\ \text{V}}{n}\log Q \quad (\text{at } 298\ \text{K})$ [20.18] The Nernst equation, expressing the effect of concentration on cell potential

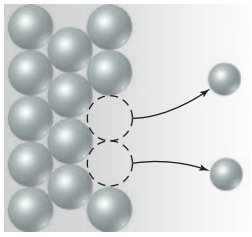
Exercises

Visualizing Concepts

20.50 In the Brønsted–Lowry concept of acids and bases, acid–base reactions are viewed as proton-transfer reactions. The stronger the acid, the weaker is its conjugate base. If we were to think of redox reactions in a similar way, what particle would be analogous to the proton? Would strong oxidizing agents be analogous to strong acids or strong bases? [Sections 20.1 and 20.2]

20.51 You may have heard that "antioxidants" are good for your health. Is an "antioxidant" an oxidizing agent or a reducing agent? [Sections 20.1 and 20.2]

20.52 The diagram that follows represents a molecular view of a process occurring at an electrode in a voltaic cell.



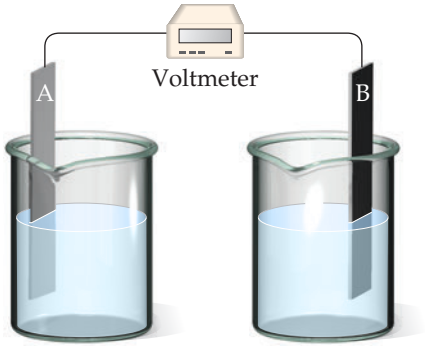
(**a**) Does the process represent oxidation or reduction? (**b**) Is the electrode the anode or cathode? (**c**) Why are the atoms in the electrode represented by larger spheres than those in the solution? [Section 20.3]

20.53 Assume that you want to construct a voltaic cell that uses the following half-reactions:

$$A^{2+}(aq) + 2\,e^- \longrightarrow A(s) \qquad E^\circ_{red} = -0.10\ \text{V}$$

$$B^{2+}(aq) + 2\,e^- \longrightarrow B(s) \qquad E^\circ_{red} = -1.10\ \text{V}$$

You begin with the incomplete cell pictured here in which the electrodes are immersed in water.



(**a**) What additions must you make to the cell for it to generate a standard emf? (**b**) Which electrode functions as the cathode? (**c**) Which direction do electrons move through the external circuit? (**d**) What voltage will the cell generate under standard conditions? [Sections 20.3 and 20.4]

20.54 For a spontaneous reaction $A(aq) + B(aq) \longrightarrow A^-(aq) + B^+(aq)$, answer the following questions:

(**a**) If you made a voltaic cell out of this reaction, what half-reaction would be occurring at the cathode, and what half-reaction would be occurring at the anode?

(**b**) Which half-reaction from (a) is higher in potential energy?

(**c**) What is the sign of E°_{cell}? [Section 20.3]

20.55 Consider the following table of standard electrode potentials for a series of hypothetical reactions in aqueous solution:

Reduction Half-Reaction	$E°$(V)
$A^+(aq) + e^- \longrightarrow A(s)$	1.33
$B^{2+}(aq) + 2\,e^- \longrightarrow B(s)$	0.87
$C^{3+}(aq) + e^- \longrightarrow C^{2+}(aq)$	−0.12
$D^{3+}(aq) + 3\,e^- \longrightarrow D(s)$	−1.59

(**a**) Which substance is the strongest oxidizing agent? Which is weakest?

(**b**) Which substance is the strongest reducing agent? Which is weakest?

(**c**) Which substance(s) can oxidize C^{2+}? [Sections 20.4 and 20.5]

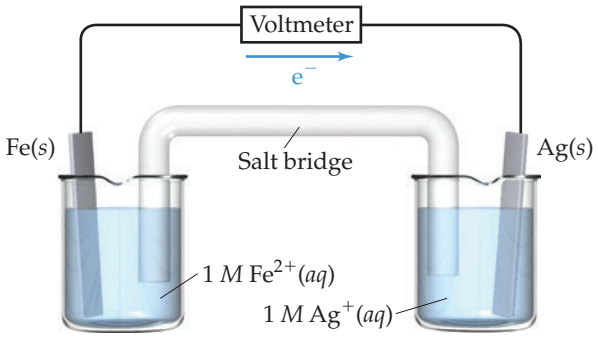
20.56 Consider a redox reaction for which $E°$ is a negative number.

(**a**) What is the sign of $\Delta G°$ for the reaction?

(**b**) Will the equilibrium constant for the reaction be larger or smaller than 1?

(**c**) Can an electrochemical cell based on this reaction accomplish work on its surroundings? [Section 20.5]

20.57 Consider the following voltaic cell:



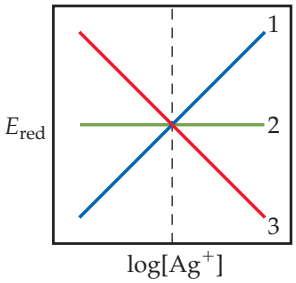
(**a**) Which electrode is the cathode?

(**b**) What is the standard emf generated by this cell?

(**c**) What is the change in the cell voltage when the ion concentrations in the cathode half-cell are increased by a factor of 10?

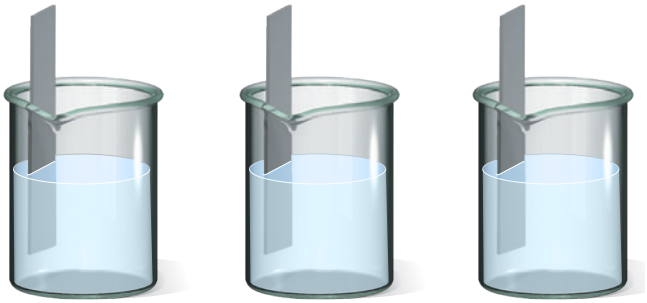
(**d**) What is the change in the cell voltage when the ion concentrations in the anode half-cell are increased by a factor of 10? [Sections 20.4 and 20.6]

20.58 Consider the half-reaction $Ag^+(aq) + e^- \longrightarrow Ag(s)$. (**a**) Which of the lines in the following diagram indicates how the reduction potential varies with the concentration of $Ag^+(aq)$? (**b**) What is the value of E_{red} when $\log[Ag^+] = 0$? [Section 20.6]



20.59 The electrodes in a silver oxide battery are silver oxide (Ag_2O) and zinc. (**a**) Which electrode acts as the anode? (**b**) Which battery do you think has an energy density most similar to the silver oxide battery: a Li-ion battery, a nickel–cadmium battery, or a lead–acid battery? [Section 20.7]

20.60 Bars of iron are put into each of the three beakers as shown here. In which beaker—A, B, or C—would you expect the iron to show the most corrosion? [Section 20.8]

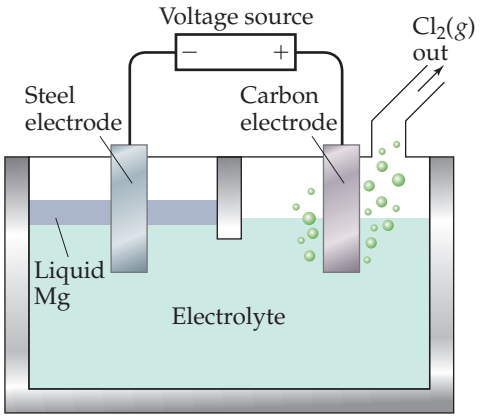


Beaker A
Pure water
pH = 7.0

Beaker B
Dilute HCl(*aq*) solution
pH = 4.0

Beaker C
Dilute NaOH(*aq*) solution
pH = 10.0

20.61 Magnesium, the element, is produced commercially by electrolysis from a molten salt (the "electrolyte") using a cell similar to the one shown here. (**a**) What is the most common oxidation number for Mg when it is part of a salt? (**b**) Chlorine gas is evolved as voltage is applied in the cell. Knowing this, identify the electrolyte. (**c**) Recall that in an electrolytic cell the anode is given the + sign and the cathode is given the – sign, which is the opposite of what we see in batteries. What half-reaction occurs at the anode in this electrolytic cell? (**d**) What half-reaction occurs at the cathode? [Section 20.9]



Oxidation–Reduction Reactions (Section 20.1)

20.62 (**a**) What is meant by the term *oxidation*? (**b**) On which side of an oxidation half-reaction do the electrons appear? (**c**) What is meant by the term *oxidant*? (**d**) What is meant by the term *oxidizing agent*?

20.63 Indicate whether each of the following statements is true or false:

(**a**) If something is oxidized, it is formally losing electrons.

(**b**) For the reaction $Fe^{3+}(aq) + Co^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Co^{3+}(aq)$, $Fe^{3+}(aq)$ is the reducing agent and $Co^{2+}(aq)$ is the oxidizing agent.

(**c**) If there are no changes in the oxidation state of the reactants or products of a particular reaction, that reaction is not a redox reaction.

20.64 For each of the following balanced oxidation–reduction reactions, (**i**) identify the oxidation numbers for all the elements in the reactants and products and (**ii**) state the total number of electrons transferred in each reaction.

(**a**) $14\,H^+(aq) + 2\,Mn^{2+}(aq) + 5\,NaBiO_3(s) \longrightarrow 7\,H_2O(l) + 2\,MnO_4^- + 5\,Bi^{3+}(aq) + 5\,Na^+(aq)$

(**b**) $2\,KMnO_4(aq) + 3\,Na_2SO_3(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,Na_2SO_4(aq) + 2\,KOH(aq)$

(**c**) $Cu(s) + 2\,AgNO_3(aq) \longrightarrow 2\,Ag(s) + Cu(NO_3)_2(aq)$

20.65 Indicate whether the following balanced equations involve oxidation–reduction. If they do, identify the elements that undergo changes in oxidation number.

(**a**) $2\,NO_2(g) + H_2O_2(aq) \longrightarrow 2\,HNO_3(aq)$

(**b**) $FeS(s) + 2\,HCl(aq) \longrightarrow FeCl_2(aq) + H_2S(g)$

(**c**) $Fe(s) + 2\,HNO_3(aq) \longrightarrow H_2O(l) + 2\,NO_2(g) + FeO(s)$

Balancing Oxidation–Reduction Reactions (Section 20.2)

20.66 The purification process of silicon involves the reaction of silicon tetrachloride vapor ($SiCl_4(g)$) with hydrogen to 1250 °C to form solid silicon and hydrogen chloride. (**a**) Write a balanced equation for this reaction. (**b**) What is being oxidized, and what is being reduced? (**c**) Which substance is the reductant, and which is the oxidant?

20.67 Complete and balance the following half-reactions. In each case, indicate whether the half-reaction is an oxidation or a reduction.

(**a**) $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$ (acidic solution)

(**b**) $Mn^{2+}(aq) \longrightarrow MnO_4^-(aq)$ (acidic solution)

(**c**) $I_2(s) \longrightarrow IO_3^-(aq)$ (acidic solution)

(**d**) $S(s)(aq) \longrightarrow H_2S(g)$ (acidic solution)

(**e**) $NO_3^-(aq) \longrightarrow NO_2^-(aq)$ (basic solution)

(**f**) $H_2O_2(aq) \longrightarrow OH^-(aq)$ (basic solution)

20.68 Complete and balance the following equations, and identify the oxidizing and reducing agents:

(**a**) $Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + IO_3^-(aq)$ (acidic solution)

(**b**) $MnO_4^-(aq) + CH_3OH(aq) \longrightarrow Mn^{2+}(aq) + HCOOH(aq)$ (acidic solution)

(**c**) $I_2(s) + OCl^-(aq) \longrightarrow IO_3^-(aq) + Cl^-(aq)$ (acidic solution)

(**d**) $As_2O_3(s) + NO_3^-(aq) \longrightarrow H_3AsO_4(aq) + N_2O_3(aq)$ (acidic solution)

(**e**) $MnO_4^-(aq) + Br^-(aq) \longrightarrow MnO_2(s) + BrO_3^-(aq)$ (basic solution)

(**f**) $Pb(OH)_4^{2-}(aq) + ClO^-(aq) \longrightarrow PbO_2(s) + Cl^-(aq)$ (basic solution)

Voltaic Cells (Section 20.3)

20.69 Indicate whether each statement is true or false: (**a**) The cathode is the electrode at which oxidation takes place. (**b**) A galvanic cell is another name for a voltaic cell. (**c**) Electrons flow spontaneously from anode to cathode in a voltaic cell.

20.70 A voltaic cell similar to that shown in Figure 20.5 is constructed. One electrode half-cell consists of a magnesium strip placed in a solution of $MgCl_2$, and the other has a nickel strip placed in a solution of $NiCl_2$. The overall cell reaction is

$$Mg(s) + Ni^{2+}(aq) \longrightarrow Ni(s) + Mg^{2+}(aq)$$

(**a**) What is being oxidized, and what is being reduced? (**b**) Write the half-reactions that occur in the two half-cells. (**c**) Which electrode is the anode, and which is the cathode? (**d**) Indicate the signs of the electrodes. (**e**) Do electrons flow from the magnesium electrode to the nickel electrode or from the nickel to the magnesium? (**f**) In which directions do the cations and anions migrate through the solution?

Cell Potentials under Standard Conditions (Section 20.4)

20.71 (**a**) What is the definition of the *volt*? (**b**) Do all voltaic cells produce a positive cell potential?

20.72 (**a**) Write the half-reaction that occurs at an oxygen electrode in acidic aqueous solution when it serves as the cathode of a voltaic cell. (**b**) Write the half-reaction that occurs at an oxygen electrode in acidic aqueous solution when it serves as the anode of a voltaic cell. (**c**) What is standard about the standard oxygen electrode?

20.73 (**a**) What conditions must be met for a reduction potential to be a *standard reduction potential*? (**b**) What is the standard reduction potential of a standard hydrogen electrode? (**c**) Why is it impossible to measure the standard reduction potential of a single half-reaction?

20.74 A voltaic cell that uses the reaction

$$Tl^{3+}(aq) + 2\,Cr^{2+}(aq) \longrightarrow Tl^+(aq) + 2\,Cr^{3+}(aq)$$

has a measured standard cell potential of +1.19 V. (**a**) Write the two half-cell reactions. (**b**) By using data from Appendix E, determine E°_{red} for the reduction of $Tl^{3+}(aq)$ to $Tl^+(aq)$. (**c**) Sketch the voltaic cell, label the anode and cathode, and indicate the direction of electron flow.

20.75 Using standard reduction potentials (Appendix E), calculate the standard emf for each of the following reactions:

(**a**) $Cl_2(g) + 2\,I^-(aq) \longrightarrow 2\,Cl^-(aq) + I_2(s)$

(**b**) $Ni(s) + 2\,Ce^{4+}(aq) \longrightarrow Ni^{2+}(aq) + 2\,Ce^{3+}(aq)$

(**c**) $Fe(s) + 2\,Fe^{3+}(aq) \longrightarrow 3\,Fe^{2+}(aq)$

(**d**) $2\,NO_3^-(aq) + 8\,H^+(aq) + 3\,Cu(s) \longrightarrow 2\,NO(g) + 4\,H_2O(l) + 3\,Cu^{2+}(aq)$

20.76 The standard reduction potentials of the following half-reactions are given in Appendix E:

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$$
$$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$$
$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$$
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

(**a**) Determine which combination of these half-cell reactions leads to the cell reaction with the largest positive cell potential and calculate the value. (**b**) Determine which combination of these half-cell reactions leads to the cell reaction with the smallest positive cell potential and calculate the value.

20.77 A 1 *M* solution of $AgNO_3$ is placed in a beaker with a strip of Ag metal. A 1 *M* solution of $Cu(NO_3)_2$ is placed in a second beaker with a strip of Cu metal. A salt bridge connects the two beakers, and wires to a voltmeter link the two metal electrodes. (**a**) Which electrode serves as the anode, and which as the cathode? (**b**) Which electrode gains mass, and which loses mass as the cell reaction proceeds? (**c**) Write the equation for the overall cell reaction. (**d**) What is the emf generated by the cell under standard conditions?

Strengths of Oxidizing and Reducing Agents (Section 20.4)

20.78 From each of the following pairs of substances, use data in Appendix E to choose the one that is the stronger reducing agent:

(**a**) Al(*s*) or Mg(*s*)

(**b**) Fe(*s*) or Ni(*s*)

(**c**) $H_2(g$, acidic solution) or Sn(*s*)

(**d**) $I^-(aq)$ or $Br^-(aq)$

20.79 By using the data in Appendix E, determine whether each of the following substances is likely to serve as an oxidant or a reductant: (**a**) $H_2(g$, basic), (**b**) $Cr_2O_7^{2-}(aq$, acidic), (**c**) $F_2(g)$, (**d**) Li(*s*).

20.80 (**a**) Assuming standard conditions, arrange the following in order of increasing strength as oxidizing agents in acidic solution: $MnO_4^-(aq)$, $O_3(g)$, $HSO_4^-(aq)$, $O_2(g)$, $HClO(aq)$. (**b**) Arrange the following in order of increasing strength as reducing agents in basic solution: $Cr(OH)_3(s)$, Fe(*s*), Ca(*s*), $H_2(g)$, Mn(*s*).

20.81 Based on the data in Appendix E, (**a**) which of the following is the strongest oxidizing agent, and which is the weakest in acidic solution: Br_2, H_2O_2, Zn, $Cr_2O_7^{2-}$? (**b**) Which of the following is the strongest reducing agent, and which is the weakest in acidic solution: F^-, Zn, $N_2H_5^+$, I_2, NO?

20.82 The standard reduction potential of $Eu^{2+}(aq)$ is −0.43 V. Using Appendix E, which of the following substances is capable of reducing $Eu^{3+}(aq)$ to $Eu^{2+}(aq)$ under standard conditions: Al, Co, H_2O_2, $N_2H_5^+$, $H_2C_2O_4$?

Free Energy and Redox Reactions (Section 20.5)

20.83 Given the following reduction half-reactions:

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq) \quad E^\circ_{red} = +0.77\ V$$

$$S_2O_6^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2SO_3(aq) \quad E^\circ_{red} = +0.60\ V$$

$$N_2O(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow N_2(g) + H_2O(l) \quad E^\circ_{red} = -1.77\ V$$

$$VO_2^+(aq) + 2\,H^+(aq) + e^- \longrightarrow VO^{2+} + H_2O(l) \quad E^\circ_{red} = +1.00\ V$$

(**a**) Write balanced chemical equations for the oxidation of $Fe^{2+}(aq)$ by $S_2O_6^{2-}(aq)$, by $N_2O(aq)$, and by $VO_2^+(aq)$. (**b**) Calculate ΔG° for each reaction at 298 K. (**c**) Calculate the equilibrium constant *K* for each reaction at 298 K.

20.84 If the equilibrium constant for a one-electron redox reaction at 298 K is 2.2×10^{-5}, calculate the corresponding ΔG° and E°.

20.85 Using the standard reduction potentials listed in Appendix E, calculate the equilibrium constant for each of the following reactions at 298 K:

(**a**) $Fe(s) + Ni^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Ni(s)$

(**b**) $Co(s) + 2\,H^+(aq) \longrightarrow Co^{2+}(aq) + H_2(g)$

(**c**) $10\,Br^-(aq) + 2\,MnO_4^-(aq) + 16\,H^+(aq) \longrightarrow 2\,Mn^{2+}(aq) + 8\,H_2O(l) + 5\,Br_2(l)$

20.86 A cell has a standard cell potential of +0.257 V at 298 K. What is the value of the equilibrium constant for the reaction (**a**) if $n = 1$? (**b**) if $n = 2$? (**c**) if $n = 3$?

20.87 A voltaic cell is based on the reaction

$$Sn(s) + I_2(s) \longrightarrow Sn^{2+}(aq) + 2\,I^-(aq)$$

Under standard conditions, what is the maximum electrical work, in joules, that the cell can accomplish if 75.0 g of Sn is consumed?

Cell EMF under Nonstandard Conditions (Section 20.6)

20.88 (**a**) In the Nernst equation, what is the numerical value of the reaction quotient, *Q*, under standard conditions? (**b**) Can the Nernst equation be used at temperatures other than room temperature?

20.89 What is the effect on the emf of the cell shown in Figure 20.5, which has the overall reaction $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$, for each of the following changes? (**a**) Zinc chloride is added to the anode half-cell. (**b**) Copper chloride is added to the anode half-cell. (**c**) The surface area of the anode is cut to half. (**d**) The cell operates for one hour.

20.90 A voltaic cell is constructed that uses the following reaction and operates at 298 K:

$$Zn(s) + Ni^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Ni(s)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Ni^{2+}] = 3.00\ M$ and $[Zn^{2+}] = 0.100\ M$? (**c**) What is the emf of the cell when $[Ni^{2+}] = 0.200\ M$ and $[Zn^{2+}] = 0.900\ M$?

20.91 A voltaic cell utilizes the following reaction:

$$4\,Fe^{2+}(aq) + O_2(g) + 4\,H^+(aq) \longrightarrow 4\,Fe^{3+}(aq) + 2\,H_2O(l)$$

(**a**) What is the emf of this cell under standard conditions? (**b**) What is the emf of this cell when $[Fe^{2+}] = 1.3\ M$, $[Fe^{3+}] = 0.010\ M$, $P_{O_2} = 50.0$ kPa, and the pH of the solution in the cathode half-cell is 3.50?

20.92 A voltaic cell is constructed with two Cu^{2+} − Cu electrodes. The two half-cells have $[Cu^{2+}] = 0.100\ M$ and $[Cu^{2+}] = 1.00 \times 10^{-4}\ M$, respectively. (**a**) Which electrode is the cathode of the cell? (**b**) What is the standard emf of the cell? (**c**) What is the cell emf for the concentrations given? (**d**) For each electrode, predict whether $[Cu^{2+}]$ will increase, decrease, or stay the same as the cell operates.

20.93 The cell in Figure 20.9 could be used to provide a measure of the pH in the cathode half-cell. Calculate the pH of the cathode half-cell solution if the cell emf at 298 K is measured to be +0.663 V when $[Zn^{2+}] = 0.10\ M$ and $P_{H_2} = 101.3$ kPa.

Batteries and Fuel Cells (Section 20.7)

20.94 During a period of discharge of a lead–acid battery, 300 g of $PbO_2(s)$ from the cathode is converted into $PbSO_4(s)$. (**a**) What mass of Pb(*s*) is oxidized at the anode during this same period? (**b**) How many coulombs of electrical charge are transferred from Pb to PbO_2?

20.95 Heart pacemakers are often powered by lithium–silver chromate "button" batteries. The overall cell reaction is

$$2\,Li(s) + Ag_2CrO_4(s) \longrightarrow Li_2CrO_4(s) + 2\,Ag(s)$$

(**a**) Lithium metal is the reactant at one of the electrodes of the battery. Is it the anode or the cathode? (**b**) Choose the two half-reactions from Appendix E that *most closely approximate* the reactions that occur in the battery. What standard emf would be generated by a voltaic cell based on these half-reactions? (**c**) The battery generates an emf of +3.5 V. How close is this value to the one calculated in part (b)? (**d**) Calculate the emf that would be generated at body temperature, 37 °C. How does this compare to the emf you calculated in part (b)?

20.96 (**a**) Suppose that an alkaline battery was manufactured using cadmium metal rather than zinc. What effect would this have on the cell emf? (**b**) What environmental advantage is provided by the use of nickel–metal hydride batteries over nickel–cadmium batteries?

20.97 In a Li-ion battery the composition of the cathode is $LiCoO_2$ when completely discharged. On charging, approximately 50% of the Li^+ ions can be extracted from the cathode and transported to the graphite anode where they intercalate between the layers. (**a**) What is the composition of the cathode when the battery is fully charged? (**b**) If the $LiCoO_2$ cathode has a mass of 10 g (when fully discharged), how many coulombs of electricity can be delivered on completely discharging a fully charged battery?

20.98 (**a**) Which reaction is spontaneous in the hydrogen fuel cell: hydrogen gas plus oxygen gas makes water, or water makes hydrogen gas plus oxygen gas? (**b**) Using the standard reduction potentials in Appendix E, calculate the standard voltage generated by the hydrogen fuel cell in acidic solution.

Corrosion (Section 20.8)

20.99 (**a**) Based on standard reduction potentials, would you expect copper metal to oxidize under standard conditions in the presence of oxygen and hydrogen ions? (**b**) When the Statue of Liberty was refurbished, Teflon spacers were placed between the iron skeleton and the copper metal on the surface of the statue. What role do these spacers play?

20.100 (**a**) Aluminum metal is used as a sacrificial anode to protect offshore pipelines in salt water from corrosion. Why is the aluminum referred to as a "sacrificial anode"? (**b**) Looking in Appendix E, suggest what metal the pipelines could be made from in order for aluminum to be successful as a sacrificial anode.

20.101 Iron corrodes to produce rust, Fe_2O_3, but other corrosion products that can form are Fe(O)(OH), iron oxyhydroxide, and magnetite, Fe_3O_4. (**a**) What is the oxidation number of Fe in iron oxyhydroxide, assuming oxygen's oxidation number is −2? (**b**) The oxidation number for Fe in magnetite was controversial for a long time. If we assume that oxygen's oxidation number is −2, and Fe has a unique oxidation number, what is the oxidation number for Fe in magnetite? (**c**) It turns out that there are two different kinds of Fe in magnetite that have different oxidation numbers. Suggest what these oxidation numbers are and what their relative stoichiometry must be, assuming oxygen's oxidation number is −2.

Electrolysis (Section 20.9)

20.102 (**a**) What is *electrolysis*? (**b**) Are electrolysis reactions thermodynamically spontaneous? (**c**) What process occurs at the anode in the electrolysis of molten NaCl? (**d**) Why is sodium metal not obtained when an aqueous solution of NaCl undergoes electrolysis?

20.103 (**a**) A $Cr^{3+}(aq)$ solution is electrolyzed, using a current of 7.60 A. What mass of $Cr(s)$ is plated out after 2.00 days? (**b**) What amperage is required to plate out 0.250 mol Cr from a Cr^{3+} solution in a period of 8.00 h?

20.104 (**a**) Calculate the mass of Li formed by electrolysis of molten LiCl by a current of 7.5×10^4 A flowing for a period of 24 h. Assume the electrolytic cell is 85% efficient. (**b**) What is the minimum voltage required to drive the reaction?

20.105 Metallic gold is collected from below the anode when a mixture of copper and gold metals is refined by electrolysis. Explain this behavior.

Additional Exercises

20.106 A disproportionation reaction is an oxidation–reduction reaction in which the same substance is oxidized and reduced. Complete and balance the following disproportionation reactions:

(**a**) $Fe^{2+}(aq) \longrightarrow Fe(s) + Fe^{3+}(aq)$

(**b**) $Br_2(l) \longrightarrow Br^-(aq) + BrO_3^-(aq)$ (acidic solution)

(**c**) $Cr^{3+}(aq) \longrightarrow Cr_2O_7^{2-}(aq) + Cr(s)$ (acidic solution)

(**d**) $NO(g) \longrightarrow N_2(g) + NO_3^-(aq)$ (acidic solution)

20.107 A common shorthand way to represent a voltaic cell is

anode|anode solution||cathode solution|cathode

A double vertical line represents a salt bridge or a porous barrier. A single vertical line represents a change in phase, such as from solid to solution. (**a**) Write the half-reactions and overall cell reaction represented by $Fe|Fe^{2+}||Ag^+|Ag$; calculate the standard cell emf using data in Appendix E. (**b**) Write the half-reactions and overall cell reaction represented by $Zn|Zn^{2+}||H^+|H_2$; calculate the standard cell emf using data in Appendix E and use Pt for the hydrogen electrode. (**c**) Using the notation just described, represent a cell based on the following reaction:

$$ClO_3^-(aq) + 3\,Cu(s) + 6\,H^+(aq) \longrightarrow Cl^-(aq) + 3\,Cu^{2+}(aq) + 3\,H_2O(l)$$

Pt is used as an inert electrode in contact with the ClO_3^- and Cl^-. Calculate the standard cell emf given: $ClO_3^-(aq) + 6\,H^+(aq) + 6\,e^- \longrightarrow Cl^-(aq) + 3\,H_2O(l)$; $E° = 1.45$ V.

20.108 Predict whether the following reactions will be spontaneous in acidic solution under standard conditions: (**a**) oxidation of Cu to Cu^{2+} by I_2 (to form I^-), (**b**) reduction of Fe^{2+} to Fe by H_2 (to form H^+), (**c**) reduction of I_2 to I^- by H_2O_2, (**d**) reduction of Ni^{2+} to Ni by Sn^{2+} (to form Sn^{4+}).

20.109 Gold exists in two common positive oxidation states, +1 and +3. The standard reduction potentials for these oxidation states are

$$Au^+(aq) + e^- \longrightarrow Au(s) \quad E°_{red} = +1.69\text{ V}$$
$$Au^{3+}(aq) + 3\,e^- \longrightarrow Au(s) \quad E°_{red} = +1.50\text{ V}$$

(**a**) Can you use these data to explain why gold does not tarnish in the air? (**b**) Suggest several substances that should be strong enough oxidizing agents to oxidize gold metal. (**c**) Miners obtain gold by soaking gold-containing ores in an aqueous solution of sodium cyanide. A very soluble complex ion of gold forms in the aqueous solution because of the redox reaction

$$4\,Au(s) + 8\,NaCN(aq) + 2\,H_2O(l) + O_2(g) \longrightarrow 4\,Na[Au(CN)_2](aq) + 4\,NaOH(aq)$$

What is being oxidized, and what is being reduced in this reaction? (**d**) Gold miners then react the basic aqueous product solution from part (c) with Zn dust to get gold metal. Write a balanced redox reaction for this process. What is being oxidized, and what is being reduced?

20.110 A voltaic cell is constructed from an $Cd^{2+}(aq)$ – $Cd(s)$ half-cell and an $Ag^{+}(aq)$ – $Ag(s)$ half-cell. The initial concentration of $Cd^{2+}(aq)$ in the $Cd^{2+}(aq)$ – $Cd(s)$ half-cell is $[Cd^{2+}] = 0.0200\,M$. The initial cell voltage is +1.102 V. (**a**) By using data in Appendix E, calculate the standard emf of this voltaic cell. (**b**) Will the concentration of $Cd^{2+}(aq)$ increase or decrease as the cell operates? (**c**) What is the initial concentration of $Ag^{+}(aq)$ in the $Ag^{+}(aq)$ – $Ag(s)$ half-cell?

20.111 A voltaic cell is constructed that uses the following half-cell reactions:

$$Ag^{+}(aq) + 2\,e^{-} \longrightarrow Ag(s)$$
$$I_2(s) + 2\,e^{-} \longrightarrow 2\,I^{-}(aq)$$

The cell is operated at 298 K with $[Ag^{+}] = 0.15\,M$ and $[I^{-}] = 0.035\,M$. (**a**) Determine E for the cell at these concentrations. (**b**) Which electrode is the anode of the cell? (**c**) Is the answer to part (b) the same as it would be if the cell were operated under standard conditions? (**d**) With $[Ag^{+}]$ equal to 0.15 M, at what concentration of I^{-} would the cell have zero potential?

20.112 Using data from Appendix E, calculate the equilibrium constant for the disproportionation of the iron(II) ion at room temperature:

$$3\,Fe^{2+}(aq) \longrightarrow Fe(s) + 2\,Fe^{3+}(aq)$$

20.113 (**a**) Write the reactions for the discharge and charge of a nickel–cadmium (nicad) rechargeable battery. (**b**) Given the following reduction potentials, calculate the standard emf of the cell:

$$Cd(OH)_2(s) + 2\,e^{-} \longrightarrow Cd(s) + 2\,OH^{-}(aq) \qquad E^{\circ}_{red} = -0.76\ V$$
$$NiO(OH)(s) + H_2O(l) + e^{-} \longrightarrow Ni(OH)_2(s) + OH^{-}(aq) \qquad E^{\circ}_{red} = +0.49\ V$$

(**c**) A typical nicad voltaic cell generates an emf of +1.30 V. Why is there a difference between this value and the one you calculated in part (b)? (**d**) Calculate the equilibrium constant for the overall nicad reaction based on this typical emf value.

20.114 The capacity of batteries such as a lithium-ion battery is expressed in units of milliamp-hours (mAh). A typical battery of this type yields a nominal capacity of 2000 mAh. (**a**) What quantity of interest to the consumer is being expressed by the units of mAh? (**b**) The starting voltage of a fresh lithium-ion battery is 3.60 V. The voltage decreases during discharge and is 3.20 V when the battery has delivered its rated capacity. If we assume that the voltage declines linearly as current is withdrawn, estimate the total maximum electrical work the battery could perform during discharge.

20.115 Disulfides are compounds that have S—S bonds, like peroxides have O—O bonds. Thiols are organic compounds that have the general formula R—SH, where R is a generic hydrocarbon. The SH^{-} ion is the sulfur counterpart of hydroxide, OH^{-}. Two thiols can react to make a disulfide, R—S—S—R. (**a**) What is the oxidation state of sulfur in a thiol? (**b**) What is the oxidation state of sulfur in a disulfide? (**c**) If you react two thiols to make a disulfide, are you oxidizing or reducing the thiols? (**d**) If you wanted to convert a disulfide to two thiols, should you add a reducing agent or oxidizing agent to the solution? (**e**) Suggest what happens to the H's in the thiols when they form disulfides.

20.116 (**a**) How many coulombs are required to plate a layer of chromium metal 0.15 mm thick on an auto bumper with a total area of 0.40 m^2 from a solution containing CrO_4^{2-}? The density of chromium metal is 7.20 g/cm^3. (**b**) What current flow is required for this electroplating if the bumper is to be plated in 20.0 s? (**c**) If the external source has an emf of +5.5 V and the electrolytic cell is 60% efficient, how much electrical energy is expended to electroplate the bumper?

20.117 Magnesium is obtained by electrolysis of molten $MgCl_2$. (**a**) Why is an aqueous solution of $MgCl_2$ not used in the electrolysis? (**b**) Several cells are connected in parallel by very large copper bars that convey current to the cells. Assuming that the cells are 96% efficient in producing the desired products in electrolysis, what mass of Mg is formed by passing a current of 97,000 A for a period of 24 h?

20.118 Calculate the number of kilowatt-hours of electricity required to produce 500 kg of aluminum by electrolysis of Al^{3+} if the applied voltage is 5.00 V and the process is 50% efficient.

20.119 Some years ago a unique proposal was made to raise the *Titanic*. The plan involved placing pontoons within the ship using a surface-controlled submarine-type vessel. The pontoons would contain cathodes and would be filled with hydrogen gas formed by the electrolysis of water. It has been estimated that it would require about 7×10^8 mol of H_2 to provide the buoyancy to lift the ship (*J. Chem. Educ.*, 1973, Vol. 50, 61). (**a**) How many coulombs of electrical charge would be required? (**b**) What is the minimum voltage required to generate H_2 and O_2 if the pressure on the gases at the depth of the wreckage (3 km) is 30 MPa? (**c**) What is the minimum electrical energy required to raise the *Titanic* by electrolysis? (**d**) What is the minimum cost of the electrical energy required to generate the necessary H_2 if the electricity costs 85 cents per kilowatt-hour to generate at the site?

Integrative Exercises

20.120 The Haber process is the principal industrial route for converting nitrogen into ammonia:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

(**a**) What is being oxidized, and what is being reduced? (**b**) Using the thermodynamic data in Appendix C, calculate the equilibrium constant for the process at room temperature. (**c**) Calculate the standard emf of the Haber process at room temperature.

20.121 In a galvanic cell the cathode is an $Ag^{+}(1.00\,M)/Ag(s)$ half-cell. The anode is a standard hydrogen electrode immersed in a buffer solution containing 0.10 M benzoic acid (C_6H_5COOH) and 0.050 M sodium benzoate ($C_6H_5COO^{-}Na^{+}$). The measured cell voltage is 1.030 V. What is the pK_a of benzoic acid?

20.122 Aqueous solutions of ammonia (NH_3) and bleach (active ingredient NaOCl) are sold as cleaning fluids, but bottles of both of them warn: "Never mix ammonia and bleach, as toxic gases may be produced." One of the toxic gases that can be produced is chloroamine, NH_2Cl. (**a**) What is the oxidation number of chlorine in bleach? (**b**) What is the oxidation number of chlorine in chloramine? (**c**) Is Cl oxidized,

reduced, or neither, upon the conversion of bleach to chloramine? (**d**) Another toxic gas that can be produced is nitrogen trichloride, NCl_3. What is the oxidation number of N in nitrogen trichloride? (**e**) Is N oxidized, reduced, or neither, upon the conversion of ammonia to nitrogen trichloride?

20.123 A voltaic cell is based on $Cu^{2+}(aq)/Cu(s)$ and $Br_2(l)/Br^-(aq)$ half-cells. (**a**) What is the standard emf of the cell? (**b**) Which reaction occurs at the cathode and which at the anode of the cell? (**c**) Use $S°$ values in Appendix C and the relationship between cell potential and free-energy change to predict whether the standard cell potential increases or decreases when the temperature is raised above 25 °C. (The standard entropy of $Cu^{2+}(aq)$ is $S° = -99.6$ J/K)

20.124 Hydrogen gas has the potential for use as a clean fuel in reaction with oxygen. The relevant reaction is

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

Consider two possible ways of utilizing this reaction as an electrical energy source: (i) Hydrogen and oxygen gases are combusted and used to drive a generator, much as coal is currently used in the electric power industry; (ii) hydrogen and oxygen gases are used to generate electricity directly by using fuel cells that operate at 85 °C. (**a**) Use data in Appendix C to calculate $\Delta H°$ and $\Delta S°$ for the reaction. We will assume that these values do not change appreciably with temperature. (**b**) Based on the values from part (a), what trend would you expect for the magnitude of ΔG for the reaction as the temperature increases? (**c**) What is the significance of the change in the magnitude of ΔG with temperature with respect to the utility of hydrogen as a fuel? (**d**) Based on the analysis here, would it be more efficient to use the combustion method or the fuel-cell method to generate electrical energy from hydrogen?

20.125 Cytochrome, a complicated molecule that we will represent as $CyFe^{2+}$, reacts with the air we breathe to supply energy required to synthesize adenosine triphosphate (ATP). The body uses ATP as an energy source to drive other reactions (Section 19.7). At pH 7.0 the following reduction potentials pertain to this oxidation of $CyFe^{2+}$:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E°_{red} = +0.82\text{ V}$$

$$CyFe^{3+}(aq) + e^- \longrightarrow CyFe^{2+}(aq) \qquad E°_{red} = +0.22\text{ V}$$

(**a**) What is ΔG for the oxidation of $CyFe^{2+}$ by air? (**b**) If the synthesis of 1.00 mol of ATP from adenosine diphosphate (ADP) requires a ΔG of 37.7 kJ, how many moles of ATP are synthesized per mole of O_2?

20.126 The standard potential for the reduction of AgCl(*s*) is +0.222 V.

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$$

Using this value and the electrode potential for $Ag^+(aq)$, calculate the K_{sp} for AgCl.

20.127 The K_{sp} value for AgI(*s*) is 8.3×10^{-17}. By using this value together with an electrode potential from Appendix E, determine the value of the standard reduction potential for the reaction

$$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$$

20.128 A student designs an ammeter (device that measures electrical current) that is based on the electrolysis of water into hydrogen and oxygen gases. When electrical current of unknown magnitude is run through the device for 90 min, 32.5 mL of water-saturated $H_2(g)$ is collected. The temperature of the system is 20 °C, and the atmospheric pressure is 101.3 kPa. What is the magnitude of the average current in amperes?

Design an Experiment

You are asked to construct a voltaic cell that would simulate an alkaline battery by providing an electrical output of 1.50 V at the beginning of its discharge. After you complete it, your voltaic cell will be used to power an external device that draws a constant current of 0.50 amperes for 2.0 hours. You are given the following supplies: electrodes of each transition metal from manganese to zinc, the chloride salts of the +2 transition metal ions from Mn^{2+} to Zn^{2+} ($MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$), two 100 mL beakers, a salt bridge, a voltmeter, and wires to make electrical connections between the electrodes and the voltmeter. (**a**) Sketch out your voltaic cell labeling the metal used for each electrode and the type and concentration of the solutions in which each electrode is immersed. Be sure to describe how many grams of the salt are dissolved and the total volume of solution in each beaker. (**b**) What will be the concentrations of the transition metal ion in each solution at the end of the 2 h discharge? (**c**) What voltage will the cell register at the end of the discharge? (**d**) How long would your cell run before it died because the reactant in one of the half-cells was completely consumed? Assume the current stays constant throughout the discharge.

21

NUCLEAR CHEMISTRY

WHAT'S AHEAD

21.1 Radioactivity and Nuclear Equations

21.2 Patterns of Nuclear Stability

21.3 Rates of Radioactive Decay

21.4 Detection of Radioactivity

21.5 Energy Changes in Nuclear Reactions

21.6 Radiation in the Environment and Living Systems

21.1 Radioactivity and Nuclear Equations



All energy that fuels life on Earth comes ultimately from sunlight. Life on Earth could not exist without energy from the sun, but where does the sun get its energy? Stars, including our sun, use **nuclear reactions** that involve changes in atomic nuclei to generate their energy. For example, the sun produces energy by fusing hydrogen atoms to form helium, releasing vast amounts of energy in the process. The fusion of hydrogen

to form helium is the dominant nuclear reaction for most of a star's lifetime. Towards the end of its life, the hydrogen in the star's core is exhausted and the helium atoms fuse to form progressively heavier elements. A select few stars end their lives in dramatic supernova explosions. The nuclear reactions that occur when a star goes supernova are responsible for the existence of all naturally occurring elements heavier than nickel.

Nuclear chemistry is the study of nuclear reactions, with an emphasis on their uses in chemistry and their effects on biological systems. Nuclear chemistry affects our lives in many ways, particularly in energy and medical applications. In rad iation therapy, for example, gamma rays from a radioactive substance such as cobalt-60 are directed to cancerous tumors to destroy them. Positron emission tomography (PET) is one example of a medical diagnostic tool that relies on decay of a radioactive element injected into the body.

The emanation of gamma rays from cobalt-60 is an example of a *nuclear reaction*, in which a change in matter originates in the nucleus of an atom. When nuclei change spontaneously, emitting radiation, they are said to be **radioactive**.

Radioactivity is also used to help determine the mechanisms of chemical reactions, to trace the movement of atoms in biological systems and the environment and to date historical artifacts.

Nuclear reactions are also used to generate electricity. Roughly 15% of the electricity generated worldwide comes from nuclear power plants, though the percentage varies from one country to the next.

The use of nuclear energy for power generation is a controversial social and political issue because of the public's conceptions about the safety of nuclear reactors and, more importantly, the difficulty of disposing of nuclear reactor waste.

At the end of this section, you should be able to

- Write balanced nuclear equations

To understand nuclear reactions, we must review and develop some ideas introduced in Section 2.3:

- Two types of subatomic particles reside in the nucleus: *protons* and *neutrons*. We will refer to these particles as **nucleons**.
- All atoms of a given element have the same number of protons; this number is the element's *atomic number*.
- Atoms of a given element can have different numbers of neutrons, which means they can have different mass numbers. The *mass number* is the total number of nucleons in the nucleus.
- Atoms with the same atomic number but different mass numbers are known as *isotopes*.

The different isotopes of an element are distinguished by their mass numbers. For example, the three naturally occurring isotopes of uranium are uranium-234, uranium-235, and uranium-238, where the numerical suffixes represent the mass numbers. These isotopes are also written $^{234}_{92}\text{U}$, $^{235}_{92}\text{U}$, and $^{238}_{92}\text{U}$, where the superscript is the mass number and the subscript is the atomic number.*

Different isotopes of an element have different natural abundances. For example, 99.3% of naturally occurring uranium is uranium-238, 0.7% is uranium-235, and only a trace is uranium-234. Different isotopes of an element also have different stabilities. Indeed, the nuclear properties of any given isotope depend on the number of protons and neutrons in its nucleus.

A *nuclide* is a nucleus containing a specified number of protons and neutrons. Nuclides that are radioactive are called **radionuclides**, and atoms containing these nuclei are called **radioisotopes**.

*As noted in Section 2.3, we often do not explicitly write the atomic number of an isotope because the element symbol is specific to the atomic number. In studying nuclear chemistry, however, it is often useful to include the atomic number in order to help us keep track of changes in the nuclei.

Nuclear Equations

Most nuclei in nature are stable and remain intact indefinitely. Radionuclides, however, are unstable and spontaneously emit particles and electromagnetic radiation. Emission of radiation is one of the ways in which an unstable nucleus is transformed into a more stable one that has less energy. The emitted radiation is the carrier of the excess energy. Uranium-238, for example, is radioactive, undergoing a nuclear reaction emitting helium-4 nuclei. The helium-4 particles are known as **alpha (α) particles**, and a stream of them is called *alpha radiation*. When a $^{238}_{92}$U nucleus loses an alpha particle, the remaining fragment has an atomic number of 90 and a mass number of 234. The element with atomic number 90 is Th, thorium. Therefore, the products of uranium-238 decomposition are an alpha particle and a thorium-234 nucleus. We represent this reaction by the *nuclear equation*

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He} \qquad [21.1]$$

When a nucleus spontaneously decomposes in this way, it is said to be *radioactive* and to have decayed or to have undergone *radioactive decay*. Because an alpha particle is involved in this reaction, scientists also describe the process as **alpha decay** or **alpha emission**.

In Equation 21.1 the sum of the mass numbers is the same on both sides of the equation ($238 = 234 + 4$). Likewise, the sum of the atomic numbers on both sides of the equation is equal ($92 = 90 + 2$). Mass numbers and atomic numbers must be balanced in all nuclear equations.

The radioactive properties of the nucleus in an atom are independent of the chemical state of the atom. In writing nuclear equations, therefore, we are not concerned with the chemical form (element or compound) of the atom in which the nucleus resides.

Sample Exercise 21.1

Predicting the Product of a Nuclear Reaction



What product is formed when radium-226 undergoes alpha emission?

SOLUTION

Analyze We are asked to determine the nucleus that results when radium-226 loses an alpha particle.

Plan We can best do this by writing a balanced nuclear reaction for the process.

Solve The periodic table shows that radium has an atomic number of 88. The complete chemical symbol for radium-226 is therefore $^{226}_{88}$Ra. An alpha particle is a helium-4 nucleus, and so its symbol is $^{4}_{2}$He. The alpha particle is a product of the nuclear reaction, and so the equation is of the form

$$^{226}_{88}\text{Ra} \longrightarrow {}^{A}_{Z}\text{X} + {}^{4}_{2}\text{He}$$

where A is the mass number of the product nucleus and Z is its atomic number. Mass numbers and atomic numbers must balance, so

$$226 = A + 4$$

and

$$88 = Z + 2$$

Hence,

$$A = 222 \quad \text{and} \quad Z = 86$$

Again, from the periodic table, the element with $Z = 86$ is radon (Rn). The product, therefore, is $^{222}_{86}$Rn, and the nuclear equation is

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

Practice Exercise

What product forms when plutonium-238 undergoes alpha emission?
(**a**) Plutonium-234 (**b**) Uranium-234 (**c**) Uranium-238
(**d**) Thorium-236 (**e**) Neptunium-237

Types of Radioactive Decay

The three most common kinds of radiation given off when a radionuclide decays are alpha (α), beta (β), and gamma (γ) radiation. Table 21.1 summarizes some of the important properties of these types of radiation.

Alpha Radiation As described earlier, alpha radiation consists of a stream of helium-4 nuclei known as alpha particles, which we denote as $^{4}_{2}$He or simply α.

TABLE 21.1 Properties of Alpha, Beta, and Gamma Radiation

	Type of Radiation		
Property	**α**	**β**	**γ**
Charge	2+	1−	0
Mass	6.64×10^{-24} g	9.11×10^{-28} g	0
Relative penetrating power	1	100	10,000
Nature of radiation	$^4_2$He nuclei	Electrons	High-energy photons

Beta Radiation *Beta radiation* consists of streams of **beta (β) particles**, which are high-speed electrons emitted by an unstable nucleus. Beta particles are represented in nuclear equations by $^0_{-1}$e or more commonly by β^-. The superscript 0 indicates that the mass of the electron is exceedingly small relative to the mass of a nucleon. The subscript −1 represents the negative charge of the beta particle, which is opposite that of the proton.

Iodine-131 is an isotope that undergoes decay by **beta emission**:

$$^{131}_{53}\text{I} \longrightarrow {}^{131}_{54}\text{Xe} + {}^0_{-1}\text{e} \qquad [21.2]$$

We see from this equation that beta decay causes the atomic number of the reactant to increase from 53 to 54, which means a proton was created. Therefore, beta emission is equivalent to the conversion of a neutron ($^1_0$n or simply n) to a proton ($^1_1$H or simply p):

$$^1_0\text{n} \longrightarrow {}^1_1\text{H} + {}^0_{-1}\text{e} \quad \text{or} \quad \text{n} \longrightarrow \text{p} + \beta^- \qquad [21.3]$$

Just because an electron is emitted from a nucleus in beta decay, we should not think that the nucleus is composed of these particles any more than we consider a match to be composed of sparks simply because it gives them off when struck. The beta-particle electron comes into being only when the nucleus undergoes a nuclear reaction. Furthermore, the speed of the beta particle is sufficiently high that it does not end up in an orbital of the decaying atom.

Gamma Radiation *Gamma (γ) radiation* (or **gamma rays**) consists of high-energy photons (that is, electromagnetic radiation of very short wavelength). It changes neither the atomic number nor the mass number of a nucleus and is represented as either $^0_0\gamma$ or simply γ. Gamma radiation usually accompanies other radioactive emission because it represents the energy lost when the nucleons in a nuclear reaction reorganize into more stable arrangements. Often gamma rays are not explicitly shown when writing nuclear equations.

Positron Emission and Electron Capture Two other types of radioactive decay are positron emission and electron capture. A **positron**, represented as $^0_{+1}$e, or simply as β^+, is a particle that has the same mass as an electron (thus, we use the letter e and superscript 0 for the mass) but the opposite charge (represented by the +1 subscript).*

The isotope carbon-11 decays by **positron emission**:

$$^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^0_{+1}\text{e} \qquad [21.4]$$

Positron emission causes the atomic number of the reactant in this equation to decrease from 6 to 5. In general, positron emission has the effect of converting a proton to a neutron, thereby decreasing the atomic number of the nucleus by 1 while not changing the mass number:

$$^1_1\text{p} \longrightarrow {}^1_0\text{n} + {}^0_{+1}\text{e} \quad \text{or} \quad \text{p} \longrightarrow \text{n} + \beta^+ \qquad [21.5]$$

Electron capture is the capture by the nucleus of an electron from the electron cloud surrounding the nucleus, as in this rubidium-81 decay:

$$^{81}_{37}\text{Rb} + {}^0_{-1}\text{e (orbital electron)} \longrightarrow {}^{81}_{36}\text{Kr} \qquad [21.6]$$

*The positron has a very short life because it is annihilated when it collides with an electron, producing gamma rays: $^0_{+1}\text{e} + {}^0_{-1}\text{e} \longrightarrow 2\,{}^0_0\gamma$.

TABLE 21.3 Types of Radioactive Decay

Type	Nuclear Equation	Change in Atomic Number	Change in Mass Number
Alpha emission	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A-4}_{Z-2}\mathrm{Y} + {}^{4}_{2}\mathrm{He}$	−2	−4
Beta emission	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A}_{Z+1}\mathrm{Y} + {}^{0}_{-1}\mathrm{e}$	+1	Unchanged
Positron emission	${}^{A}_{Z}\mathrm{X} \longrightarrow {}^{A}_{Z-1}\mathrm{Y} + {}^{0}_{+1}\mathrm{e}$	−1	Unchanged
Electron capture*	${}^{A}_{Z}\mathrm{X} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{A}_{Z-1}\mathrm{Y}$	−1	Unchanged

*The electron captured comes from the electron cloud surrounding the nucleus.

TABLE 21.2 Particles Found in Nuclear Reactions

Particle	Symbol
Neutron	${}^{1}_{0}\mathrm{n}$ or n
Proton	${}^{1}_{1}\mathrm{H}$ or p
Electron	${}^{0}_{-1}\mathrm{e}$
Alpha particle	${}^{4}_{2}\mathrm{He}$ or α
Beta particle	${}^{0}_{-1}\mathrm{e}$ or β^-
Positron	${}^{0}_{+1}\mathrm{e}$ or β^+

Because the electron is consumed rather than formed in the process, it is shown on the reactant side of the equation. Electron capture, like positron emission, has the effect of converting a proton to a neutron:

$$ {}^{1}_{1}\mathrm{p} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{1}_{0}\mathrm{n} \qquad [21.7] $$

Table 21.2 summarizes the symbols used to represent the particles commonly encountered in nuclear reactions. The various types of radioactive decay are summarized in Table 21.3.

Sample Exercise 21.2

Writing Nuclear Equations

Write nuclear equations for (**a**) mercury-201 undergoing electron capture; (**b**) thorium-231 decaying to protactinium-231.

SOLUTION

Analyze We must write balanced nuclear equations in which the masses and charges of reactants and products are equal.

Plan We can begin by writing the complete chemical symbols for the nuclei and decay particles that are given in the problem.

Solve

(**a**) The information given in the question can be summarized as

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{A}_{Z}\mathrm{X} $$

The mass numbers must have the same sum on both sides of the equation:

$$ 201 + 0 = A $$

Thus, the product nucleus must have a mass number of 201. Similarly, balancing the atomic numbers gives

$$ 80 - 1 = Z $$

Thus, the atomic number of the product nucleus must be 79, which identifies it as gold (Au):

$$ {}^{201}_{80}\mathrm{Hg} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{201}_{79}\mathrm{Au} $$

(**b**) In this case, we must determine what type of particle is emitted in the course of the radioactive decay:

$$ {}^{231}_{90}\mathrm{Th} \longrightarrow {}^{231}_{91}\mathrm{Pa} + {}^{A}_{Z}\mathrm{X} $$

From $231 = 231 + A$ and $90 = 91 + Z$, we deduce $A = 0$ and $Z = -1$. According to Table 21.2, the particle with these characteristics is the beta particle (electron). We therefore write

$$ {}^{231}_{90}\mathrm{Th} \longrightarrow {}^{231}_{91}\mathrm{Pa} + {}^{0}_{-1}\mathrm{e} \quad \text{or} \quad {}^{231}_{90}\mathrm{Th} \longrightarrow {}^{231}_{91}\mathrm{Pa} + \beta^- $$

Practice Exercise

The radioactive decay of thorium-232 occurs in multiple steps, called a *radioactive decay chain*. The second product produced in this chain is actinium-228. Which of the following processes could lead to this product starting with thorium-232?

(**a**) Alpha decay followed by beta emission
(**b**) Beta emission followed by electron capture
(**c**) Positron emission followed by alpha decay
(**d**) Electron capture followed by positron emission
(**e**) More than one of these is consistent with the observed transformation.

Self-Assessment Exercise

21.1 Carbon-11 decays by positron emission and is one radioisotope used in PET scans. What is the nuclear equation for its decay?

(**a**) ${}^{11}_{6}\mathrm{C} \longrightarrow {}^{11}_{5}\mathrm{C} + {}^{0}_{+1}\mathrm{e}$
(**b**) ${}^{11}_{6}\mathrm{C} \longrightarrow {}^{11}_{5}\mathrm{B} + {}^{0}_{+1}\mathrm{e}$
(**b**) ${}^{11}_{6}\mathrm{C} \longrightarrow {}^{11}_{7}\mathrm{N} + {}^{0}_{+1}\mathrm{e}$

Exercises

21.2 Indicate the number of protons and neutrons in the following nuclei: (**a**) $^{214}_{83}$Bi, (**b**) $^{210}_{82}$Pb, (**c**) uranium-235.

21.3 What do these symbols stand for? (**a**) $^{0}_{0}\gamma$, (**b**) $^{4}_{2}$He, (**c**) $^{1}_{0}$n.

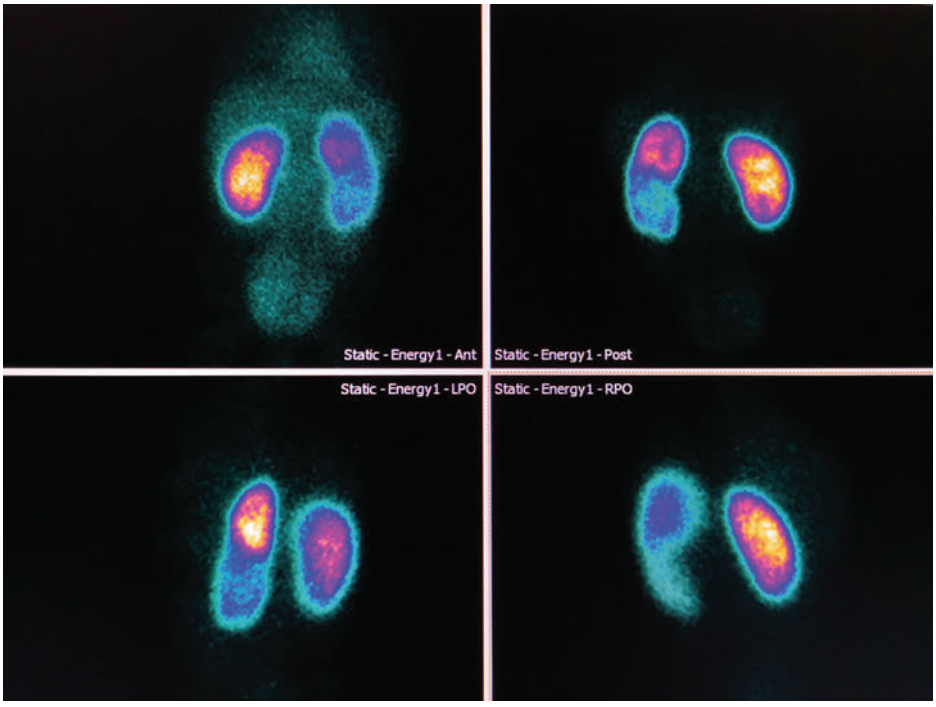
21.4 Write balanced nuclear equations for the following transformations: (**a**) polonium-210 emits alpha particle; (**b**) neptunium-235 undergoes electron capture; (**c**) fluorine-18 emits beta particle; (**d**) carbon-14 decays by beta emission.

21.5 What particle is produced during the following decay processes: (**a**) actinium-215 decays to francium-211; (**b**) boron-13 decays to carbon-13; (**c**) holmium-151 decays to terbium-147; (**d**) carbon-11 decays to boron-11?

Answers to Self-Assessment Exercise

21.1 (b)

21.2 Patterns of Nuclear Stability



One of the most useful radionuclides in diagnostic medicine is technetium-99m, ^{99m}Tc. The 'm' stands for 'metastable,' indicating that the isotope is in an excited state. The excess energy the isotope contains is emitted as easily detectable gamma rays in the absence of alpha or beta particles. The isotope can be used to study the brain, heart, thyroid, lungs, liver, kidneys (pictured), blood, and in the detection of bone cancer. This wide applicability and a short lifetime mean that nearly 95% decays to ^{99}Tc in 24 hours, by which time most of it has been flushed from the body. In turn, technetium-99 is unusual because it emits β radiation in the absence of γ radiation and this, in combination with a long half-life, makes it useful for the calibration of some types of equipment.

In this section, we look at nuclear stability. Some nuclides, such as $^{12}_{6}$C and $^{13}_{6}$C are stable, whereas others, such as $^{14}_{6}$C, are unstable and undergo radioactive decay. Why does a small difference in the number of neutrons affect the stability of a nuclide? No single rule allows us to predict whether a particular nucleus is radioactive and, if it is, how it might decay. However, several empirical observations can help us predict the stability of a nucleus.

By the end of this section, you should be able to

- Predict nuclear stability and expected type of nuclear decay from the neutron-to-proton ratio of an isotope.
- Write balanced nuclear equations for nuclear transmutation

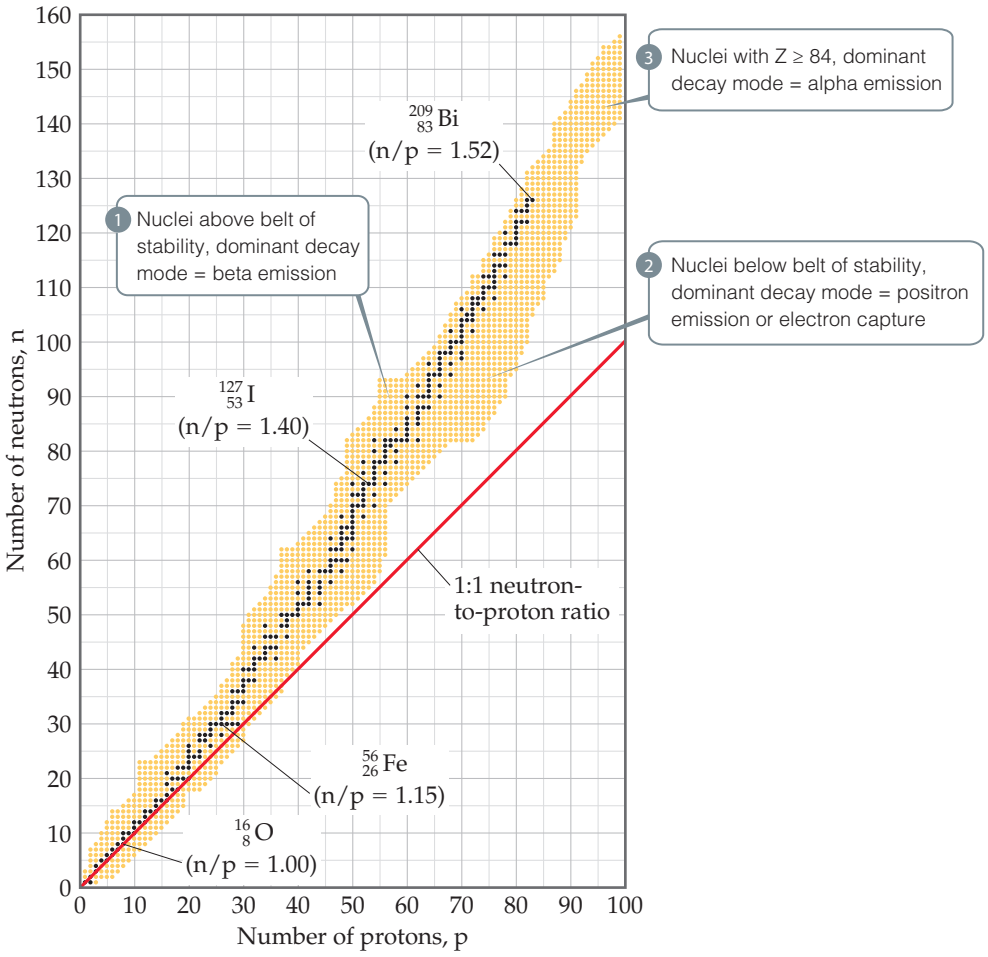
Neutron-to-Proton Ratio

Because like charges repel each other, it may seem surprising that a large number of protons can reside within the small volume of the nucleus. At close distances, however, a strong force of attraction, called the *strong nuclear force*, exists between nucleons. Neutrons are intimately involved in this attractive force.

All nuclei other than $^{1}_{1}H$ contain neutrons. As the number of protons in a nucleus increases, there is an ever greater need for neutrons to counteract the proton–proton repulsions. Stable nuclei with atomic numbers up to about 20 have approximately equal numbers of neutrons and protons. For nuclei with atomic number above 20, the number of neutrons exceeds the number of protons. Indeed, the number of neutrons necessary to create a stable nucleus increases more rapidly than the number of protons. Thus, the neutron-to-proton ratios of stable nuclei increase with increasing atomic number, as illustrated by the following isotopes: $^{12}_{6}C$ (n/p = 1), manganese, $^{55}_{25}Mn$ (n/p = 1.20), and gold, $^{197}_{79}Au$ (n/p = 1.49).

Figure 21.1 shows all known isotopes of the elements up to $Z = 100$ plotted according to their numbers of protons and neutrons. Notice how the plot goes above the line for 1:1 neutron-to-proton for heavier elements. The dark blue dots in the figure represent stable (nonradioactive) isotopes, the remainder being radioactive isotopes. The region of the graph covered by these dark blue dots is known as the *belt of stability*. The belt of

Go Figure Estimate the optimal number of neutrons for a nucleus containing 70 protons.



▲ **Figure 21.1 Stable and radioactive isotopes as a function of numbers of neutrons and protons in a nucleus.** The stable nuclei (dark blue dots) define a region known as the belt of stability.

stability ends at element 83 (bismuth), which means that *all nuclei with 84 or more protons are radioactive*. For example, all isotopes of uranium, $Z = 92$, are radioactive.

Different radionuclides decay in different ways. The type of decay that occurs depends largely on a nuclide's neutron-to-proton ratio and how it compares with the ratio of nearby nuclei that lie within the belt of stability. We can envision three general situations, which are labeled 1, 2, and 3, in Figure 21.1.

1. **Nuclei above the belt of stability (high neutron-to-proton ratios).** These neutron-rich nuclei can lower their ratio and thereby move toward the belt of stability by emitting a beta particle because beta emission decreases the number of neutrons and increases the number of protons (Equation 21.3).
2. **Nuclei below the belt of stability (low neutron-to-proton ratios).** These proton-rich nuclei can increase their ratio and so move closer to the belt of stability by either positron emission or electron capture because both decays increase the number of neutrons and decrease the number of protons (Equations 21.5 and 21.7). Positron emission is more common among lighter nuclei. Electron capture becomes increasingly common as the nuclear charge increases.
3. **Nuclei with atomic numbers ≥ 84.** These heavy nuclei tend to undergo alpha emission, which decreases both the number of neutrons and the number of protons by two, moving the nucleus diagonally toward the belt of stability.

Sample Exercise 21.3

Predicting Modes of Nuclear Decay

Predict the mode of decay of (**a**) carbon-14, (**b**) xenon-118.

SOLUTION

Analyze We are asked to predict the modes of decay of two nuclei.

Plan To do this, we must locate the respective nuclei in Figure 21.1 and determine their positions with respect to the belt of stability in order to predict the most likely mode of decay.

Solve

(**a**) Carbon is element 6. Thus, carbon-14 has 6 protons and $14 - 6 = 8$ neutrons, giving it a neutron-to-proton ratio of 1.25. Elements with $Z < 20$ normally have stable nuclei that contain approximately equal numbers of neutrons and protons (n/p = 1). Thus, carbon-14 is located above the belt of stability, and we expect it to decay by emitting a beta particle to decrease the n/p ratio:

$$^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$

This is indeed the mode of decay observed for carbon-14, a reaction that lowers the n/p ratio from 1.25 to 1.0.

(**b**) Xenon is element 54. Thus, xenon-118 has 54 protons and $118 - 54 = 64$ neutrons, giving it an n/p ratio of 1.18. According to Figure 21.1, stable nuclei in this region of the belt of stability have higher neutron-to-proton ratios than xenon-118. The nucleus can increase this ratio by either positron emission or electron capture:

$$^{118}_{54}\text{Xe} \longrightarrow {}^{118}_{53}\text{I} + {}^{0}_{+1}\text{e}$$

$$^{118}_{54}\text{Xe} + {}^{0}_{-1}\text{e} \longrightarrow {}^{118}_{53}\text{I}$$

In this case, both modes of decay are observed.

Comment Keep in mind that our guidelines do not always work. For example, thorium-233, which we might expect to undergo alpha decay, actually undergoes beta emission. Furthermore, a few radioactive nuclei lie within the belt of stability. Both $^{146}_{60}$Nd and $^{148}_{60}$Nd, for example, are stable and lie in the belt of stability. $^{147}_{60}$Nd, however, which lies between them, is radioactive.

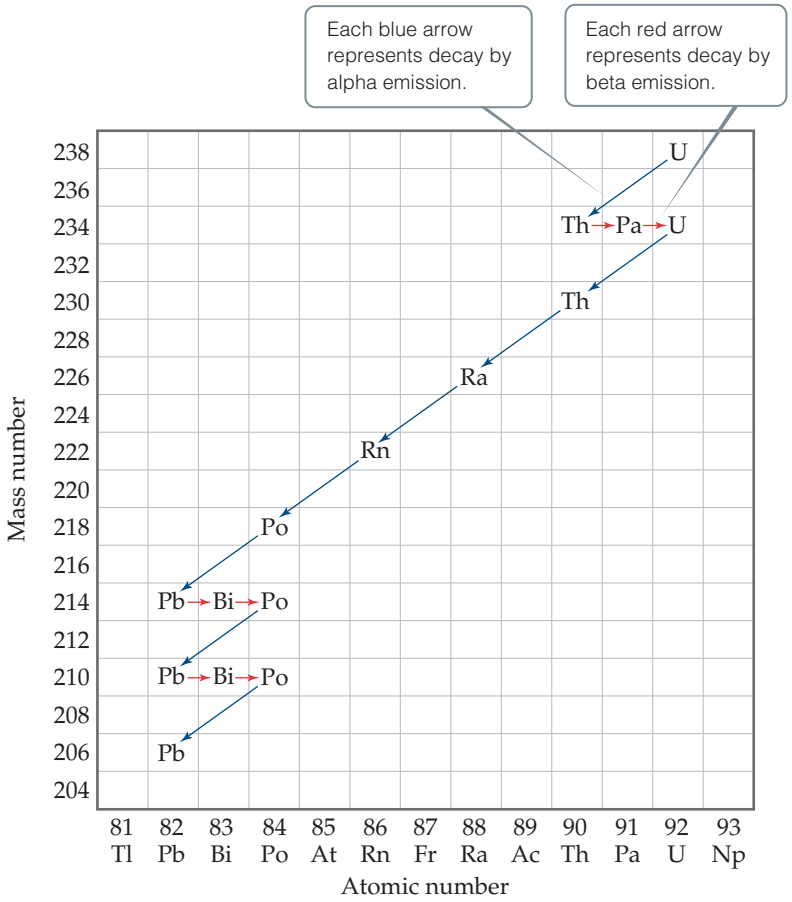
Practice Exercise

Which of the following radioactive nuclei is most likely to decay via emission of a β^- particle?
(**a**) nitrogen-13 (**b**) magnesium-23 (**c**) rubidium-83
(**d**) iodine-131 (**e**) neptunium-237

Radioactive Decay Chains

Some nuclei cannot gain stability by a single emission. Consequently, a series of successive emissions occurs as shown for uranium-238 in **Figure 21.2**. Decay continues until a stable nucleus—lead-206 in this case—is formed. A series of nuclear reactions that begins with an unstable nucleus and terminates with a stable one is known as a **radioactive decay chain** or a **nuclear disintegration series**. Three such series occur in nature: uranium-238 to lead-206, uranium-235 to lead-207, and thorium-232 to lead-208. All of the decay processes in these series are either alpha emissions or beta emissions.

Go Figure Write the nuclear equation for the step shown for the first decay of Th.



▲ **Figure 21.2 Nuclear decay chain for uranium-238.** The decay continues until the stable nucleus ^{206}Pb is formed.

Further Observations

Two further observations can help us to predict stable nuclei:

- Nuclei with the **magic numbers** of 2, 8, 20, 28, 50, or 82 protons or 2, 8, 20, 28, 50, 82, or 126 neutrons are generally more stable than nuclei that do not contain these numbers of nucleons.
- Nuclei with even numbers of protons, neutrons, or both are more likely to be stable than those with odd numbers of protons and/or neutrons. Approximately 60% of stable nuclei have an even number of both protons and neutrons, whereas less than 2% have odd numbers of both (Table 21.4).

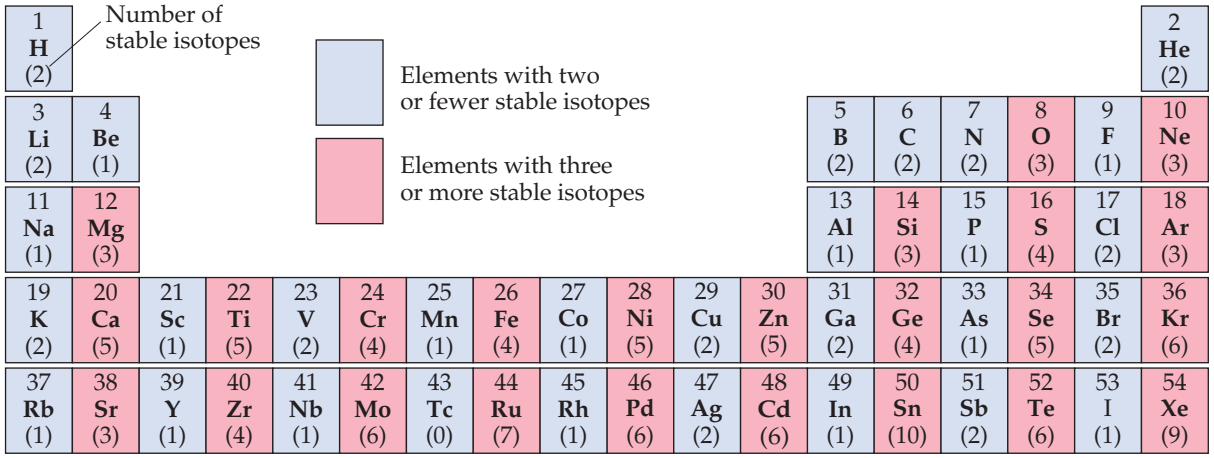
These observations can be understood in terms of the *shell model of the nucleus*, in which nucleons are described as residing in shells analogous to the shell structure for electrons in atoms. Just as certain numbers of electrons correspond to stable filled-shell electron configurations, so too do certain numbers (known as magic numbers) of nucleons represent filled shells in nuclei.

There are several examples of the stability of nuclei with magic numbers of nucleons. For example, the radioactive series in Figure 21.2 ends with the stable $^{206}_{82}$Pb nucleus, which has a magic number of protons (82). Another example is the observation that tin, which has a magic number of protons (50), has ten stable isotopes, more than any other element.

TABLE 21.4 Number of Stable Isotopes with Even and Odd Numbers of Protons and Neutrons

Number of Stable Isotopes	Proton Number	Neutron Number
157	Even	Even
53	Even	Odd
50	Odd	Even
5	Odd	Odd

Go Figure Among the elements shown here, how many have an even number of protons and fewer than three stable isotopes? How many have an odd number of protons and more than two stable isotopes?



1 H (2)																	2 He (2)
3 Li (2)	4 Be (1)											5 B (2)	6 C (2)	7 N (2)	8 O (3)	9 F (1)	10 Ne (3)
11 Na (1)	12 Mg (3)											13 Al (1)	14 Si (3)	15 P (1)	16 S (4)	17 Cl (2)	18 Ar (3)
19 K (2)	20 Ca (5)	21 Sc (1)	22 Ti (5)	23 V (2)	24 Cr (4)	25 Mn (1)	26 Fe (4)	27 Co (1)	28 Ni (5)	29 Cu (2)	30 Zn (5)	31 Ga (2)	32 Ge (4)	33 As (1)	34 Se (5)	35 Br (2)	36 Kr (6)
37 Rb (1)	38 Sr (3)	39 Y (1)	40 Zr (4)	41 Nb (1)	42 Mo (6)	43 Tc (0)	44 Ru (7)	45 Rh (1)	46 Pd (6)	47 Ag (2)	48 Cd (6)	49 In (1)	50 Sn (10)	51 Sb (2)	52 Te (6)	53 I (1)	54 Xe (9)

▲ **Figure 21.3** Number of stable isotopes for elements 1–54.

Evidence also suggests that pairs of protons and pairs of neutrons have a special stability, analogous to the pairs of electrons in molecules. This evidence accounts for the observation that stable nuclei with an even number of protons and/or neutrons are far more numerous than those with odd numbers. The preference for even numbers of protons is illustrated in **Figure 21.3**, which shows the number of stable isotopes for all elements up to Xe. Notice that once we move past nitrogen, the elements with an odd number of protons invariably have fewer stable isotopes than their neighbors with an even number of protons.

Nuclear Transmutations

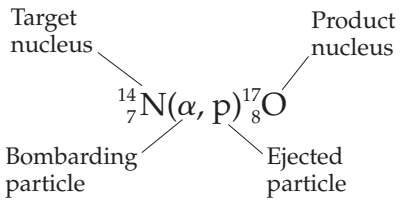
Thus far we have examined nuclear reactions in which a nucleus decays spontaneously. A nucleus can also change identity if it is struck by a neutron or by another nucleus. Nuclear reactions induced in this way are known as **nuclear transmutations**.

In 1919, Ernest Rutherford performed the first conversion of one nucleus into another, using alpha particles emitted by radium to convert nitrogen-14 into oxygen-17:

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H} \quad \text{or} \quad {}^{14}_{7}\text{N} + \alpha \longrightarrow {}^{17}_{8}\text{O} + \text{p} \qquad [21.8]$$

Such reactions have allowed scientists to synthesize hundreds of radioisotopes in the laboratory.

A shorthand notation often used to represent nuclear transmutations lists the target nucleus, the bombarding particle and the ejected particle in parentheses, followed by the product nucleus. Using this condensed notation we see that, Equation 21.8 becomes



Sample Exercise 21.4

Writing a Balanced Nuclear Equation

Write the balanced nuclear equation for the process summarized as $^{27}_{13}\text{Al}(\text{n}, \alpha)^{24}_{11}\text{Na}$.

SOLUTION

Analyze We must go from the condensed descriptive form of the reaction to the balanced nuclear equation.

Plan We arrive at the balanced equation by writing n and α, each with its associated subscripts and superscripts.

Solve The n is the abbreviation for a neutron (^1_0n), and α represents an alpha particle (^4_2He). The neutron is the bombarding particle, and the alpha particle is a product. Therefore, the nuclear equation is

$$^{27}_{13}\text{Al} + {}^1_0\text{n} \longrightarrow {}^{24}_{11}\text{Na} + {}^4_2\text{He} \quad \text{or} \quad {}^{27}_{13}\text{Al} + \text{n} \longrightarrow {}^{24}_{11}\text{Na} + \alpha$$

Practice Exercise

Consider the following nuclear transmutation: $^{238}_{92}\text{U}(\text{n}, \beta^-)\text{X}$. What is the identity of nucleus X?

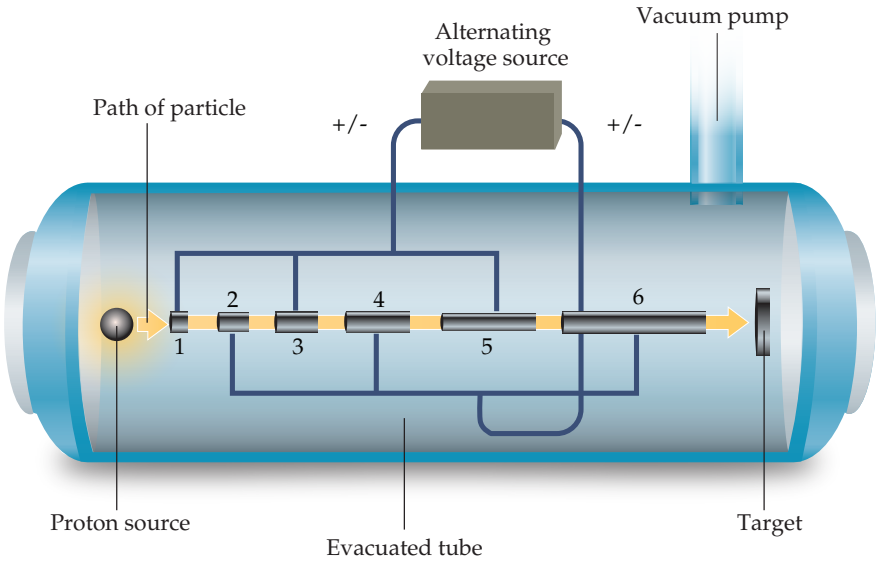
(a) $^{238}_{93}\text{Np}$ **(b)** $^{239}_{92}\text{U}$ **(c)** $^{239}_{92}\text{U}^+$ **(d)** $^{235}_{90}\text{Th}$ **(e)** $^{239}_{93}\text{Np}$

Accelerating Charged Particles

Alpha particles and other positively charged particles must move very fast to overcome the electrostatic repulsion between them and the target nucleus. The higher the nuclear charge on either the bombarding particle or the target nucleus, the faster the bombarding particle must move to bring about a nuclear reaction. Many methods have been devised to accelerate charged particles, using strong magnetic and electrostatic fields. These **particle accelerators**, popularly called "atom smashers," bear such names as *cyclotron* and *synchrotron*.

A common theme of all particle accelerators is the need to create charged particles so that they can be manipulated by electric and magnetic fields. In addition, the region through which the particles move must be kept at high vacuum so that they do not collide with any gas-phase molecules.

Figure 21.4(**a**) shows a multistage linear accelerator. A charged particle, such as a proton, is accelerated through a series of tubes of increasing length. The electrical charge on the tubes is changed from positive to negative, so that the particle is always attracted to the tube it is approaching and repelled by the one it is leaving. As a result, the particle accelerates until it has sufficient kinetic energy to smash into a target nucleus. Figure 21.4(**b**) shows the Stanford linear accelerator, which is 3.2 km in length.

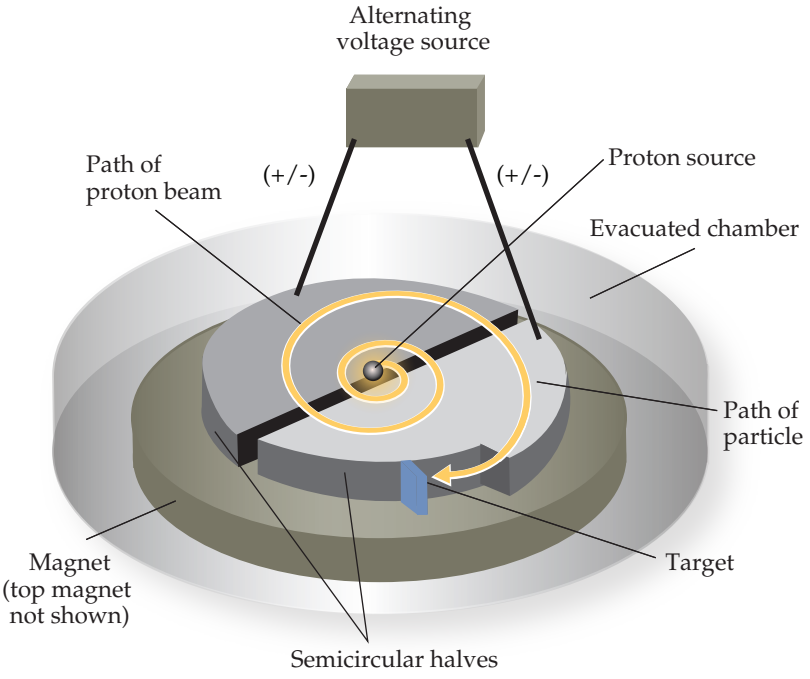


(a)



(b)

▲ Figure 21.4 The linear accelerator.



(a)



(b)

▲ **Figure 21.5** The cyclotron.

Figure 21.5(**a**) shows a *cyclotron*. In this device, charged particles move in a spiral path within two D-shaped electrodes. Alternating charges on the electrodes accelerate the particles, while magnets above and below the device constrain the particles to a spiral path of increasing radius. In a *synchrotron*, the magnetic fields are synchronized so that the particle moves in a circular rather than a spiral path. Figure 21.5(**b**) shows the Fermi National Accelerator Lab at Batavia, Illinois, which has a circumference of 6.3 km.

Reactions Involving Neutrons

Most synthetic isotopes used in medicine and scientific research are made using neutrons as the bombarding particles. Because neutrons are neutral, they are not repelled by the nucleus. Consequently, they do not need to be accelerated to cause nuclear reactions. The neutrons are produced in nuclear reactors (see Section 21.5). For example, cobalt-60, which is used in cancer radiation therapy, is produced by neutron capture. Iron-58 is placed in a nuclear reactor and bombarded by neutrons to trigger the following sequence of reactions:

$$^{58}_{26}\text{Fe} + {}^{1}_{0}\text{n} \longrightarrow {}^{59}_{26}\text{Fe} \qquad [21.9]$$

$$^{59}_{26}\text{Fe} \longrightarrow {}^{59}_{27}\text{Co} + {}^{0}_{-1}\text{e} \qquad [21.10]$$

$$^{59}_{27}\text{Co} + {}^{1}_{0}\text{n} \longrightarrow {}^{60}_{27}\text{Co} \qquad [21.11]$$

Transuranium Elements

Nuclear transmutations have been used to produce the elements with atomic number above 92, collectively known as the **transuranium elements** because they follow uranium in the periodic table. Elements 93 (neptunium, Np) and 94 (plutonium, Pu) were produced in 1940 by bombarding uranium-238 with neutrons:

$$^{238}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{239}_{92}\text{U} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}\text{e} \qquad [21.12]$$

$$^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{0}_{-1}\text{e} \qquad [21.13]$$

Elements with still larger atomic numbers are normally formed in small quantities in particle accelerators. Curium-242, for example, is formed when a plutonium-239 target is bombarded with accelerated alpha particles:

$$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n} \qquad [21.14]$$

New advances in the detection of the decay patterns of single atoms have led to recent additions to the periodic table. Between 1994 and 2010, elements 110 through 118 were discovered via the nuclear reactions that occur when nuclei of much lighter elements collide with high energy. For example, in 1996 a team of European scientists based in Germany synthesized element 112, copernicium, Cn, by bombarding a lead target continuously for three weeks with a beam of zinc atoms:

$$^{208}_{82}\text{Pb} + {}^{70}_{30}\text{Zn} \longrightarrow {}^{277}_{112}\text{Cn} + {}^{1}_{0}\text{n} \qquad [21.15]$$

Amazingly, their discovery was based on the detection of only one atom of the new element, which decays after roughly 100 μs by alpha decay to form darmstadtium-273 (element 110). Within one minute, another five alpha decays take place producing fermium-253 (element 100). The finding has been verified in both Japan and Russia.

Because experiments to create new elements are very complicated and produce only a very small number of atoms of the new elements, they need to be carefully evaluated and reproduced before the new element is made an official part of the periodic table.

The International Union for Pure and Applied Chemistry (IUPAC) is the international body that authorizes names of new elements after their experimental discovery and confirmation. According to the IUPAC, new elements can be named after a mythological concept, a mineral, a place or country, a property, or a scientist. In 2016, IUPAC approved the following names and symbols for elements 113, 115, 117, and 118, as suggested by their discoverers: nihonium, Nh, for element 113; moscovium, Mc, for element 115; tennessine, Ts, for element 117; and organesson, Og, for element 118.

Self-Assessment Exercises

21.6 Cobalt-60 is used in radiotherapy, in industrial radiography, and in sterilizing food and equipment. Which nuclear equation represents the likely decay route of Co-60? (Hint: You may find it useful to refer to Figure 21.1)

(a) $^{60}_{27}\text{Co} \longrightarrow {}^{56}_{25}\text{Mn} + {}^{4}_{2}\alpha$

(b) $^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\text{e}$

(c) $^{60}_{27}\text{Co} \longrightarrow {}^{60}_{26}\text{Fe} + {}^{0}_{+1}\text{e}$

21.7 Which nuclear equation represents the nuclear transmutation: $^{11}_{6}\text{C(n,p)}^{11}_{5}\text{B}$

(a) $^{11}_{6}\text{C} + {}^{1}_{0}\text{n} \longrightarrow {}^{1}_{1}\text{p} + {}^{11}_{5}\text{B}$

(b) $^{11}_{6}\text{C} + {}^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{11}_{5}\text{B}$

(c) $^{11}_{5}\text{B} + {}^{1}_{1}\text{p} \longrightarrow {}^{1}_{0}\text{n} + {}^{11}_{6}\text{C}$

Exercises

21.8 Each of the following nuclei undergoes either beta decay or positron emission. Predict the type of emission for each: (**a**) $^{90}_{38}\text{Sr}$, (**b**) $^{85}_{38}\text{Sr}$, (**c**) potassium-40, (**d**) sulfur-30.

21.9 One nuclide in each of these pairs is radioactive. Predict which is radioactive and which is stable: (**a**) $^{40}_{20}\text{Ca}$ and $^{45}_{20}\text{Ca}$, (**b**) ^{12}C and ^{14}C, (**c**) lead-206 and thorium-230. Explain your choice in each case.

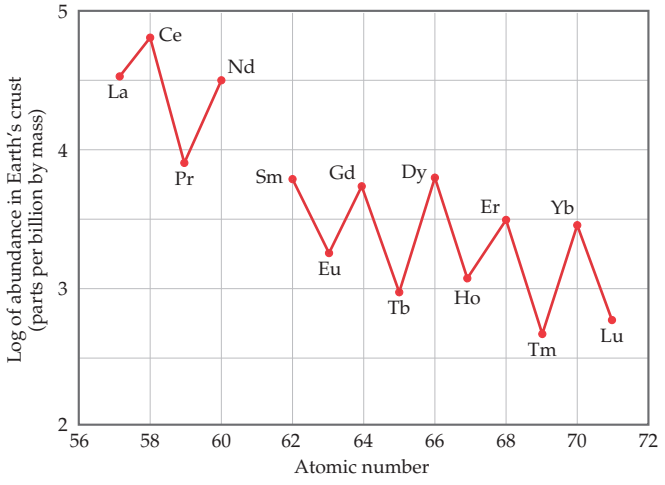
21.10 Despite the similarities in the chemical reactivity of elements in the lanthanide series, their abundances in Earth's crust vary by two orders of magnitude. This graph shows the relative abundance as a function of atomic number. Which of the following statements best explains the sawtooth variation across the series?

(**a**) The elements with an odd atomic number lie above the belt of stability.

(**b**) The elements with an odd atomic number lie below the belt of stability.

(**c**) The elements with an even atomic number have a magic number of protons.

(**d**) Pairs of protons have a special stability.



21.11 Which of the following nuclides would you expect to be radioactive: $^{58}_{26}\text{Fe}$, $^{60}_{27}\text{Co}$, $^{92}_{41}\text{Nb}$, mercury-202, radium-226? Justify your choices.

21.12 A radioactive decay series that begins with $^{232}_{90}\text{Th}$ ends with formation of the stable nuclide $^{208}_{82}\text{Pb}$. How many alpha-particle emissions and how many beta-particle emissions are involved in the sequence of radioactive decays?

21.13 In 1930 the American physicist Ernest Lawrence designed the first cyclotron in Berkeley, California. In 1937 Lawrence bombarded a molybdenum target with deuterium ions, producing for the first time an element not found in nature. What was this element? Starting with molybdenum-96 as your reactant, write a nuclear equation to represent this process.

21.14 Complete and balance the following nuclear equations by supplying the missing particle:

(**a**) $^{106}_{47}\text{Ag} + {}^{0}_{-1}\text{e} \longrightarrow ?$

(**b**) $^{263}_{106}\text{Sg} \longrightarrow {}^{4}_{2}\text{He} + ?$

(**c**) $^{216}_{84}\text{Po} \longrightarrow {}^{212}_{82}\text{Pb} + ?$

(**d**) $^{10}_{5}\text{B} + ? \longrightarrow {}^{7}_{3}\text{Li} + {}^{4}_{2}\text{He}$

(**e**) $^{220}_{86}\text{Rn} \longrightarrow {}^{4}_{2}\text{He} + ?$

21.15 Write balanced equations for each of the following nuclear reactions: (**a**) $^{238}_{92}\text{U}(\text{n},\gamma)^{239}_{92}\text{U}$, (**b**) $^{16}_{8}\text{O}(\text{p},\alpha)^{13}_{7}\text{N}$, (**c**) $^{18}_{8}\text{O}(\text{n},\beta^-)^{19}_{9}\text{F}$.

Answers to Self-Assessment Exercises

21.6 (b) **21.7** (a)

21.3 Rates of Radioactive Decay



The discovery of radiocarbon dating around 1950 had a profound effect on archaeology. For the first time, it was possible to obtain the date of an organic object (for example, cloth, bone, parchment, or charcoal from a fire) without reference to stratigraphy. It also made possible the comparison of sites that were distant from one another showing that the same innovation could arise independently in two or more places. It had previously been thought that all innovations spread slowly across the pre-historic landscape as people migrated, traded, and invaded neighboring regions.

By the end of this section, you should be able to

- Use the half-life of selected radionuclides to calculate the ages of objects

Some radioisotopes, such as uranium-238, are found in nature even though they are not stable. Other radioisotopes do not exist in nature but can be synthesized in nuclear reactions. To understand this distinction, we must realize that different nuclei undergo radioactive decay at different rates. Many radioisotopes decay essentially completely in fractions of a second, so we do not find them in nature. Uranium-238, on the other hand, decays very slowly. Therefore, despite its instability, we can still observe what remains from its formation in the early history of the universe.

Radioactive decay is a first-order kinetic process. Recall that a first-order process has a characteristic **half-life**, which is the time required for half of any given quantity of a substance to react. Nuclear decay rates are commonly expressed in terms of half-lives. Each radioisotope has its own characteristic half-life. For example, strontium-90 has a half-life of 28.8 yr:

$$^{90}_{38}\text{Sr} \longrightarrow {}^{90}_{39}\text{Y} + {}^{0}_{-1}\text{e} \qquad t_{1/2} = 28.8\ \text{yr} \qquad [21.16]$$

TABLE 21.5 The Half-Lives and Type of Decay for Several Radioisotopes

	Isotope	Half-Life (yr)	Type of Decay
Natural radioisotopes	$^{238}_{92}U$	4.5×10^9	Alpha
	$^{235}_{92}U$	7.0×10^8	Alpha
	$^{232}_{90}Th$	1.4×10^{10}	Alpha
	$^{40}_{19}K$	1.3×10^9	Beta
	$^{14}_{6}C$	5700	Beta
Synthetic radioisotopes	$^{239}_{94}Pu$	24,000	Alpha
	$^{137}_{55}Cs$	30.2	Beta
	$^{90}_{38}Sr$	28.8	Beta
	$^{131}_{53}I$	0.022	Beta

Thus, if we start with 10.0 g of strontium-90, only 5.0 g of that isotope remains after 28.8 yr, 2.5 g remains after another 28.8 yr, and so on (Figure 21.6).

Half-lives as short as millionths of a second and as long as billions of years are known. The half-lives of some radioisotopes are listed in Table 21.5. One important feature of half-lives for nuclear decay is that they are unaffected by external conditions such as temperature, pressure, or state of chemical combination. Unlike toxic chemicals, therefore, radioactive atoms cannot be rendered harmless by chemical reaction or by any other practical treatment.

Radiometric Dating

Because the half-life of any particular nuclide is constant, the half-life can serve as a "nuclear clock" to determine the age of objects. The method of dating objects based on their isotopes and isotope abundances is called *radiometric dating*.

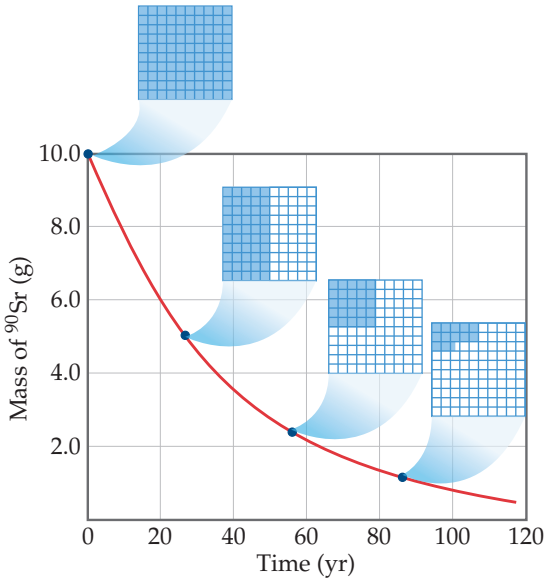
When carbon-14 is used in radiometric dating, the technique is known as *radiocarbon dating*. The procedure is based on the formation of carbon-14 as neutrons created by cosmic rays in the upper atmosphere convert nitrogen-14 into carbon-14 (Figure 21.7). The ^{14}C reacts with oxygen to form $^{14}CO_2$ in the atmosphere, and this "labeled" CO_2 is taken up by plants and introduced into the food chain through photosynthesis. This process provides a small but reasonably constant source of carbon-14, which is radioactive and undergoes beta decay with a half-life of 5700 yr (to two significant figures):

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e \qquad [21.17]$$

Because a living plant or animal has a constant intake of carbon compounds, it is able to maintain a ratio of carbon-14 to carbon-12 that is nearly identical with that of the atmosphere.

Go Figure

If we start with a 50.0-g sample, how much remains after three half-lives have passed?



▲ **Figure 21.6 Decay of a 10.0 g sample of strontium-90 ($t_{1/2}$ = 28.8 yr).** The 10 × 10 grids show how much of the radioactive isotope remains after various amounts of time.

Sample Exercise 21.5

Calculation Involving Half-Lives

The half-life of cobalt-60 is 5.27 yr. How much of a 1.000 mg sample of cobalt-60 is left after 15.81 yr?

SOLUTION

Analyze We are given the half-life for cobalt-60 and asked to calculate the amount of cobalt-60 remaining from an initial 1.000 mg sample after 15.81 yr.

Plan We will use the fact that the amount of a radioactive substance decreases by 50% for every half-life that passes.

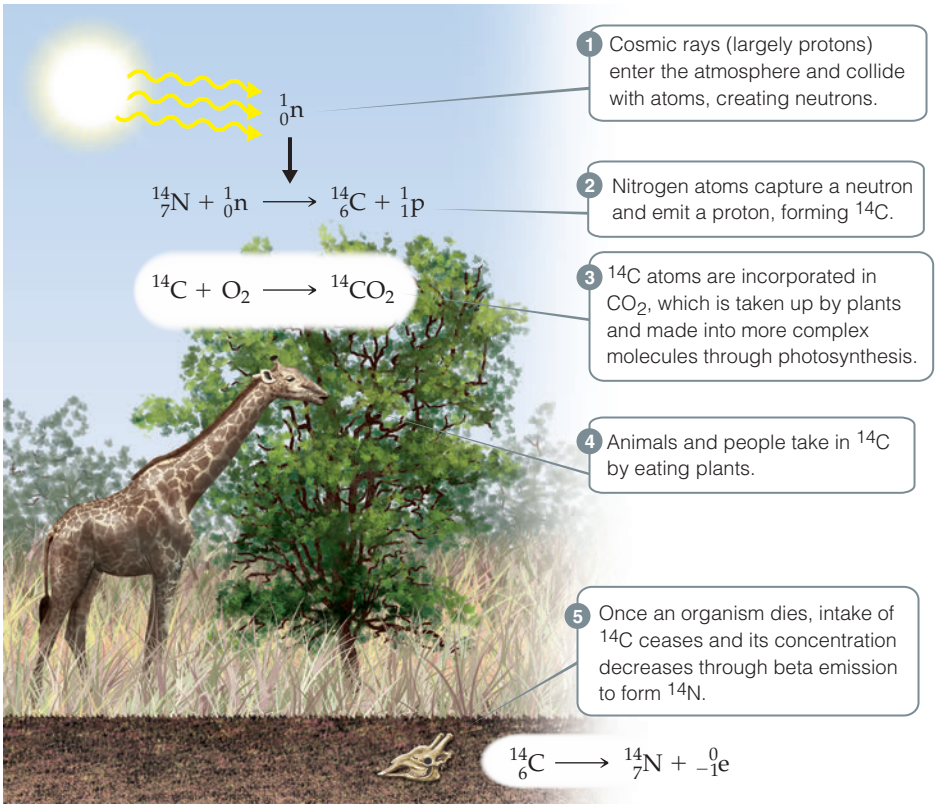
Solve Because $5.27 \times 3 = 15.81$, 15.81 yr is three half-lives for cobalt-60. At the end of one half-life, 0.500 mg of cobalt-60 remains, 0.250 mg at the end of two half-lives, and 0.125 mg at the end of three half-lives.

Practice Exercise

A radioisotope of technetium is useful in medical imaging techniques. A sample initially contains 80.0 mg of this isotope. After 24.0 h, only 5.0 mg of the technetium isotope remains. What is the half-life of the isotope?
(**a**) 3.0 h (**b**) 6.0 h (**c**) 12.0 h (**d**) 16.0 h (**e**) 24.0 h

Once the organism dies, however, it no longer ingests carbon compounds to replenish the carbon-14 lost through radioactive decay. The ratio of carbon-14 to carbon-12 therefore decreases. By measuring this ratio and comparing it with that of the atmosphere, we can estimate the age of an object. For example, if the ratio diminishes to half that of the atmosphere, we can conclude that the object is one half-life, or 5700 yr, old.

Go Figure How does $^{14}CO_2$ become incorporated into the mammalian food chain?



▲ **Figure 21.7 Creation and distribution of carbon-14.** The ratio of carbon-14 to carbon-12 in a dead animal or plant is related to the time since death occurred.

This method cannot be used to date objects older than about 50,000 yr because after this length of time the radioactivity is too low to be measured accurately.

In radiocarbon dating, a reasonable assumption is that the ratio of carbon-14 to carbon-12 in the atmosphere has been relatively constant for the past 50,000 yr. However, because variations in solar activity control the amount of carbon-14 produced in the atmosphere, that ratio can fluctuate. We can correct for this effect by using other kinds of data. Recently, scientists have compared carbon-14 data with data from tree rings, corals, lake sediments, ice cores, and other natural sources to correct variations in the carbon-14 "clock" back to 26,000 yr.

Other isotopes can be similarly used to date other types of objects. For example, it takes 4.5×10^9 yr for half of a sample of uranium-238 to decay to lead-206. The age of rocks containing uranium can therefore be determined by measuring the ratio of lead-206 to uranium-238. If the lead-206 had somehow become incorporated into the rock by normal chemical processes instead of by radioactive decay, the rock would also contain large amounts of the more abundant isotope lead-208. In the absence of large amounts of this "geonormal" isotope of lead, it is assumed that all of the lead-206 was at one time uranium-238.

The oldest rocks found on Earth are approximately 3×10^9 yr old. This age indicates that Earth's crust has been solid for at least this length of time. Scientists estimate that it required 1×10^9 to 1.5×10^9 yr for Earth to cool and its surface to become solid, making the age of Earth 4.0 to 4.5×10^9 yr.

Calculations Based on Half-Life

The rate at which a sample decays is called its **activity**, and it is often expressed as number of disintegrations per unit time. The **becquerel** (Bq) is the SI unit for expressing activity. A becquerel is defined as one nuclear disintegration per second. An older, but still widely used, unit of activity is the **curie** (Ci), defined as 3.7×10^{10} disintegrations per second, which is the rate of decay of 1 g of radium. Thus, a 4.0 mCi sample of cobalt-60 undergoes

$$4.0 \times 10^{-3}\,\cancel{\text{Ci}} \times \frac{3.7 \times 10^{10}\ \text{disintegrations/s}}{1\,\cancel{\text{Ci}}} = 1.5 \times 10^8\ \text{disintegrations/s}$$

and so has an activity of 1.5×10^8 Bq.

As a radioactive sample decays, the amount of radiation emanating from the sample decays as well. For example, the half-life of cobalt-60 is 5.27 yr. The 4.0 mCi sample of cobalt-60 would, after 5.27 yr, have a radiation activity of 2.0 mCi, or 7.5×10^7 Bq.

Because radioactive decay is a first-order kinetic process, its rate is proportional to the number of radioactive nuclei N in a sample:

$$\text{Rate} = kN \qquad [21.18]$$

The first-order rate constant, k, is called the *decay constant* and is related to the half-life:

$$k = \frac{0.693}{t_{1/2}} \qquad [21.19]$$

Thus, if we know the value of either the half-life or the decay constant, we can calculate the value of the other.

As we saw in Section 14.4, a first-order rate law can be expressed in the following form:

$$\ln \frac{N_t}{N_0} = -kt \qquad [21.20]$$

In this equation t is the time interval of decay, k is the decay constant, N_0 is the initial number of nuclei (at time zero), and N_t is the number remaining after the time interval. Both the mass of a particular radioisotope and its activity are proportional to the number of radioactive nuclei. Thus, either the ratio of the mass at any time t to the mass at time $t = 0$ or the ratio of the activities at time t and $t = 0$ can be substituted for N_t/N_0 in Equation 21.20.

Sample Exercise 21.6

Calculating the Age of Objects Using Radioactive Decay

A rock contains 0.257 mg of lead-206 for every milligram of uranium-238. The half-life for the decay of uranium-238 to lead-206 is 4.5×10^9 yr. How old is the rock?

SOLUTION

Analyze We are asked to calculate the age of a rock containing uranium-238 and lead-206, given the half-life of the uranium-238 and the relative amounts of the uranium-238 and lead-206.

Plan Lead-206 is the product of the radioactive decay of uranium-238. We will assume that the only source of lead-206 in the rock is from the decay of uranium-238, which has a known half-life. To apply first-order kinetics expressions (Equations 21.19 and 21.20) to calculate the time elapsed since the rock was formed, we first need to calculate how much initial uranium-238 there was for every 1 mg that remains today.

Solve Let's assume that the rock currently contains 1.000 mg of uranium-238 and therefore 0.257 mg of lead-206. The amount of uranium-238 in the rock when it was first formed therefore equals 1.000 mg plus the quantity that has decayed to lead-206. Because the mass of lead atoms is not the same as the mass of uranium atoms, we cannot just add 1.000 mg and 0.257 mg. We have to multiply the present mass of lead-206 (0.257 mg) by the ratio of the mass number of uranium to that of lead, into which it has decayed. Therefore, the original mass of $^{238}_{92}\text{U}$ was

$$\text{Original } ^{238}_{92}\text{U} = 1.000\text{ mg} + \frac{238}{206}(0.257\text{ mg})$$

$$= 1.297\text{ mg}$$

Using Equation 21.19, we can calculate the decay constant for the process from its half-life:

$$k = \frac{0.693}{4.5 \times 10^9\text{ yr}} = 1.5 \times 10^{-10}\text{ yr}^{-1}$$

Rearranging Equation 21.20 to solve for time, t, and substituting known quantities gives

$$t = -\frac{1}{k}\ln\frac{N_t}{N_0} = -\frac{1}{1.5 \times 10^{-10}\text{ yr}^{-1}}\ln\frac{1.000}{1.297} = 1.7 \times 10^9\text{ yr}$$

Practice Exercise

Cesium-137, which has a half-life of 30.2 yr, is a component of the radioactive waste from nuclear power plants. If the activity due to cesium-137 in a sample of radioactive waste has decreased to 35.2% of its initial value, how old is the sample? (**a**) 1.04 yr (**b**) 15.4 yr (**c**) 31.5 yr (**d**) 45.5 yr (**e**) 156 yr

Sample Exercise 21.7

Calculations Involving Radioactive Decay and Time

If we start with 1.000 g of strontium-90, 0.953 g will remain after 2.00 yr. (**a**) What is the half-life of strontium-90? (**b**) How much strontium-90 will remain after 5.00 yr?

SOLUTION

Analyze (**a**) We are asked to calculate a half-life, $t_{1/2}$, based on data that tell us how much of a radioactive nucleus has decayed in a time interval $t = 2.00$ yr and the information $N_0 = 1.000$ g, $N_t = 0.953$ g. (**b**) We are asked to calculate the amount of a radionuclide remaining after a given period of time.

Plan (**a**) We first calculate the rate constant for the decay, k, and then we use that to compute $t_{1/2}$. (**b**) We need to calculate N_t, the amount of strontium present at time t, using the initial quantity, N_0, and the rate constant for decay, k, calculated in part (a).

Solve

(**a**) Equation 21.20 is solved for the decay constant, k, and then Equation 21.19 is used to calculate half-life, $t_{1/2}$:

$$k = -\frac{1}{t}\ln\frac{N_t}{N_0} = -\frac{1}{2.00\text{ yr}}\ln\frac{0.953\text{ g}}{1.000\text{ g}}$$

$$= -\frac{1}{2.00\text{ yr}}(-0.0481) = 0.0241\text{ yr}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0241\text{ yr}^{-1}} = 28.8\text{ yr}$$

Continued

(**b**) Again using Equation 21.20, with $k = 0.0241\ \text{yr}^{-1}$, we have:

$$\ln \frac{N_t}{N_0} = -kt = -(0.0241\ \text{yr}^{-1})(5.00\ \text{yr}) = -0.120$$

N_t/N_0 is calculated from $\ln(N_t/N_0) = -0.120$ using the e^x or INV LN function of a calculator:

$$\frac{N_t}{N_0} = e^{-0.120} = 0.887$$

Because $N_0 = 1.000$ g, we have:

$$N_t = (0.887)N_0 = (0.887)(1.000\ \text{g}) = 0.887\ \text{g}$$

Practice Exercise

As mentioned in the previous Practice Exercise, cesium-137, a component of radioactive waste, has a half-life of 30.2 yr. If a sample of waste has an initial activity of 15.0 Ci due to cesium-137, how long will it take for the activity due to cesium-137 to drop to 0.250 Ci?
(**a**) 0.728 yr (**b**) 60.4 yr (**c**) 78.2 yr (**d**) 124 yr (**e**) 178 yr

Self-Assessment Exercise

21.16 A one-gram sample of carbon from peat moss has an activity of 0.350 mCi. A reference or modern standard sample yields 0.446 mCi. What is the radiocarbon age of the peat moss given a half-life of $^{14}C = 5700$ years?

(a) Age = 880 yr old
(b) Age = 1400 yr old
(c) Age = 2000 yr old

Exercises

21.17 It has been suggested that strontium-90 (generated by nuclear testing) deposited in the hot desert will undergo radioactive decay more rapidly because it will be exposed to much higher average temperatures. (**a**) Is this a reasonable suggestion? (**b**) Does the process of radioactive decay have an activation energy, like the Arrhenius behavior of many chemical reactions (Section 14.5)?

21.18 It takes 180 minutes for a 200 mg sample of an unknown radioactive substance to decay to 112 mg. What is the half-life of this substance?

21.19 How much time is required for a 5.00 g sample of ^{233}Pa to decay to 0.625 g if the half-life for the beta decay of ^{233}Pa is 27.4 days?

21.20 Iodine-131, which undergoes beta decay, has a half-life of 8.02 days. (**a**) How many beta particles are emitted in 1 min by a 5.00 mg sample of ^{131}I? (**b**) What is the activity of the sample in Bq?

21.21 A wooden artifact from an Indian temple has a ^{14}C activity of 42 counts per minute as compared with an activity of 58.2 counts per minute for a standard zero age. From the half-life of ^{14}C decay, 5715 years, calculate the age of the artifact.

21.22 Iodine-131 is used as a nuclear medicine to treat hyperthyroidism. The half-life of ^{131}I is 8.04 days. How long will it take for a 500 mg sample of ^{131}I to decay into 1% of its original mass?

Answers to Self-Assessment Exercise

21.16 (c)

21.4 Detection of Radioactivity

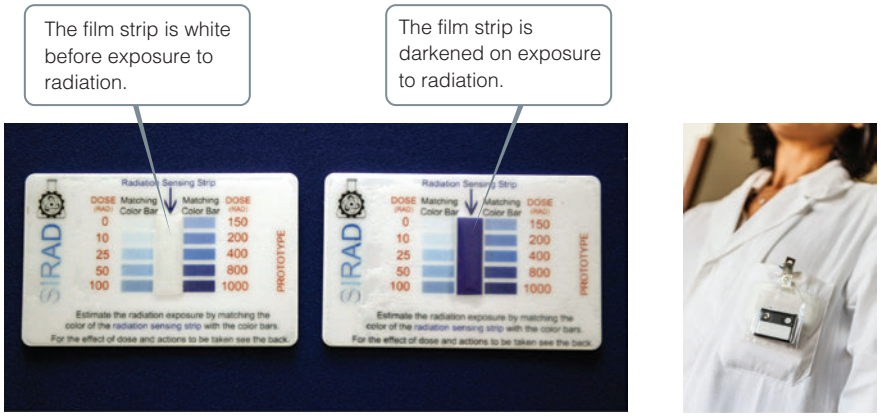


Domestic smoke alarms of the 'ionization' type contain a small amount of radioactive material (usually Am-241). This ionizes the air in a chamber in the alarm allowing a small current to flow. If there is smoke present, this disrupts the flow of ions, which triggers an alarm to sound. This is just one common device in which radionuclides are present. In order to ensure such devices are safe to have in the home the amount of radiation they emit is carefully regulated. In this section, we look at the ways to quantify radiation. By the end of this section, you should

- Appreciate the two main ways to detect radioactivity

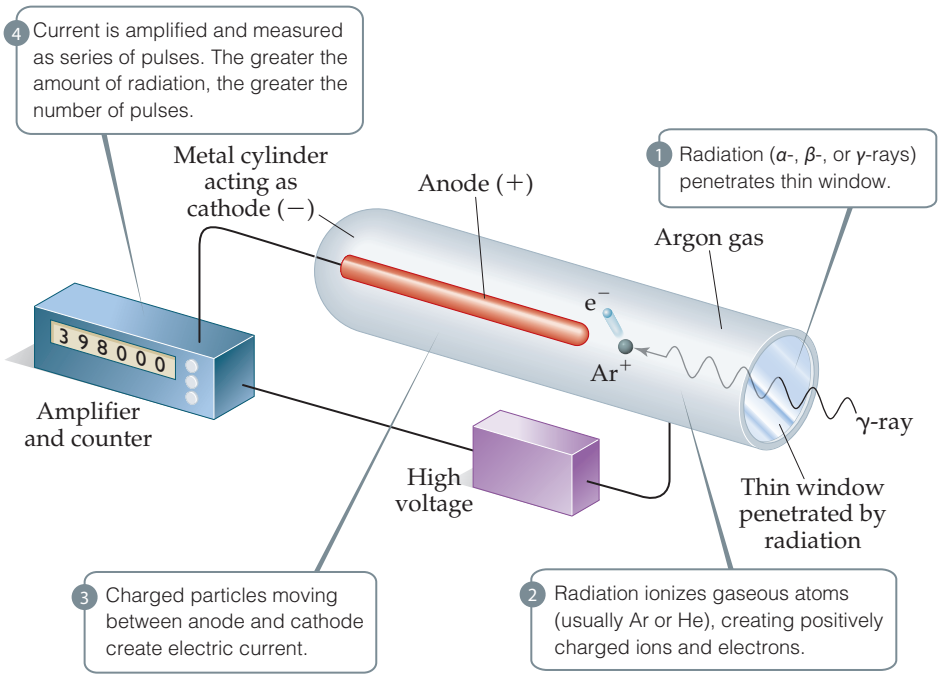
A variety of methods have been devised to detect emissions from radioactive substances. Henri Becquerel discovered radioactivity because radiation caused fogging of photographic plates, and since that time photographic plates and film have been used to detect radioactivity. The radiation affects photographic film in much the same way as X-rays do. The greater the extent of exposure to radiation, the darker the area of the developed negative. People who work with radioactive substances carry film badges to record the extent of their exposure to radiation (**Figure 21.8**).

Go Figure Which type of radiation—alpha, beta, or gamma—is likely to fog a film that is sensitive to X rays?



▲ Figure 21.8 Badge dosimeters monitor the extent to which the individual has been exposed to high-energy radiation. The radiation dose is determined from the extent of darkening of the film in the dosimeter.

Go Figure Which property of the atoms of gas inside a Geiger counter is most relevant to the operation of the device?



▲ **Figure 21.9** **Schematic drawing of a Geiger counter.**

Radioactivity can also be detected and measured by a Geiger counter. The operation of this device is based on the fact that radiation is able to ionize matter. The ions and electrons produced by the ionizing radiation permit conduction of an electrical current. The basic design of a Geiger counter is shown in **Figure 21.9**. A current pulse between the anode and the metal cylinder occurs whenever entering radiation produces ions. Each pulse is counted in order to estimate the amount of radiation.

Some substances, called *phosphors*, emit light when radiation strikes or passes through them. The radioactivity excites the atoms, ions, or molecules of the phosphor to a higher energy state, and they release this energy as light as they return to their ground states. For example, ZnS responds this way to alpha radiation. An instrument called a *scintillation counter* detects and counts the flashes of light produced when radiation strikes the phosphor. The flashes of light are magnified electronically and counted to measure the amount of radiation.

Radiotracers

Because radioisotopes can be detected readily, they can be used to follow an element through its chemical reactions. The incorporation of carbon atoms from CO_2 into glucose during photosynthesis, for example, has been studied using CO_2 enriched in carbon-14:

$$6\ {}^{14}CO_2 + 6\ H_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} {}^{14}C_6H_{12}O_6 + 6\ O_2 \qquad [21.21]$$

Use of the carbon-14 label provides direct experimental evidence that carbon dioxide in the environment is chemically converted to glucose in plants. Analogous labeling experiments using oxygen-18 show that the O_2 produced during photosynthesis comes from water, not carbon dioxide. When it is possible to isolate and purify intermediates and products from reactions, detection devices such as scintillation counters can be used to "follow" the radioisotope as it moves from starting material through intermediates to final product. These types of experiments are useful for identifying elementary steps in a reaction mechanism.

The use of radioisotopes is possible because all isotopes of an element have essentially identical chemical properties. When a small quantity of a radioisotope is mixed with the naturally occurring stable isotopes of the same element, all the isotopes go through the same reactions together. The element's path is revealed by the radioactivity of the radioisotope. Because the radioisotope can be used to trace the path of the element, it is called a **radiotracer**.

CHEMISTRY AND LIFE Medical Applications of Radiotracers

Radiotracers have found wide use as diagnostic tools in medicine. Table 21.6 lists some radiotracers and their uses. These radioisotopes are incorporated into a compound that is administered to the patient, usually intravenously. The diagnostic use of these isotopes is based on the ability of the radioactive compound to localize and concentrate in the organ or tissue under investigation. Iodine-131, for example, has been used to test the activity of the thyroid gland. This gland is the only place in which iodine is incorporated significantly in the body. The patient drinks a solution of NaI containing iodine-131. Only a very small amount is used so that the patient does not receive a harmful dose of radioactivity. A Geiger counter placed close to the thyroid, in the neck region, determines the ability of the thyroid to take up the iodine. A normal thyroid will absorb about 12% of the iodine within a few hours.

The medical applications of radiotracers are further illustrated by *positron emission tomography* (PET). PET is used for clinical diagnosis of many diseases. In this method, compounds containing radionuclides that decay by positron emission are injected into a patient. These compounds are chosen to enable researchers to monitor blood flow, oxygen and glucose metabolic rates, and other biological functions. Some of the most interesting work involves study of the brain, which depends on glucose for most of its energy. Changes in how this sugar is metabolized or used by the brain may signal a disease such as cancer, epilepsy, Parkinson's disease, or schizophrenia.

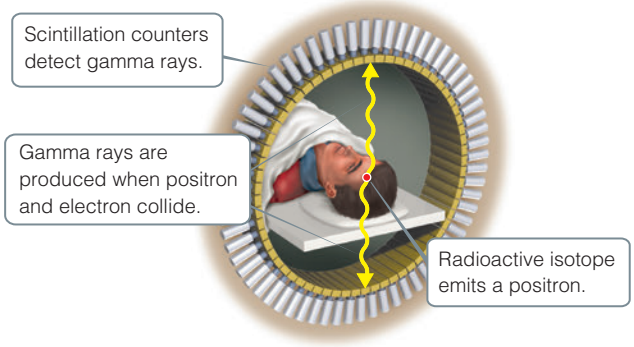
The radionuclides that are most widely used in PET are carbon-11 ($t_{1/2}$ = 20.4 min), fluorine-18 ($t_{1/2}$ = 110 min), oxygen-15 ($t_{1/2}$ = 2 min), and nitrogen-13 ($t_{1/2}$ = 10 min). Glucose, for example, can be labeled with carbon-11. Because the half-lives of positron emitters are so short, they must be generated on site using a cyclotron and the chemist must quickly incorporate the radionuclide into the sugar (or other appropriate) molecule and inject the compound immediately. The patient is placed in an instrument that measures the positron emission and constructs a computer-based image of the organ in which the emitting compound is localized. When the element decays, the emitted positron quickly collides with an electron. The positron and electron are annihilated in the collision, producing two gamma rays that move in opposite directions. The gamma rays are detected by an encircling ring of scintillation counters (Figure 21.10). Because the rays move in opposite directions but were created in the same place at the same time, it is possible to accurately locate the point in the body where the radioactive isotope decayed. The nature of this image provides clues to the presence of disease or other abnormality and helps medical researchers understand how a particular disease affects the functioning of the brain. For example, the images shown in Figure 21.11 reveal that levels of activity in brains of patients with Alzheimer's disease are different from the levels in those without the disease.

Related Exercises: 21.24, 21.64, 21.89

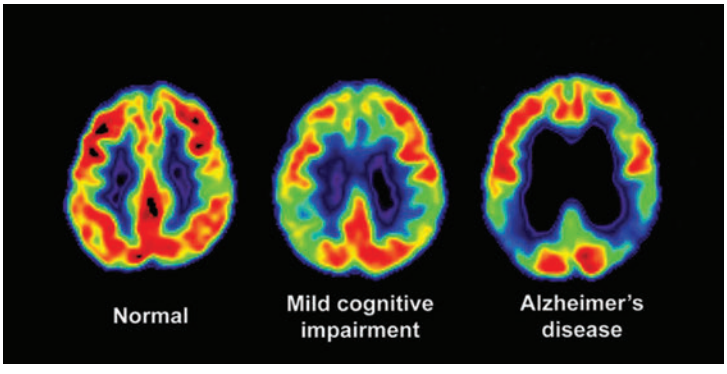
TABLE 21.6 Some Radionuclides Used as Radiotracers

Nuclide	Half-Life	Area of the Body Studied
Iodine-131	8.04 days	Thyroid
Iron-59	44.5 days	Red blood cells
Phosphorus-32	14.3 days	Eyes, liver, tumors
Technetium-99[a]	6.0 hours	Heart, bones, liver, and lungs
Thallium-201	73 hours	Heart, arteries
Sodium-24	14.8 hours	Circulatory system

[a]The isotope of technetium is actually a special isotope of Tc-99 called Tc-99*m*, where the *m* indicates a so-called *metastable* isotope.



▲ **Figure 21.10 Schematic representation of a positron emission tomography (PET) scanner.**



▲ **Figure 21.11 Positron emission tomography (PET) scans showing glucose metabolism levels in the brain.** Red and yellow colors show higher levels of glucose metabolism.

Self-Assessment Exercise

21.23 The luminous dial of an old watch contains a radioisotope and a material called a phosphor, which glows when energized. What type of radiation detector uses a similar mechanism?

(a) A Geiger counter

(b) A scintillation counter

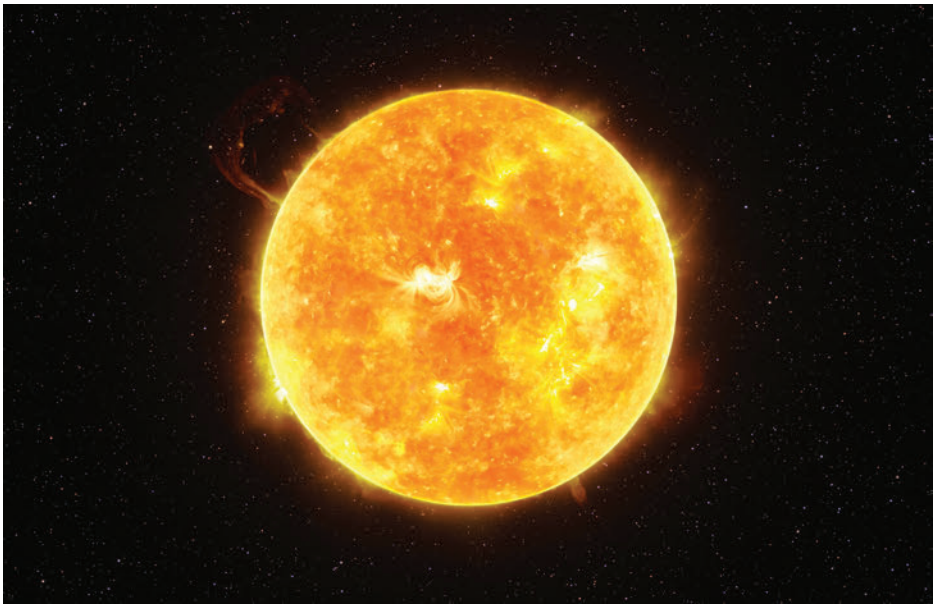
Exercise

21.24 Iodine-131 is a convenient radioisotope to monitor thyroid activity in humans. It is a beta emitter with a half-life of 8.02 days. The thyroid is the only gland in the body that uses iodine. A person undergoing a test of thyroid activity drinks a solution of NaI, in which only a small fraction of the iodide is radioactive. (**a**) Why is NaI a good choice for the source of iodine? (**b**) If a Geiger counter is placed near the person's thyroid (which is near the neck) right after the sodium iodide solution is taken, what will the data look like as a function of time? (**c**) A normal thyroid will take up about 12% of the ingested iodide in a few hours. How long will it take for the radioactive iodide taken up and held by the thyroid to decay to 0.01% of the original amount?

Answers to Self-Assessment Exercises

21.23 (b)

21.5 Energy Changes in Nuclear Reactions



The sun is a huge sphere so hot that nuclei and electrons move independently. It accounts for 99.86% of the mass of our solar system and is composed of 73.8% hydrogen, 24.8% helium, and 1.4% other elements. Most of the Sun's energy is generated in its core by the fusion of hydrogen nuclei to form helium nuclei. Such nuclear reactions can release enormous amounts of energy—far more than the amounts involved in even

the most energetic chemical reactions. The Sun's surface releases this energy as electromagnetic radiation accompanied by a stream of charged particles called solar wind. Bursts of radiation and particles continuously erupt from the surface, producing solar flares.

In this section, we discuss the processes involved in nuclear reactions and our attempts to harness them. By the end of the section, you should be able to

- Calculate mass and energy changes for nuclear reactions.
- Describe the difference between fission and fusion.

Why are the energies associated with nuclear reactions so large, in many cases orders of magnitude larger than those associated with nonnuclear chemical reactions? The answer to this question begins with Einstein's celebrated equation from the theory of relativity that relates mass and energy:

$$E = mc^2 \qquad [21.22]$$

In this equation E stands for energy, m for mass, and c for the speed of light, 2.9979×10^8 m/s. This equation states that mass and energy are equivalent and can be converted into one another. If a system loses mass, it loses energy; if it gains mass, it gains energy. Because the proportionality constant between energy and mass, c^2, is such a large number, even small changes in mass are accompanied by large changes in energy.

The mass changes in chemical reactions are too small to detect. For example, the mass change associated with the combustion of 1 mol of CH_4 (an exothermic process) is -9.9×10^{-9} g. Because the mass change is so small, it is possible to treat chemical reactions as though mass is conserved.

The mass changes and the associated energy changes in nuclear reactions are much greater than those in chemical reactions. The mass change accompanying the radioactive decay of 1 mol of uranium-238, for example, is 50,000 times greater than that for the combustion of 1 mol of CH_4. Let's examine the energy change for the nuclear reaction

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

The masses of the nuclei are $^{238}_{92}$U, 238.0003 u; $^{234}_{90}$Th, 233.9942 u; and $^{4}_{2}$He, 4.0015 u. The mass change, Δm, is the total mass of the products minus the total mass of the reactants. The mass change for the decay of 1 mol of uranium-238 can then be expressed in grams:

$$233.9942\ \text{g} + 4.0015\ \text{g} - 238.0003\ \text{g} = -0.0046\ \text{g}$$

The fact that the system has lost mass indicates that the process is exothermic. All spontaneous nuclear reactions are exothermic.

The energy change per mole associated with this reaction is

$$\begin{aligned}\Delta E &= \Delta(mc^2) = c^2\Delta m \\ &= (2.9979 \times 10^8\ \text{m/s})^2(-0.0046\ \text{g})\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right) \\ &= -4.1 \times 10^{11}\frac{\text{kg-m}^2}{\text{s}^2} = -4.1 \times 10^{11}\ \text{J}\end{aligned}$$

Notice that Δm must be converted to kilograms, the SI unit of mass, to obtain ΔE in joules, the SI unit of energy. The negative sign for the energy change indicates that energy is released in the reaction—in this case, over 400 billion joules per mole of uranium! This energy would provide the average annual household electricity for about 10,000 homes.

Sample Exercise 21.8

Calculating Mass Change in a Nuclear Reaction

How much energy is lost or gained when 1 mol of cobalt-60 undergoes beta decay, $^{60}_{27}\text{Co} \longrightarrow {}^{60}_{28}\text{Ni} + {}^{0}_{-1}\text{e}$? The mass of a $^{60}_{27}\text{Co}$ atom is 59.933819 u, and that of a $^{60}_{28}\text{Ni}$ atom is 59.930788 u.

SOLUTION

Analyze We are asked to calculate the energy change in a nuclear reaction.

Plan We must first calculate the mass change in the process. We are given atomic masses, but we need the masses of the nuclei in the reaction. We calculate these by taking account of the masses of the electrons that contribute to the atomic masses.

Solve

A $^{60}_{27}\text{Co}$ atom has 27 electrons. The mass of an electron is 5.4858×10^{-4} u. (See the list of fundamental constants in the back inside cover.) We subtract the mass of the 27 electrons from the mass of the $^{60}_{27}\text{Co}$ *atom* to find the mass of the $^{60}_{27}\text{Co}$ *nucleus*:

$$59.933819\text{ u} - (27)(5.4858 \times 10^{-4}\text{ u}) = 59.919007\text{ u (or } 59.919007\text{ g/mol)}$$

Likewise, for $^{60}_{28}\text{Ni}$, the mass of the nucleus is:

$$59.930788\text{ u} - (28)(5.4858 \times 10^{-4}\text{ u}) = 59.915428\text{ u (or } 59.915428\text{ g/mol)}$$

The mass change in the nuclear reaction is the total mass of the products minus the mass of the reactant:

$$\begin{aligned}\Delta m &= \text{mass of electron} + \text{mass } {}^{60}_{28}\text{Ni nucleus} - \text{mass of } {}^{60}_{27}\text{Co nucleus}\\ &= 0.00054858\text{ u} + 59.915428\text{ u} - 59.919007\text{ u}\\ &= -0.003030\text{ u}\end{aligned}$$

Thus, when a mole of cobalt-60 decays,

$$\Delta m = -0.003030\text{ g}$$

Because the mass decreases ($\Delta m < 0$), energy is released ($\Delta E < 0$). The quantity of energy released *per mole* of cobalt-60 is calculated using Equation 21.22:

$$\begin{aligned}\Delta E &= c^2\Delta m\\ &= (2.9979 \times 10^8\text{ m/s})^2(-0.003030\text{ g})\left(\frac{1\text{ kg}}{1000\text{ g}}\right)\\ &= -2.723 \times 10^{11}\,\frac{\text{kg-m}^2}{\text{s}^2} = -2.723 \times 10^{11}\text{ J}\end{aligned}$$

Practice Exercise

Positron emission from ^{11}C, $^{11}_{6}\text{C} \longrightarrow {}^{11}_{5}\text{B} + {}^{0}_{+1}\text{e}$, occurs with release of 2.87×10^{11} J per mole of ^{11}C. What is the mass change per mole of ^{11}C in this nuclear reaction? The masses of ^{11}B and ^{11}C are 11.009305 and 11.011434 u, respectively.

Nuclear Binding Energies

Scientists discovered in the 1930s that the masses of nuclei are always less than the masses of the individual nucleons of which they are composed. For example, the helium-4 nucleus (an alpha particle) has a mass of 4.00150 u. The mass of a proton is 1.00728 u and that of a neutron is 1.00866 u. Consequently, two protons and two neutrons have a total mass of 4.03188 u:

$$\begin{aligned}\text{Mass of two protons} &= 2(1.00728\text{ u}) = 2.01456\text{ u}\\ \text{Mass of two neutrons} &= 2(1.00866\text{ u}) = \underline{2.01732\text{ u}}\\ \text{Total mass} &= 4.03188\text{ u}\end{aligned}$$

TABLE 21.7 Mass Defects and Binding Energies for Three Nuclei

Nucleus	Mass of Nucleus (u)	Mass of Individual Nucleons (u)	Mass Defect (u)	Binding Energy (J)	Binding Energy per Nucleon (J)
$^{4}_{2}\text{He}$	4.00150	4.03188	0.03038	4.53×10^{-12}	1.13×10^{-12}
$^{56}_{26}\text{Fe}$	55.92068	56.44914	0.52846	7.90×10^{-11}	1.41×10^{-12}
$^{238}_{92}\text{U}$	238.00031	239.93451	1.93420	2.89×10^{-10}	1.21×10^{-12}

The mass of the individual nucleons is 0.03038 u greater than that of the helium-4 nucleus:

$$\begin{aligned}\text{Mass of two protons and two neutrons} &= 4.03188\ \text{u}\\ \text{Mass of } ^{4}_{2}\text{He nucleus} &= \underline{4.00150\ \text{u}}\\ \text{Mass difference } \Delta m &= 0.03038\ \text{u}\end{aligned}$$

The mass difference between a nucleus and its constituent nucleons is called the **mass defect**. The origin of the mass defect is readily understood if we consider that energy must be added to a nucleus to break it into separated protons and neutrons:

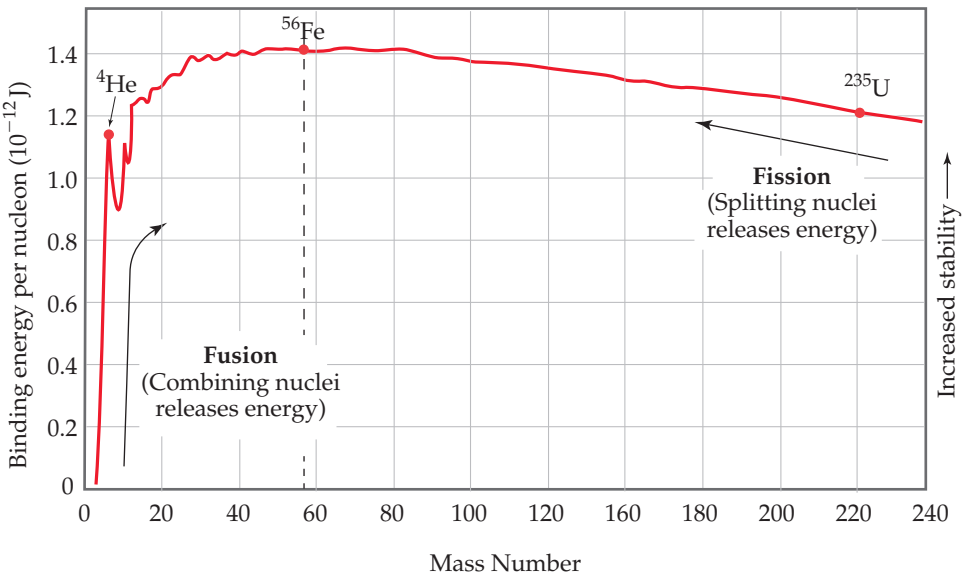
$$\text{Energy} + {}^{4}_{2}\text{He} \longrightarrow 2\,{}^{1}_{1}\text{H} + 2\,{}^{1}_{0}\text{n} \qquad [21.23]$$

By Einstein's relation, the addition of energy to a system must be accompanied by a proportional increase in mass. The mass change we just calculated for the conversion of helium-4 into separated nucleons is $\Delta m = 0.03038$ u. Therefore, the energy required for this process is

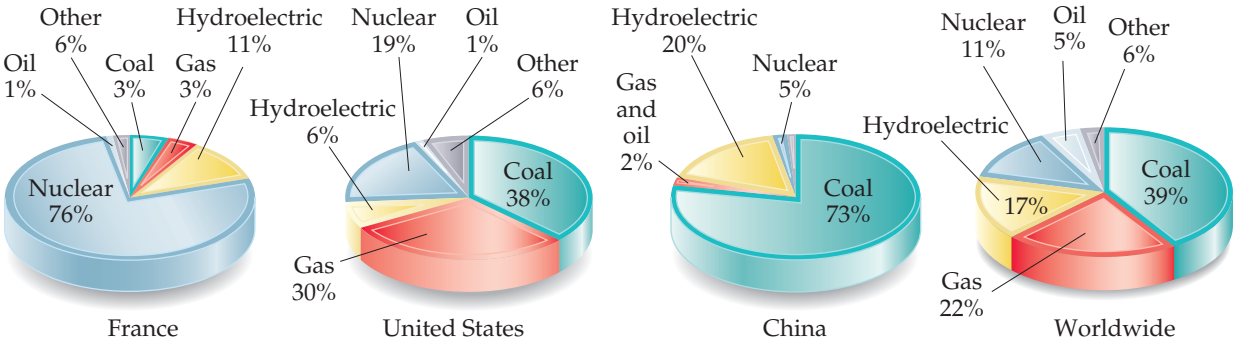
$$\begin{aligned}\Delta E &= c^2 \Delta m\\ &= (2.9979 \times 10^{8}\ \text{m/s})^2 (0.03038\ \cancel{\text{u}}) \left(\frac{1\ \cancel{\text{g}}}{6.022 \times 10^{23}\ \cancel{\text{u}}}\right)\left(\frac{1\ \text{kg}}{1000\ \cancel{\text{g}}}\right)\\ &= 4.534 \times 10^{-12}\ \text{J}\end{aligned}$$

The energy required to separate a nucleus into its individual nucleons is called the **nuclear binding energy**. The mass defect and nuclear binding energy for three elements are compared in Table 21.7.

Values of binding energies per nucleon can be used to compare the stabilities of different combinations of nucleons (such as two protons and two neutrons arranged either as $^{4}_{2}\text{He}$ or as $2\,{}^{2}_{1}\text{H}$). Figure 21.12 shows average binding energy per nucleon plotted



▲ **Figure 21.12 Nuclear binding energies.** The average binding energy per nucleon increases initially as the mass number increases and then decreases slowly. Because of these trends, fusion of light nuclei and fission of heavy nuclei are exothermic processes.



▲ **Figure 21.13** **Sources of electricity generation, worldwide and for select countries.** (***Sources:*** The Shift Project and the World Bank, 2014 data)

against mass number. Binding energy per nucleon at first increases in magnitude as mass number increases, reaching about 1.4×10^{-12} J for nuclei whose mass numbers are in the vicinity of iron-56. It then decreases slowly to about 1.2×10^{-12} J for very heavy nuclei. *This trend indicates that nuclei of intermediate mass numbers are more tightly bound (and therefore more stable) than those with either smaller or larger mass numbers.*

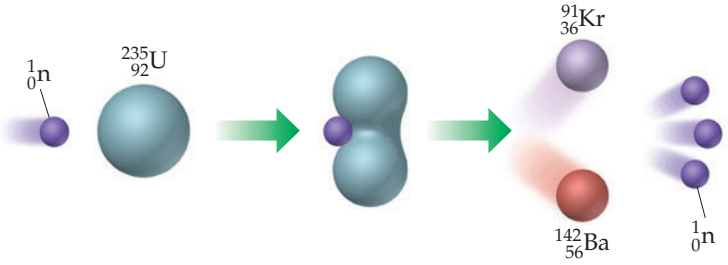
This trend has two significant consequences: First, heavy nuclei gain stability and therefore give off energy if they are fragmented into two midsized nuclei. This process, known as **fission**, is used to generate energy in nuclear power plants. Second, because of the sharp increase in the graph for small mass numbers, even greater amounts of energy are released if very light nuclei are combined, or fused together, to give more massive nuclei. This **fusion** process is the essential energy-producing process in the Sun and other stars.

Nuclear Power: Fission

Nuclear fission is the process used to generate energy in nuclear power plants. Over 11% of the electricity generated worldwide comes from nuclear power plants, though the percentage varies from one country to the next, as **Figure 21.13** shows. There are 440 commercial nuclear power plants in operation in 30 countries, and approximately another 65 are under construction.

Most nuclear reactors rely on the fission of uranium-235. This was the first nuclear fission reaction to be discovered. This nucleus, as well as those of uranium-233 and plutonium-239, undergoes fission when struck by a slow-moving neutron (**Figure 21.14**).*

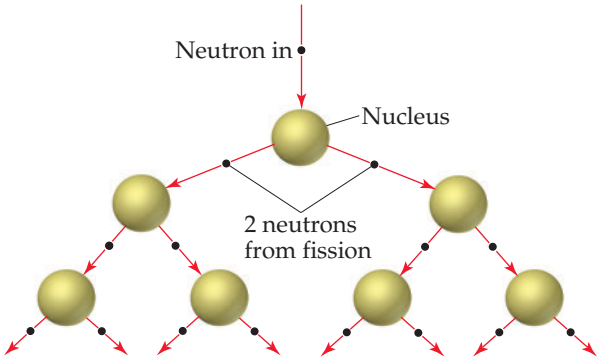
Go Figure What is the relationship between the sum of the mass numbers on the two sides of this reaction?



▲ **Figure 21.14** **Uranium-235 fission.** This is just one of many fission patterns. In this reaction, 3.5×10^{-11} J of energy is released per ^{235}U nucleus that is split.

*Other heavy nuclei can also undergo fission. However, these three are the only ones of practical importance.

Go Figure If this figure were extended one more "generation" down, how many neutrons would be produced?



▲ **Figure 21.15** **Fission chain reaction.**

A heavy nucleus can split in many ways, giving rise to a variety of smaller nuclei. Two ways that the uranium-235 nucleus splits, for instance, are

$$^{1}_{0}\text{n} + {}^{235}_{92}\text{U} \longrightarrow {}^{137}_{52}\text{Te} + {}^{97}_{40}\text{Zr} + 2\,{}^{1}_{0}\text{n} \qquad [21.24]$$

$$^{1}_{0}\text{n} + {}^{235}_{92}\text{U} \longrightarrow {}^{142}_{56}\text{Ba} + {}^{91}_{36}\text{Kr} + 3\,{}^{1}_{0}\text{n} \qquad [21.25]$$

The nuclei produced in Equations 21.24 and 21.25—called the *fission products*—are themselves radioactive and undergo further nuclear decay. More than 200 isotopes of 35 elements have been found among the fission products of uranium-235. Most of them are radioactive.

Slow-moving neutrons are required for the fission of uranium-235 because the process involves initial absorption of the neutron by the nucleus. The resulting more massive nucleus is extremely unstable and spontaneously undergoes fission. Fast neutrons tend to bounce off the nucleus, and little fission occurs.

Note that the coefficients of the neutrons produced in Equations 21.24 and 21.25 are 2 and 3, respectively. On average, 2.4 neutrons are produced by every fission of a uranium-235 nucleus. If one fission produces two neutrons, the two neutrons can cause two additional fissions, each producing two neutrons. The four neutrons thereby released can produce four fissions, and so forth, as shown in **Figure 21.15**. The number of fissions and the energy released quickly escalate, and if the process is unchecked, the result is a violent explosion. Reactions that multiply in this fashion are called **chain reactions**.

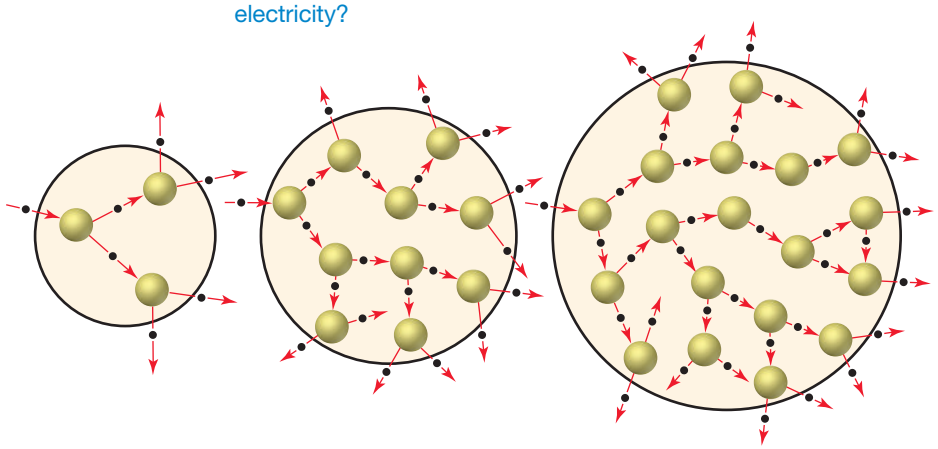
For a fission chain reaction to occur, the sample of fissionable material must have a certain minimum mass. Otherwise, neutrons escape from the sample before they have the opportunity to strike other nuclei and cause additional fission. The amount of fissionable material large enough to maintain a chain reaction with a constant rate of fission is called the **critical mass**. When a critical mass of material is present, one neutron on average from each fission is subsequently effective in producing another fission and the fission continues at a constant, controllable rate. The critical mass of uranium-235 is about 50 kg for a bare sphere of the metal.*

If more than a critical mass of fissionable material is present, very few neutrons escape. The chain reaction thus multiplies the number of fissions, which can lead to a nuclear explosion. A mass in excess of a critical mass is referred to as a **supercritical mass**. The effect of mass on a fission reaction is illustrated in **Figure 21.16**.

Figure 21.17 shows a schematic diagram of the first atomic bomb used in warfare, the bomb, code-named "Little Boy," that was dropped on Hiroshima, Japan, on August 6, 1945. The bomb contained about 64 kg of uranium-235, which had been separated

*The exact value of the critical mass depends on the shape of the radioactive substance. The critical mass can be reduced if the radioisotope is surrounded by a material that reflects some neutrons.

Go Figure Which of these criticality scenarios—subcritical, critical, or supercritical—is desirable in a nuclear power plant that generates electricity?

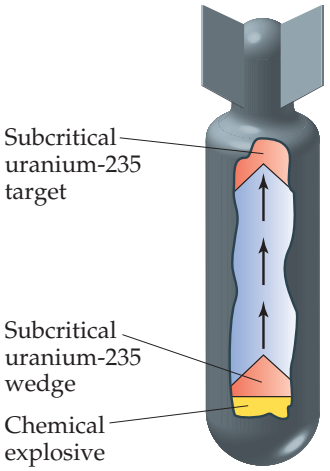


Subcritical mass
Rate of neutron loss > rate of neutron creation by fission

Critical mass
Rate of neutron loss = rate of neutron creation by fission

Supercritical mass
Rate of neutron loss < rate of neutron creation by fission

▲ **Figure 21.16** **Subcritical, critical, and supercritical nuclear fission.**



▲ **Figure 21.17** **Schematic drawing of an atomic bomb.** A conventional explosive is used to bring two subcritical masses together to form a supercritical mass.

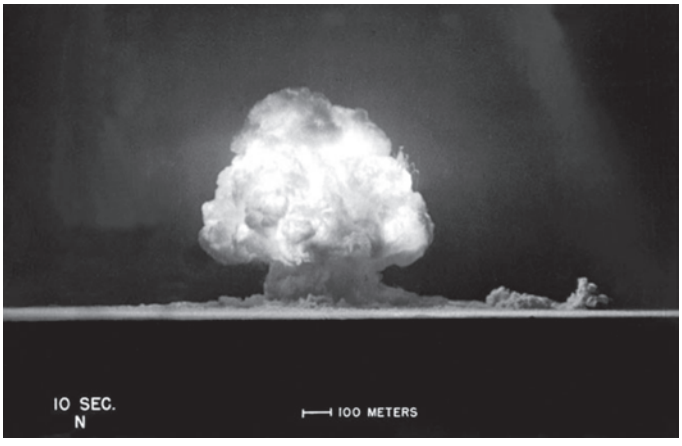
A CLOSER LOOK The Dawning of the Nuclear Age

Uranium-235 fission was first achieved during the late 1930s by Enrico Fermi and coworkers in Rome and shortly thereafter by Otto Hahn and coworkers in Berlin. Both groups were trying to produce transuranium elements. In 1938, Hahn identified barium among his reaction products. He was puzzled by this observation and questioned the identification because the presence of barium was so unexpected. He sent a letter describing his experiments to Lise Meitner, a former coworker who had been forced to leave Germany because of the anti-Semitism of the Third Reich and had settled in Sweden. She surmised that Hahn's experiment indicated a nuclear process was occurring in which the uranium-235 split. She called this process *nuclear fission*.

Meitner passed word of this discovery to her nephew, Otto Frisch, a physicist working at Niels Bohr's institute in Copenhagen. Frisch repeated the experiment, verifying Hahn's observations, and found that tremendous energies were involved. In January 1939, Meitner and Frisch published a short article describing the reaction. In March 1939, Leo Szilard and Walter Zinn at Columbia University discovered that more neutrons are produced than are used in each fission. As we have seen, this result allows a chain reaction to occur.

News of these discoveries and an awareness of their potential use in explosive devices spread rapidly within the scientific community. Several scientists finally persuaded Albert Einstein, the most famous physicist of the time, to write a letter to President Franklin D. Roosevelt explaining the implications of these discoveries. Einstein's letter, written in August 1939, outlined the possible military applications of nuclear fission and emphasized the danger that weapons based on fission would pose if they were developed by the Nazis. Roosevelt judged it imperative that the United States investigate the possibility of such weapons. Late in 1941, the decision was made to build a bomb based on the fission reaction. An enormous research project, known as the Manhattan Project, began.

On December 2, 1942, the first artificial self-sustaining nuclear fission chain reaction was achieved in an abandoned squash court at the University of Chicago. This accomplishment led to the development of the first atomic bomb, at Los Alamos National Laboratory in New Mexico in July 1945 (**Figure 21.18**). In August 1945 the United States dropped atomic bombs on two Japanese cities, Hiroshima and Nagasaki. The nuclear age had arrived, albeit in a sadly destructive fashion. Humanity has struggled with the conflict between the positive potential of nuclear energy and its terrifying potential as a weapon ever since.



▲ **Figure 21.18** **The Trinity test for the atom bomb developed during World War II.** The first human-made nuclear explosion took place on July 16, 1945, on the Alamogordo test range in New Mexico.

from the nonfissionable uranium-238 primarily by gaseous diffusion of uranium hexafluoride, UF_6. To trigger the fission reaction, two subcritical masses of uranium-235 were slammed together using chemical explosives. The combined masses of the uranium formed a supercritical mass, which led to a rapid, uncontrolled chain reaction and, ultimately, a nuclear explosion. The energy released by the bomb dropped on Hiroshima was equivalent to that of 16,000 tons of TNT (it therefore is called a *16-kiloton* bomb). Unfortunately, the basic design of a fission-based atomic bomb is quite simple, and the fissionable materials are potentially available to any nation with a nuclear reactor. The combination of design simplicity and materials availability has generated international concerns about the proliferation of atomic weapons.

Nuclear Reactors

Nuclear power plants use nuclear fission to generate energy. The core of a typical nuclear reactor consists of four principal components: fuel elements, control rods, a moderator, and a primary coolant (**Figure 21.19**). The fuel is a fissionable substance, such as uranium-235. The natural isotopic abundance of uranium-235 is only 0.7%, too low to sustain a chain reaction in most reactors. Therefore, the ^{235}U content of the fuel must be enriched to 3–5% for use in a reactor. The *fuel elements* contain enriched uranium in the form of UO_2 pellets encased in zirconium or stainless steel tubes.

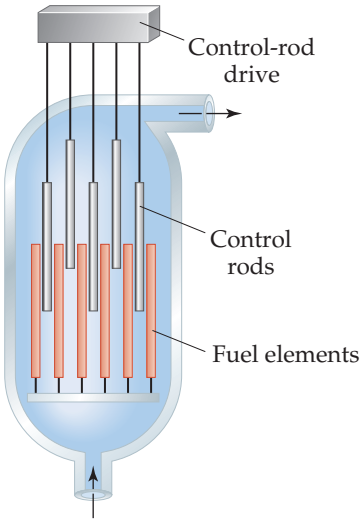
The *control rods* are composed of materials that absorb neutrons, such as boron-10 or an alloy of silver, indium, and cadmium. These rods regulate the flux of neutrons to keep the reaction chain self-sustaining and also prevent the reactor core from overheating.*

The probability that a neutron will trigger fission of a ^{235}U nucleus depends on the speed of the neutron. The neutrons produced by fission have high speeds (typically in excess of 10,000 km/s). The function of the *moderator* is to slow down the neutrons (to speeds of a few kilometers per second) so that they can be captured more readily by the fissionable nuclei. The moderator is typically either water or graphite.

The *primary coolant* is a substance that transports the heat generated by the nuclear chain reaction away from the reactor core. In a *pressurized water reactor*, which is the most common commercial reactor design, water acts as both the moderator and the primary coolant.

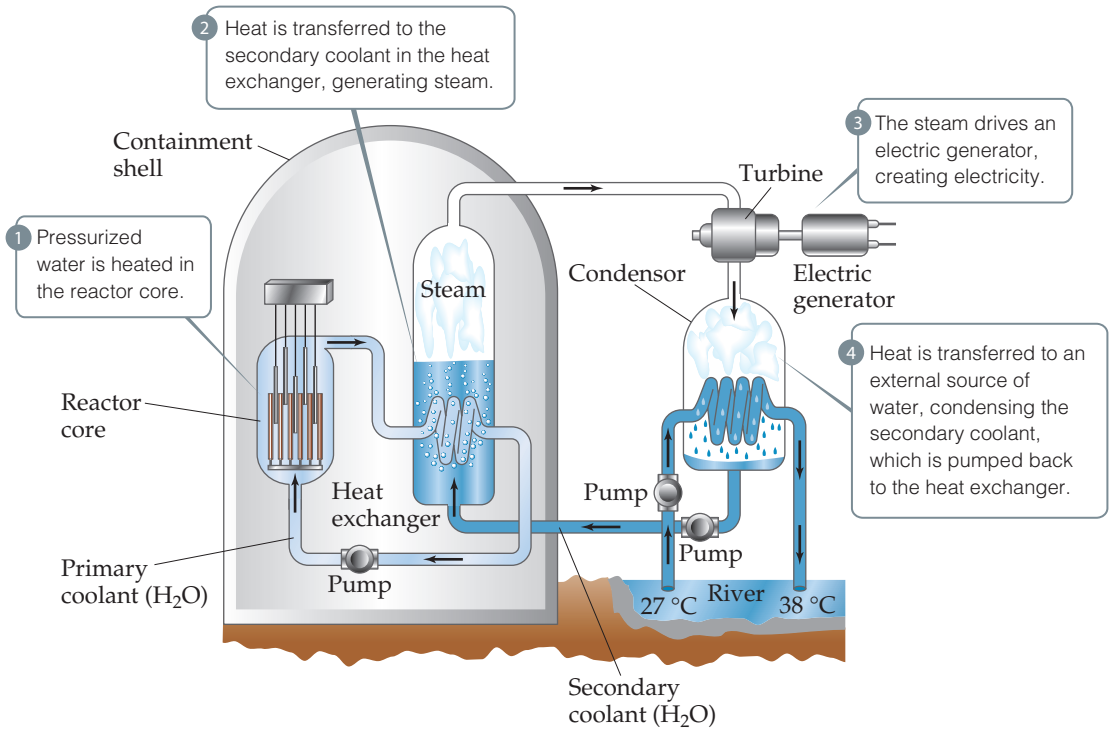
The design of a nuclear power plant is basically the same as that of a power plant that burns fossil fuel (except that the burner is replaced by a reactor core). The nuclear power plant design shown in **Figure 21.20**, a pressurized water reactor, is currently the most popular. The primary coolant passes through the core in a closed system, which lessens the chance that radioactive products could escape the core. As an added safety precaution, the reactor is surrounded by a reinforced concrete *containment shell* to shield personnel and nearby residents from radiation and to protect the reactor from external forces. After passing through the reactor core, the very hot primary coolant passes through a heat exchanger where much of its heat is transferred to a *secondary coolant*, converting the latter to high-pressure steam that is used to drive a turbine. The secondary coolant is then condensed by transferring heat to an external source of water, such as a river or lake. The cooling systems of nuclear power plants are necessary for proper and safe operation. The nuclear disaster in Fukushima, Japan, in March 2011 occurred when a tsunami damaged the reactor cooling systems, resulting in a large-scale release of radioactive materials.

Although about two-thirds of all commercial reactors are pressurized water reactors, there are several variations on this basic design, each with advantages and disadvantages. A *boiling water reactor* generates steam by boiling the primary coolant; thus, no secondary coolant is needed. The reactors at Fukushima, Japan, were boiling water reactors. Pressurized water reactors and boiling water reactors are collectively referred to as *light water reactors* because they use H_2O as moderator and primary coolant. A *heavy water reactor* uses D_2O (D = deuterium, ^2H) as moderator and primary coolant, and a *gas-cooled reactor* uses a gas, typically CO_2, as primary coolant and graphite as the moderator.



▲ **Figure 21.19 Schematic diagram of a pressurized water reactor core.**

*The reactor core cannot reach supercritical levels and explode with the violence of an atomic bomb because the concentration of uranium-235 is too low. However, if the core overheats, sufficient damage can lead to release of radioactive materials into the environment.



▲ **Figure 21.20** **Basic design of a pressurized water reactor nuclear power plant.**

Use of either D_2O or graphite as the moderator has the advantage that both substances absorb fewer neutrons than H_2O. Consequently, the uranium fuel does not need to be as enriched.

Nuclear Waste

The fission products that accumulate as a reactor operates decrease the efficiency of the reactor by capturing neutrons. For this reason, commercial reactors must be stopped periodically to either replace or reprocess the nuclear fuel. When the fuel elements are removed from the reactor, they are initially very radioactive. It was originally intended that they be stored for several months in pools at the reactor site to allow decay of short-lived radioactive nuclei. They were then to be transported in shielded containers to reprocessing plants where the unspent fuel would be separated from the fission products. Reprocessing plants have been plagued with operational difficulties, however, and there is intense opposition in some countries to the transport of nuclear wastes on the nation's roads and rails. Spent fuel is reprocessed, however, in France, Russia, the United Kingdom, India, and Japan.

Storage of spent nuclear fuel poses a major problem because the fission products are extremely radioactive. It is estimated that 10 half-lives are required for their radioactivity to reach levels acceptable for biological exposure. Based on the 28.8-yr half-life of strontium-90, one of the longer-lived and most dangerous of the products, the wastes must be stored for nearly 300 yr. Plutonium-239 is one of the by-products present in spent fuel elements. It is formed by absorption of a neutron by uranium-238, followed by two successive beta emissions. (Remember that most of the uranium in the fuel elements is uranium-238.) If the elements are reprocessed, the plutonium-239 is largely recovered because it can be used as a nuclear fuel. However, if the plutonium is not removed, spent elements must be stored for a very long time because plutonium-239 has a half-life of 24,000 yr.

A *fast breeder reactor* offers one approach to getting more power out of existing uranium sources and potentially reducing radioactive waste. This type of reactor is so named because it creates ("breeds") more fissionable material than it consumes. The reactor operates without a moderator, which means the neutrons used are not slowed down.

In order to capture the fast neutrons, the fuel must be highly enriched with both uranium-235 and plutonium-239. Water cannot be used as a primary coolant because it would moderate the neutrons, and so a liquid metal, usually sodium, is used. The core is surrounded by a blanket of uranium-238 that captures neutrons that escape the core, producing plutonium-239 in the process. The plutonium can later be separated by reprocessing and used as fuel in a future cycle.

Because fast neutrons are more effective at decaying many radioactive nuclides, the material separated from the uranium and plutonium during reprocessing is less radioactive than waste from other reactors. However, generation of relatively high levels of plutonium coupled with the need for reprocessing is problematic in terms of nuclear nonproliferation. Thus, political factors coupled with increased safety concerns and higher operational costs make fast breeder reactors quite rare.

A considerable amount of research is being devoted to disposal of radioactive wastes. At present, the most attractive possibilities appear to be formation of glass, ceramic, or synthetic rock from the wastes as a means of immobilizing them. These solid materials would then be placed in containers of high corrosion resistance and durability and buried deep underground. The process of selecting appropriate deep repositories for high-level waste and spent fuel is now under way in several countries.

In spite of these difficulties, nuclear power is making a modest comeback as an energy source. Concerns about climate change caused by escalating atmospheric CO_2 levels have increased support for nuclear power as a major energy source in the future. Increasing demand for power in rapidly developing countries, particularly China, has sparked a rise in construction of new nuclear power plants in those parts of the world.

Nuclear Power: Fusion

Energy is produced when light nuclei fuse into heavier ones. Reactions of this type are responsible for the energy produced by the Sun. The following reactions are among the numerous fusion processes believed to occur in the Sun:

$$^{1}_{1}\mathrm{H} + {}^{1}_{1}\mathrm{H} \longrightarrow {}^{2}_{1}\mathrm{H} + {}^{0}_{+1}\mathrm{e} \qquad [21.26]$$

$$^{1}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \longrightarrow {}^{3}_{2}\mathrm{He} \qquad [21.27]$$

$$^{3}_{2}\mathrm{He} + {}^{3}_{2}\mathrm{He} \longrightarrow {}^{4}_{2}\mathrm{He} + 2\,{}^{1}_{1}\mathrm{H} \qquad [21.28]$$

$$^{3}_{2}\mathrm{He} + {}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{0}_{+1}\mathrm{e} \qquad [21.29]$$

Fusion is appealing as an energy source because of the availability of light isotopes on Earth and because fusion products are generally not radioactive. Despite this fact, fusion is not presently used to generate energy. The problem is that extremely high temperatures and pressures are needed to overcome the electrostatic repulsion between nuclei in order to fuse them. The lowest temperature required for any fusion is about 40,000,000 K, the temperature needed to fuse deuterium and tritium:

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} \qquad [21.30]$$

Fusion reactions are therefore also known as **thermonuclear reactions**.

Such high temperatures have been achieved by using an atomic bomb to initiate fusion. This is the operating principle behind a thermonuclear, or hydrogen, bomb. This approach is obviously unacceptable, however, for a power generation plant.*

Numerous problems must be overcome before fusion becomes a practical energy source. In addition to the high temperatures necessary to initiate the reaction, there is the problem of confining the reaction. No known structural material is able to withstand the enormous temperatures necessary for fusion. Much research has centered on the use of an apparatus called a *tokamak*, which uses strong magnetic fields to contain and to heat the reaction. Temperatures of over 100,000,000 K have been achieved in a tokamak. Unfortunately, scientists have not yet been able to generate more power than is consumed over a sustained period of time.

*Historically, a nuclear weapon that relies solely on a fission process to release energy is called an atomic bomb, whereas one that also releases energy via a fusion reaction is called a hydrogen bomb.

A CLOSER LOOK Nuclear Synthesis of the Elements

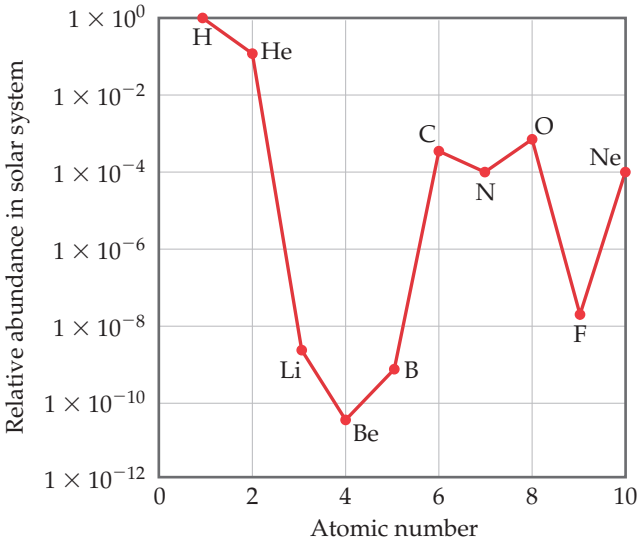
The lightest elements—hydrogen and helium along with very small amounts of lithium and beryllium—were formed as the universe expanded in the moments following the Big Bang. All the heavier elements owe their existence to subsequent nuclear reactions that occur in stars. These heavier elements are not all created in equal amounts, however. In our solar system, for example, carbon and oxygen are a million times more abundant than lithium and boron, and over 100 million times more abundant than beryllium (**Figure 21.21**)! In fact, of the elements heavier than helium, carbon and oxygen are the most abundant. This is more than an academic curiosity given the fact that these elements, together with hydrogen, are the most important elements for life on Earth. Let's look at the factors responsible for the relatively high abundance of carbon and oxygen in the universe.

A star is born from a cloud of gas and dust called a *nebula*. When conditions are right, gravitational forces collapse the cloud, and its core density and temperature rise until nuclear fusion commences. Hydrogen nuclei fuse to form deuterium, $^{2}_{1}H$, and eventually $^{4}_{2}He$ through the reactions shown in Equations 21.26—21.29. Because $^{4}_{2}He$ has a larger binding energy than any of its immediate neighbors (Figure 21.12), these reactions release an enormous amount of energy. This process, called *hydrogen burning*, is the dominant process for most of a star's lifetime.

Once a star's supply of hydrogen is nearly exhausted, several important changes occur as the star enters the next the phase of its life, and is transformed into a *red giant*. The decrease in nuclear fusion causes the core to contract, triggering an increase in core temperature and pressure. At the same time, the outer regions expand and cool enough to make the star emit red light (thus, the name *red giant*). The star now must use $^{4}_{2}He$ nuclei as its fuel. The simplest reaction that can occur in the He-rich core, fusion of two alpha particles to form a $^{8}_{4}Be$ nucleus, does occur. The binding energy per nucleon for $^{8}_{4}Be$ is very slightly smaller than that for $^{4}_{2}He$, so this fusion process is very slightly endothermic. The $^{8}_{4}Be$ nucleus is highly unstable (half-life of 7×10^{-17} s) and so falls apart almost immediately. In a tiny fraction of cases, however, a third $^{4}_{2}He$ collides with a $^{8}_{4}Be$ nucleus before it decays, forming carbon-12:

$$^{4}_{2}He + {}^{4}_{2}He \longrightarrow {}^{8}_{4}Be$$

$$^{8}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C$$



▲ **Figure 21.21 Relative abundance of elements 1–10 in the solar system.** Note the logarithmic scale used for the *y*-axis.

Some of the $^{12}_{6}C$ nuclei go on to react with alpha particles to form oxygen-16:

$$^{12}_{6}C + {}^{4}_{2}He \longrightarrow {}^{16}_{8}O$$

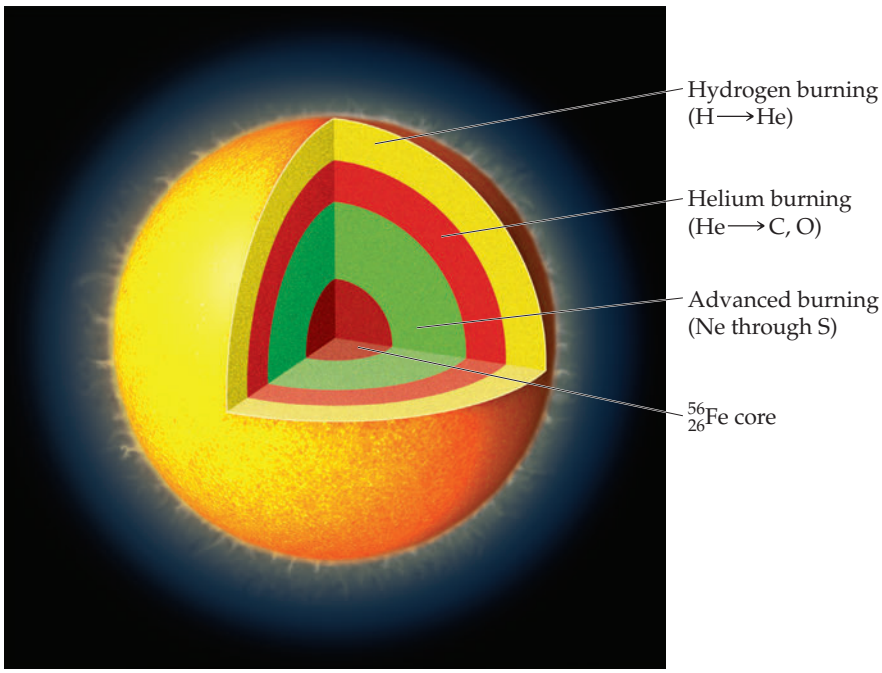
This stage of nuclear fusion is called *helium burning*. Notice that carbon, element 6, is formed without prior formation of elements 3, 4, and 5, explaining in part their unusually low abundance. Nitrogen is relatively abundant because it can be produced from carbon through a series of reactions involving proton capture and positron emission.

Most stars gradually cool and dim as the helium is converted to carbon and oxygen, ending their lives as *white dwarfs*, a phase in which stars become incredibly dense—generally about one million times denser than the Sun. The extreme density of white dwarfs is accompanied by much higher temperatures and pressures at the core, where a variety of fusion processes lead to synthesis of the elements from neon to sulfur. These fusion reactions are collectively called *advanced burning*.

Eventually, progressively heavier elements form at the core until it becomes predominantly ^{56}Fe, as shown in **Figure 21.22**. Because this is such a stable nucleus, further fusion to heavier nuclei consumes energy rather than releasing it. When this happens, the fusion reactions that power the star diminish, and immense gravitational forces lead to a dramatic collapse called a supernova *explosion*. Neutron capture coupled with subsequent radioactive decays in the dying moments of such a star are responsible for the presence of all elements heavier than iron and nickel.

Without these dramatic supernova events in the past history of the universe, heavier elements that are so familiar to us, such as silver, gold, iodine, lead, and uranium, would not exist.

Related Exercises: 21.81, 21.83



▲ **Figure 21.22 Fusion processes going on in a red giant just prior to a supernova explosion.**

Self-Assessment Exercise

21.25 Based on the following atomic mass values, calculate the energy released per mole in the following nuclear reaction:

^{1}H 1.00782 u; ^{2}H, 2.01410 u; ^{3}He, 3.01603 u; ^{4}He, 4.00260 u

$$^{2}_{1}H + {}^{3}_{2}He \longrightarrow {}^{1}_{1}H + {}^{4}_{2}He$$

(a) -5.909×10^{3} J

(b) -1.771×10^{12} J

(b) -1.771×10^{15} J

21.26 Would fusing two stable nuclei that have mass numbers in the vicinity of 100 be an energy-releasing process?

(a) Yes

(b) No

Exercises

21.27 How much energy must be supplied to break a single ^{21}Ne nucleus into separated protons and neutrons if the nucleus has a mass of 20.98846 u? What is the nuclear binding energy for 1 mol of ^{21}Ne?

21.28 The atomic masses of nitrogen-14, titanium-48, and xenon-129 are 13.999234 u, 47.935878 u, and 128.904779 u, respectively. For each isotope, calculate (**a**) the nuclear mass, (**b**) the nuclear binding energy, (**c**) the nuclear binding energy per nucleon.

21.29 The energy from solar radiation falling on Earth is 1.07×10^{16} kJ/min. (**a**) How much loss of mass from the Sun occurs in one day from just the energy falling on Earth? (**b**) If the energy released in the reaction

$$^{235}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n$$

(^{235}U nuclear mass, 234.9935 u; ^{141}Ba nuclear mass, 140.8833 u; ^{92}Kr nuclear mass, 91.9021 u) is taken as typical of that occurring in a nuclear reactor, what mass of uranium-235 is required to equal 0.10% of the solar energy that falls on Earth in 1.0 day?

21.30 Using Figure 21.12, predict which of the following nuclei are likely to have the largest mass defect per nucleon: (**a**) ^{27}Al, (**b**) ^{55}Mn, (**c**) ^{165}Ho, (**d**) ^{209}Bi?

21.31 Which of the following statements about the uranium used in nuclear reactors is or are true? (i) Natural uranium has too little ^{235}U to be used as a fuel. (ii) ^{238}U cannot be used as a fuel because it forms a supercritical mass too easily. (iii) To be used as fuel, uranium must be enriched so that it is more than 50% ^{235}U in composition. (iv) The neutron-induced fission of ^{235}U releases more neutrons per nucleus than fission of ^{238}U.

21.32 (**a**) What is the function of the moderator in a nuclear reactor? (**b**) What substance acts as the moderator in a pressurized water generator? (**c**) What other substances are used as a moderator in nuclear reactor designs?

21.33 Complete and balance the nuclear equations for the following fission reactions:

(**a**) $^{239}_{94}Pu + {}^{1}_{0}n \longrightarrow {}^{137}_{52}Te + {}^{100}_{42}Mo + _$

(**b**) $^{256}_{100}Fm + {}^{1}_{0}n \longrightarrow {}^{113}_{46}Pd + _ + 4\,{}^{1}_{0}n$

21.34 Which type or types of nuclear reactors have these characteristics?

(**a**) Can use natural uranium as a fuel

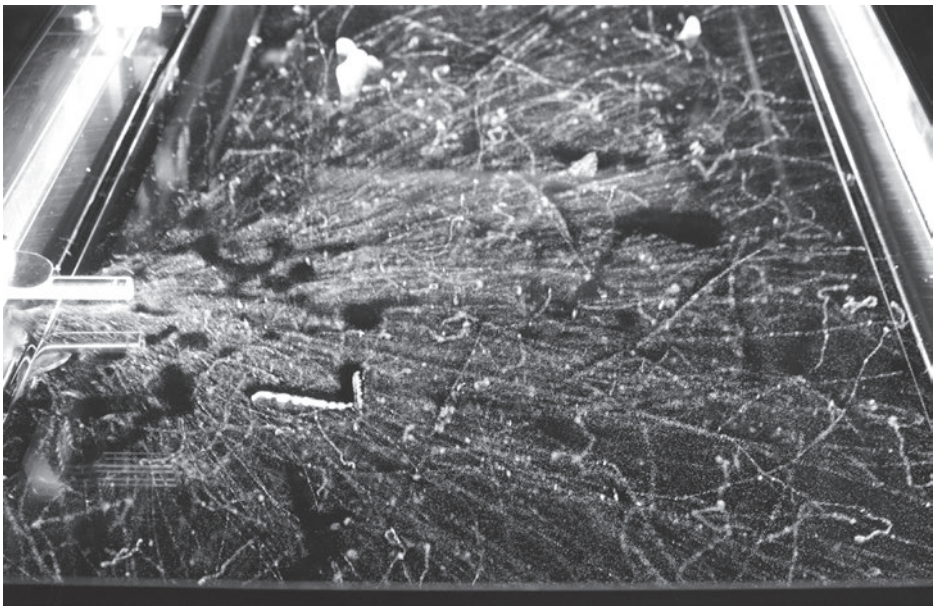
(**b**) Does not use a moderator

(**c**) Can be refueled without shutting down

Answers to Self-Assessment Exercises

21.25 (b) **21.26** (a)

21.6 Radiation in the Environment and Living Systems



A cloud chamber is a device that detects particles that have been ionized by ionizing radiation. Our exposure to natural radiation is from cosmic rays and terrestrial sources. Radon is produced by the radioactive decay of uranium and is one of the most important contributors to natural radiation from the earth. This noble gas seeps out of the ground and is dispersed by the wind. Being a heavy gas, it can accumulate in basements that are poorly sealed from the ground and have little ventilation. While radon has a short half-life, some of its decay products are more persistent. In this section, we look at a few of the effects of radiation on our bodies. By the end of this section, you should be able to

- Compare different measurements and units of radiation dosage and describe the biological effects of radiation

We are continuously bombarded by radiation from both natural and artificial sources. We are exposed to infrared, ultraviolet, and visible radiation from the Sun; radio waves from radio and television stations; microwaves from microwave ovens; X rays from medical procedures; and radioactivity from natural materials (Table 21.8). Understanding the

TABLE 21.8 Average Abundances and Activities of Natural Radionuclides†

	Potassium-40	Rubidium-87	Thorium-232	Uranium-238
Land elemental abundance (ppm)	28,000	112	10.7	2.8
Land activity (Bq/kg)	870	102	43	35
Ocean elemental concentration (mg/L)	339	0.12	1×10^{-7}	0.0032
Ocean activity (Bq/L)	12	0.11	4×10^{-7}	0.040
Ocean sediments elemental abundance (ppm)	17,000	—	5.0	1.0
Ocean sediments activity (Bq/kg)	500	—	20	12
Human body activity (Bq)	4000	600	0.08	0.4‡

†Data from "Ionizing Radiation Exposure of the Population of the United States," Report 93, 1987, and Report 160, 2009, National Council on Radiation Protection.

‡Includes lead-210 and polonium-210, daughter nuclei of uranium-238.

different energies of these various kinds of radiation is necessary in order to understand their different effects on matter.

When matter absorbs radiation, the radiation energy can cause atoms in the matter to be either excited or ionized. In general, radiation that causes ionization, called **ionizing radiation**, is far more harmful to biological systems than radiation that does not cause ionization. The latter, called **nonionizing radiation**, is generally of lower energy, such as radiofrequency electromagnetic radiation or slow-moving neutrons.

Most living tissue contains at least 70% water by mass. When living tissue is irradiated, water molecules absorb most of the energy of the radiation. Thus, it is common to define ionizing radiation as radiation that can ionize water, a process requiring a minimum energy of 1216 kJ/mol. Alpha, beta, and gamma rays (as well as X rays and higher-energy ultraviolet radiation) possess energies in excess of this quantity and are therefore forms of ionizing radiation.

When ionizing radiation passes through living tissue, electrons are removed from water molecules, forming highly reactive H_2O^+ ions. An H_2O^+ ion can react with another water molecule to form an H_3O^+ ion and a neutral OH molecule:

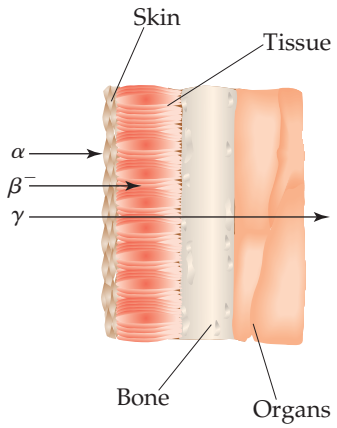
$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \qquad [21.31]$$

The unstable and highly reactive OH molecule is a **free radical**, a substance with one or more unpaired electrons, as seen in the Lewis structure shown in the margin. The OH molecule is also called the *hydroxyl radical*, and the presence of the unpaired electron is often emphasized by writing the species with a single dot, ·OH. In cells and tissues, hydroxyl radicals can attack biomolecules to produce new free radicals, which in turn attack yet other biomolecules. Thus, the formation of a single hydroxyl radical via Equation 21.31 can initiate a large number of chemical reactions that are ultimately able to disrupt the normal operations of cells.

The damage produced by radiation depends on the activity and energy of the radiation, the length of exposure, and whether the source is inside or outside the body. Gamma rays are particularly harmful outside the body because they penetrate human tissue very effectively, just as X rays do. Consequently, their damage is not limited to the skin. In contrast, most alpha rays are stopped by skin, and beta rays are able to penetrate only about 1 cm beyond the skin surface (**Figure 21.23**). Therefore, neither alpha rays nor beta rays are as dangerous as gamma rays, *unless* the radiation source somehow enters the body. Within the body, alpha rays are particularly dangerous because they transfer their energy efficiently to the surrounding tissue, causing considerable damage.

Go Figure

Why are alpha rays much more dangerous when the source of radiation is located inside the body?



▲ **Figure 21.23** **Relative penetrating abilities of alpha, beta, and gamma radiation.**

In general, the tissues damaged most by radiation are those that reproduce rapidly, such as bone marrow, blood-forming tissues, and lymph nodes. The principal effect of extended exposure to low doses of radiation is to cause cancer. Cancer is caused by damage to the growth-regulation mechanism of cells, inducing the cells to reproduce uncontrollably. Leukemia, which is characterized by excessive growth of white blood cells, is probably the major type of radiation-caused cancer.

In light of the biological effects of radiation, it is important to determine whether any levels of exposure are safe. Unfortunately, we are hampered in our attempts to set realistic standards because we do not fully understand the effects of long-term exposure. Scientists concerned with setting health standards have used the hypothesis that the effects of radiation are proportional to exposure. *Any* amount of radiation is assumed to cause some finite risk of injury, and the effects of high dosage rates are extrapolated to those of lower ones. Other scientists believe, however, that there is a threshold below which there are no radiation risks. Until scientific evidence enables us to settle the matter with some confidence, it is safer to assume that even low levels of radiation present some danger.

Radiation Doses

Two units are commonly used to measure exposure to radiation. The **gray** (Gy), the SI unit of absorbed dose, corresponds to the absorption of 1 J of energy per

TABLE 21.9 Effects of Short-Term Exposures to Radiation

Dose (Sv)	Effect
0–0.25	No detectable clinical effects
0.25–0.50	Slight, temporary decrease in white blood cell counts
1–2	Nausea; marked decrease in white blood cell counts
5	Death of half the exposed population within 30 days

kilogram of tissue. The **rad** (*r*adiation *a*bsorbed *d*ose) corresponds to the absorption of 1×10^{-2} J of energy per kilogram of tissue. Thus, 1 Gy = 100 rad. The rad is the unit most often used in medicine.

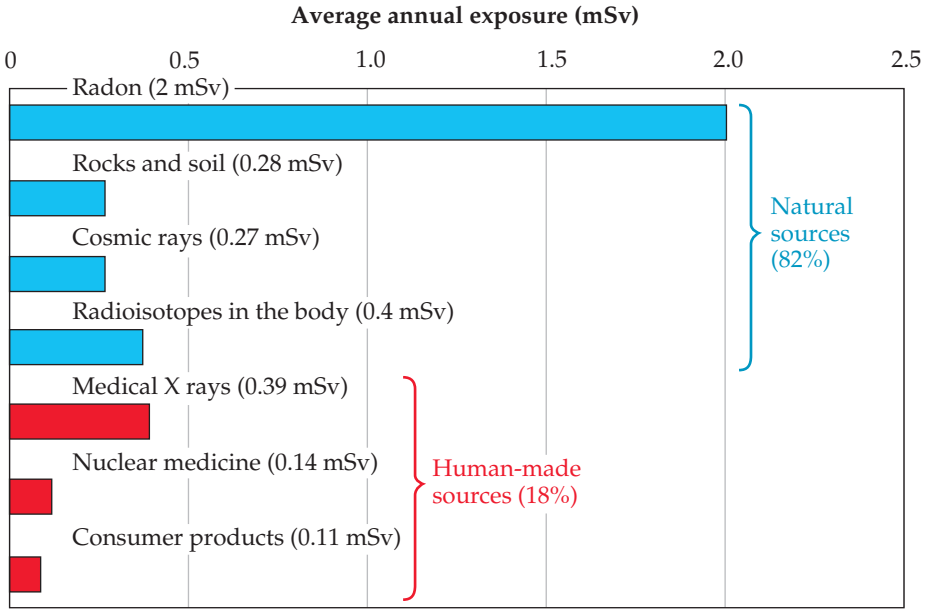
Not all forms of radiation harm biological materials to the same extent even at the same level of exposure. For example, 1 rad of alpha radiation can produce more damage than 1 rad of beta radiation. To correct for these differences, the radiation dose is multiplied by a factor that measures the relative damage caused by the radiation. This multiplication factor is known as the *relative biological effectiveness*, *RBE*. The RBE is approximately 1 for gamma and beta radiation, and 10 for alpha radiation.

The exact value of the RBE varies with dose rate, total dose, and type of tissue affected. The product of the radiation dose in rads and the RBE of the radiation give the *effective dosage* in **rem** (*r*oentgen *e*quivalent for *m*an):

$$\text{Number of rem} = (\text{number of rad})(\text{RBE}) \qquad [21.32]$$

The SI unit for effective dose is the *sievert* (Sv), obtained by multiplying the RBE times the SI unit for radiation dose, the gray; because a gray is 100 times larger than a rad, 1 Sv = 100 rem. The rem is the unit of radiation damage usually used in medicine.

The effects of short-term exposure to radiation appear in Table 21.9. An exposure of 6 Sv is fatal to most humans. To put this number in perspective, a typical dental X ray entails an exposure of about 5 μSv. The average exposure for a person in 1 yr due to all natural sources of ionizing radiation (called *background radiation*) is about 3.6 mSv (Figure 21.24).



▲ **Figure 21.24 Sources of U.S. average annual exposure to high-energy radiation.** The total average annual exposure is 3.6 mSv.
Data from "Ionizing Radiation Exposure of the Population of the United States," Report 93, 1987 and Report 160, 2009, National Council on Radiation Protection.

CHEMISTRY AND LIFE Radiation Therapy

Healthy cells are either destroyed or damaged by high-energy radiation, leading to physiological disorders. This radiation can also destroy *unhealthy* cells, however, including cancerous cells. All cancers are characterized by runaway cell growth that can produce *malignant tumors*. These tumors can be caused by the exposure of healthy cells to high-energy radiation. Paradoxically, however, they can be destroyed by the same radiation that caused them because the rapidly reproducing cells of the tumors are very susceptible to radiation damage. Thus, cancerous cells are more susceptible to destruction by radiation than healthy ones, allowing radiation to be used effectively in the treatment of cancer. As early as 1904, physicians used the radiation emitted by radioactive substances to treat tumors by destroying the mass of unhealthy tissue. The treatment of disease by high-energy radiation is called *radiation therapy*.

Many radionuclides are currently used in radiation therapy. Some of the more commonly used ones are listed in Table 21.10. Most of them have short half-lives, meaning that they emit a great deal of radiation in a short period of time.

The radiation source used in radiation therapy may be inside or outside the body. In almost all cases, radiation therapy uses gamma radiation emitted by radioisotopes. Any alpha or beta radiation that is emitted concurrently can be blocked by appropriate packaging.

TABLE 21.10 Some Radioisotopes Used in Radiation Therapy

Isotope	Half-Life	Isotope	Half-Life
^{32}P	14.3 days	^{137}Cs	30 yr
^{60}Co	5.27 yr	^{192}Ir	74.2 days
^{90}Sr	28.8 yr	^{198}Au	2.7 days
^{125}I	60.25 days	^{222}Rn	3.82 days
^{131}I	8.04 days	^{226}Ra	1600 yr

For example, ^{192}Ir is often administered as "seeds" consisting of a core of radioactive isotope coated with 0.1 mm of platinum metal. The platinum coating stops the alpha and beta rays, but the gamma rays penetrate it readily. The radioactive seeds can be surgically implanted in a tumor.

In some cases, human physiology allows a radioisotope to be ingested. For example, most of the iodine in the human body ends up in the thyroid gland, so thyroid cancer can be treated by using large doses of ^{131}I. Radiation therapy on deep organs, where a surgical implant is impractical, often uses a ^{60}Co "gun" outside the body to shoot a beam of gamma rays at the tumor. Particle accelerators are also used as an external source of high-energy radiation for radiation therapy.

Because gamma radiation is so strongly penetrating, it is nearly impossible to avoid damaging healthy cells during radiation therapy. Many cancer patients undergoing radiation treatment experience unpleasant and dangerous side effects such as fatigue, nausea, hair loss, a weakened immune system, and occasionally even death. However, if other treatments such as *chemotherapy* (the use of drugs to combat cancer) fail, radiation therapy can be a good option.

Much current research in radiation therapy is engaged in developing new drugs that specifically target tumors using a method called *neutron capture therapy*. In this technique, a nonradioactive isotope, usually boron-10, is concentrated in the tumor by using specific tumor-seeking reagents. The boron-10 is then irradiated with neutrons, where it undergoes the following nuclear reaction producing alpha particles:

$$^{10}_{5}B + {}^{1}_{0}n \longrightarrow {}^{7}_{3}Li + {}^{4}_{2}He$$

Tumor cells are killed or damaged by exposure to the alpha particles. Healthy tissue farther away from the tumor is unaffected because of the short-range penetrating power of alpha particles. Thus, neutron-capture therapy has the promise to be a "silver bullet" that specifically targets unhealthy cells for exposure to radiation.

Related Exercises: 21.24, 21.60, 21.64

Sample Integrative Exercise

Putting Concepts Together

Potassium ion is present in foods and is an essential nutrient in the human body. One of the naturally occurring isotopes of potassium, potassium-40, is radioactive. Potassium-40 has a natural abundance of 0.0117% and a half-life $t_{1/2} = 1.28 \times 10^9$ yr. It undergoes radioactive decay in three ways: 98.2% is by electron capture, 1.35% is by beta emission, and 0.49% is by positron emission. (**a**) Why should we expect ^{40}K to be radioactive? (**b**) Write the nuclear equations for the three modes by which ^{40}K decays. (**c**) How many $^{40}K^+$ ions are present in 1.00 g of KCl? (**d**) How long does it take for 1.00% of the ^{40}K in a sample to undergo radioactive decay?

SOLUTION

(**a**) The ^{40}K nucleus contains 19 protons and 21 neutrons. There are very few stable nuclei with odd numbers of both protons and neutrons (Section 21.2).

(**b**) Electron capture is capture of an inner-shell electron by the nucleus:

$$^{40}_{19}K + {}^{0}_{-1}e \longrightarrow {}^{40}_{18}Ar$$

Beta emission is loss of a beta particle ($^{0}_{-1}e$) by the nucleus:

$$^{40}_{19}K \longrightarrow {}^{40}_{20}Ca + {}^{0}_{-1}e$$

Positron emission is loss of a positron ($^{0}_{+1}e$) by the nucleus:

$$^{40}_{19}K \longrightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e$$

Continued

(c) The total number of K^+ ions in the sample is:

$$(1.00\ \text{g KCl})\left(\frac{1\ \text{mol KCl}}{74.55\ \text{g KCl}}\right)\left(\frac{1\ \text{mol K}^+}{1\ \text{mol KCl}}\right)\left(\frac{6.022 \times 10^{23}\ \text{K}^+}{1\ \text{mol K}^+}\right) = 8.08 \times 10^{21}\ \text{K}^+\ \text{ions}$$

Of these, 0.0117% are $^{40}K^+$ ions:

$$(8.08 \times 10^{21}\ \text{K}^+\ \text{ions})\left(\frac{0.0117\ ^{40}\text{K}^+\ \text{ions}}{100\ \text{K}^+\ \text{ions}}\right) = 9.45 \times 10^{17}\ ^{40}\text{K}^+\ \text{ions}$$

(d) The decay constant (the rate constant) for the radioactive decay can be calculated from the half-life, using Equation 21.19:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.28 \times 10^9\ \text{yr}} = (5.41 \times 10^{-10})/\text{yr}$$

The rate equation, Equation 21.20, then allows us to calculate the time required:

$$\ln\frac{N_t}{N_0} = -kt$$

$$\ln\frac{99}{100} = -[(5.41 \times 10^{-10})/\text{yr}]t$$

$$-0.01005 = -[(5.41 \times 10^{-10})/\text{yr}]t$$

$$t = \frac{-0.01005}{(-5.41 \times 10^{-10})/\text{yr}} = 1.86 \times 10^7\ \text{yr}$$

That is, it would take 18.6 million years for just 1.00% of the ^{40}K in a sample to decay.

Self-Assessment Exercise

21.35 If a person is uniformly irradiated by 0.010 J/kg alpha radiation, what is the effective dosage in rem?

(a) 0.010 rem
(b) 1.0 rem
(c) 10 rem

Exercises

21.36 Hydroxyl radicals can pluck hydrogen atoms from molecules ("hydrogen abstraction"), and hydroxide ions can pluck protons from molecules ("deprotonation"). Write the reaction equations and Lewis dot structures for the hydrogen abstraction and deprotonation reactions for the generic carboxylic acid R—COOH with hydroxyl radical and hydroxide ion, respectively. Why is hydroxyl radical more toxic to living systems than hydroxide ion?

21.37 A 65-kg person is accidentally exposed for 240 s to a 15-mCi source of beta radiation coming from a sample of ^{90}Sr. (**a**) What is the activity of the radiation source in disintegrations per second? In becquerels? (**b**) Each beta particle has an energy of 8.75×10^{-14} J. and 7.5% of the radiation is absorbed by the person. Assuming that the absorbed radiation is spread over the person's entire body, calculate the absorbed dose in rads and in grays. (**c**) If the RBE of the beta particles is 1.0, what is the effective dose in mrem and in sieverts? (**d**) Is the radiation dose equal to, greater than, or less than that for a typical mammogram (3 mSv)?

Answers to Self-Assessment Exercises

21.35 (c)

Chapter Summary and Key Terms

INTRODUCTION TO RADIOACTIVITY AND NUCLEAR EQUATIONS (SECTION 21.1) The nucleus of an atom contains protons and neutrons, both of which are called **nucleons**. Reactions that involve changes in atomic nuclei are called **nuclear reactions**. Nuclei that spontaneously change by emitting radiation are said to be **radioactive**. Radioactive nuclei are called **radionuclides**, and the atoms containing them are called **radioisotopes**. Radionuclides spontaneously change through a process called radioactive decay. The three most important types of radiation given off as a result of radioactive decay are **alpha (α) particles** ($^4_2$He or α), **beta (β)**

particles ($_{-1}^{0}e$ or β^-), and **gamma (γ) radiation** ($_{0}^{0}\gamma$ or γ). **Positrons** ($_{+1}^{0}e$ or β^+), which are particles with the same mass as an electron but the opposite charge, can also be produced when a radioisotope decays.

In nuclear equations, reactant and product nuclei are represented by giving their mass numbers and atomic numbers, as well as their chemical symbol. The totals of the mass numbers on both sides of the equation are equal; the totals of the atomic numbers on both sides are also equal. There are four common modes of radioactive decay: **alpha emission**, which reduces the atomic number by 2 and the mass number by 4; **beta emission**, which increases the atomic number by 1 and leaves the mass number unchanged; and **positron emission** and **electron capture**, both of which reduce the atomic number by 1 and leave the mass number unchanged.

PATTERNS OF NUCLEAR STABILITY (SECTION 21.2) The neutron-to-proton ratio is an important factor determining nuclear stability. By comparing a nuclide's neutron-to-proton ratio with those of stable nuclei, we can predict the mode of radioactive decay. In general, neutron-rich nuclei tend to emit beta particles; proton-rich nuclei tend to either emit positrons or undergo electron capture; and heavy nuclei tend to emit alpha particles. The presence of **magic numbers** of nucleons and an even number of protons and neutrons also help determine the stability of a nucleus. A nuclide may undergo a series of decay steps before a stable nuclide forms. This series of steps is called a **radioactive decay chain** or a **nuclear disintegration series**.

Nuclear transmutations, induced conversions of one nucleus into another, can be brought about by bombarding nuclei with either charged particles or neutrons. **Particle accelerators** increase the kinetic energies of positively charged particles, allowing these particles to overcome their electrostatic repulsion by the nucleus. Nuclear transmutations are used to produce the **transuranium elements**, those elements with atomic numbers greater than that of uranium.

RADIOACTIVE DECAY RATES AND DETECTION OF RADIOACTIVITY (SECTIONS 21.3 AND 21.4) The SI unit for the activity of a radioactive source is the **becquerel** (Bq), defined as one nuclear disintegration per second. A related unit, the **curie** (Ci), corresponds to 3.7×10^{10} disintegrations per second. Nuclear decay is a first-order process. The decay rate (**activity**) is therefore directly proportional to the number of radioactive nuclei. The **half-life** of a radionuclide, which is a constant independent of temperature, is the time needed for one-half of the nuclei to decay. Some radioisotopes can be used to date objects; ^{14}C, for example, is used to date organic objects. Geiger counters and scintillation counters count the emissions from radioactive samples. The ease of detection of radioisotopes also permits their use as **radiotracers** to follow elements through reactions.

ENERGY CHANGES IN NUCLEAR REACTIONS (SECTION 21.5) The energy produced in nuclear reactions is accompanied by measurable changes of mass in accordance with Einstein's relationship, $\Delta E = c^2\Delta m$. The difference in mass between nuclei and the nucleons of which they are composed is known as the **mass defect**. The mass defect of a nuclide makes it possible to calculate its **nuclear binding energy**, the energy required to separate the nucleus into individual nucleons. Because of trends in the nuclear binding energy with atomic number, energy is produced when heavy nuclei split (**fission**) and when light nuclei fuse (**fusion**).

Uranium-235, uranium-233, and plutonium-239 undergo fission when they capture a neutron, splitting into lighter nuclei and releasing more neutrons. The neutrons produced in one fission can cause further fission reactions, which can lead to a nuclear **chain reaction**. A reaction that maintains a constant rate is said to be critical, and the mass necessary to maintain this constant rate is called a **critical mass**. A mass in excess of the critical mass is termed a **supercritical mass**.

In nuclear reactors, the fission rate is controlled to generate a constant power. The reactor core consists of fuel elements containing fissionable nuclei, control rods, a moderator, and a primary coolant. A nuclear power plant resembles a conventional power plant except that the reactor core replaces the fuel burner. There is concern about the disposal of highly radioactive nuclear wastes that are generated in nuclear power plants.

Nuclear fusion requires high temperatures because nuclei must have large kinetic energies to overcome their mutual repulsions. Fusion reactions are therefore called **thermonuclear reactions**. It is not yet possible to generate power on Earth through a controlled fusion process.

NUCLEAR CHEMISTRY AND LIVING SYSTEMS (SECTION 21.6) **Ionizing radiation** is energetic enough to remove an electron from a water molecule; radiation with less energy is called **nonionizing radiation**. Ionizing radiation generates **free radicals**, reactive substances with one or more unpaired electrons. The effects of long-term exposure to low levels of radiation are not completely understood, but there is evidence that the extent of biological damage varies in direct proportion to the level of exposure.

The amount of energy deposited in biological tissue by radiation is called the radiation dose and is measured in units of gray or rad. One **gray** (Gy) corresponds to a dose of 1 J/kg of tissue. It is the SI unit of radiation dose. The **rad** is a smaller unit; 100 rad = 1 Gy. The effective dose, which measures the biological damage created by the deposited energy, is measured in units of rem or sievert (Sv). The **rem** is obtained by multiplying the number of rad by the relative biological effectiveness (RBE); 100 rem = 1 Sv.

Learning Outcomes After studying this chapter, you should be able to:

- Write balanced nuclear equations. (Section 21.1) *Related Exercises: 21.4, 21.49*
- Predict nuclear stability and expected type of nuclear decay from the neutron-to-proton ratio of an isotope. (Section 21.2) *Related Exercises: 21.38, 21.51*
- Write balanced nuclear equations for nuclear transmutations. (Section 21.3) *Related Exercises: 21.56, 21.57*
- Calculate ages of objects and/or the amount of a radionuclide remaining after a given period of time using the half-life of the radionuclide in question. (Section 21.4) *Related Exercises: 21.43, 21.60*
- Calculate mass and energy changes for nuclear reactions. (Section 21.6) *Related Exercises: 21.29, 21.65*
- Calculate the binding energies for nuclei. (Section 21.6) *Related Exercises: 21.67, 21.68*
- Describe the difference between fission and fusion and explain how a nuclear power plant operates. (Sections 21.7 and 21.8) *Related Exercises: 21.71, 21.76*
- Compare different measurements and units of radiation dosage and describe the biological effects of radiation. (Section 21.9) *Related Exercises: 21.36, 21.78*

Key Equations

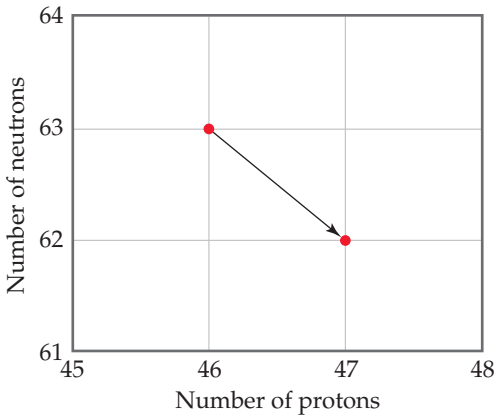
- $k = \dfrac{0.693}{t_{1/2}}$ [21.19] Relationship between nuclear decay constant and half-life; this is derived from the following equation at $N_t = \frac{1}{2}N_0$
- $\ln\dfrac{N_t}{N_0} = -kt$ [21.20] First-order rate law for nuclear decay
- $E = mc^2$ [21.22] Einstein's equation that relates mass and energy

Exercises

Visualizing Concepts

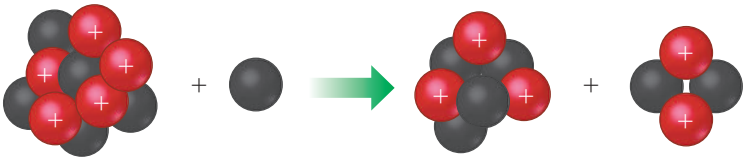
21.38 Indicate whether each of the following nuclides lies within the belt of stability in Figure 21.2: (**a**) neon-24, (**b**) chlorine-32, (**c**) tin-108, (**d**) polonium-216. For any that do not, describe a nuclear decay process that would alter the neutron-to-proton ratio in the direction of increased stability. [Section 21.2]

21.39 Write the balanced nuclear equation for the reaction represented by the diagram shown here. [Section 21.2]

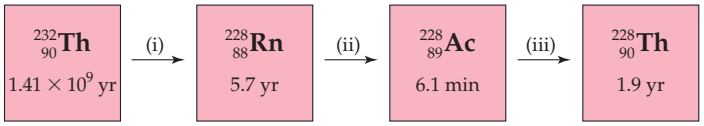


21.40 Draw a diagram similar to that shown in Exercise 21.39 that illustrates the nuclear reaction $^{211}_{83}\text{Bi} \longrightarrow {}^{4}_{2}\text{He} + {}^{207}_{81}\text{Tl}$. [Section 21.2]

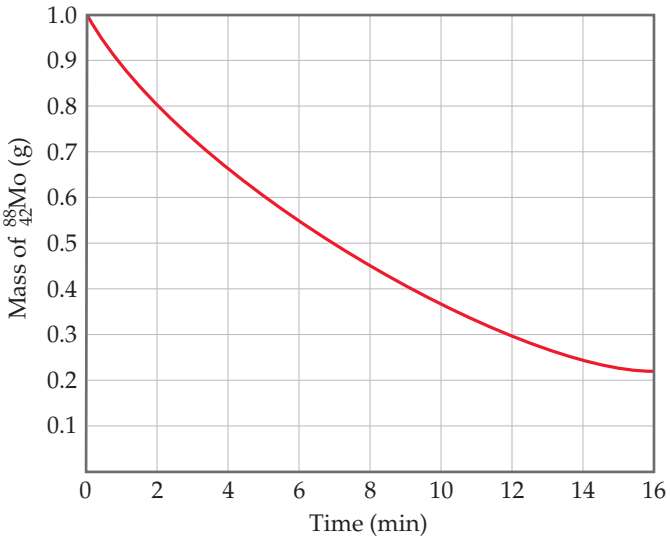
21.41 In this sketch, the red spheres represent protons and the gray spheres represent neutrons. (**a**) What are the identities of the four particles involved in the reaction depicted? (**b**) Write the transformation represented here using condensed notation. (**c**) Based on its atomic number and mass number, do you think the product nucleus is stable or radioactive? [Section 21.2]



21.42 The steps drawn here show three of the steps in the radioactive decay chain for $^{232}_{90}\text{Th}$. The half-life of each isotope is shown below the symbol of the isotope. (**a**) Identify the type of radioactive decay for each of the steps (i), (ii), and (iii). (**b**) Which of the isotopes shown has the highest activity? (**c**) Which of the isotopes shown has the lowest activity? (**d**) The next step in the decay chain is an alpha emission. What is the next isotope in the chain? [Sections 21.2 and 21.3]

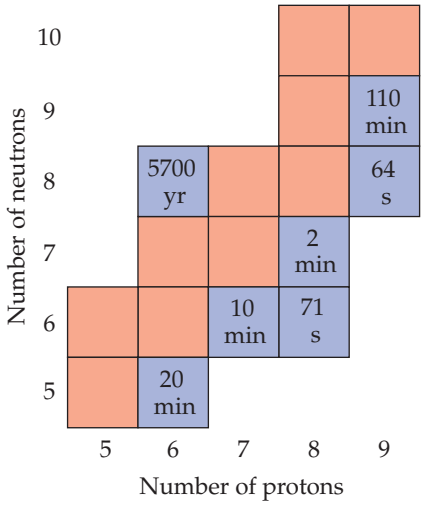


21.43 The accompanying graph illustrates the decay of $^{88}_{42}\text{Mo}$, which decays via positron emission. (**a**) What is the half-life of the decay? (**b**) What is the rate constant for the decay? (**c**) What fraction of the original sample of $^{88}_{42}\text{Mo}$ remains after 12 min? (**d**) What is the product of the decay process? [Section 21.3]

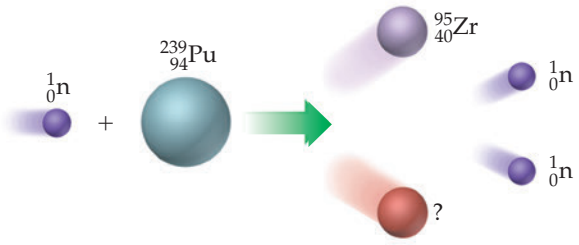


21.44 All the stable isotopes of boron, carbon, nitrogen, oxygen, and fluorine are shown in the accompanying chart (in red), along with their radioactive isotopes with $t_{1/2} > 1$ min (in blue). (**a**) Write the chemical symbols, including mass and atomic numbers, for all of the stable isotopes. (**b**) Which radioactive isotopes are most likely to decay by beta

emission? (**c**) Some of the isotopes shown are used in positron emission tomography. Which ones would you expect to be most useful for this application? (**d**) Which isotope would decay to 12.5% of its original concentration after 1 hour? [Sections 21.2, 21.3, and 21.4]



21.45 The diagram shown here illustrates a fission process. (**a**) What is the unidentified product of the fission? (**b**) Use Figure 21.2 to predict whether the nuclear products of this fission reaction are stable. [Section 21.5]



Radioactivity and Nuclear Equations (Section 21.1)

21.46 Indicate the number of protons and neutrons in the following nuclei: (**a**) $^{239}_{94}$Pu, (**b**) $^{142}_{56}$Ba, (**c**) potassium-41.

21.47 What do these symbols stand for? (**a**) $^{1}_{1}$p, (**b**) $^{0}_{-1}$e, (**c**) $^{0}_{+1}$e

21.48 Write balanced nuclear equations for the following processes: (**a**) radon-198 undergoes alpha emission; (**b**) thorium-234 undergoes beta emission; (**c**) copper-61 undergoes positron emission; (**d**) silver-106 undergoes electron capture.

21.49 Decay of which nucleus will lead to the following products: (**a**) uranium-235 by alpha decay; (**b**) aluminum-26 by positron emission; (**c**) deuterium by alpha decay; (**d**) yttrium-90 by beta decay?

21.50 The naturally occurring radioactive decay series that begins with $^{235}_{92}$U stops with formation of the stable $^{207}_{82}$Pb nucleus. The decays proceed through a series of alpha-particle and beta-particle emissions. How many of each type of emission are involved in this series?

Patterns of Nuclear Stability (Section 21.2)

21.51 Predict the type of radioactive decay process for the following radionuclides: (**a**) $^{15}_{8}$O, (**b**) $^{41}_{21}$Sc, (**c**) uranium-237, (**d**) sulphur-35.

21.52 One of the nuclides in each of the following pairs is radioactive. Predict which is radioactive and which is stable: (**a**) $^{92}_{44}$Ru and $^{102}_{44}$Ru, (**b**) $^{138}_{56}$Ba and $^{139}_{56}$Ba, (**c**) tin-109 and tin-120.

21.53 Which of the following nuclides have magic numbers of both protons and neutrons: (**a**) beryllium-10, (**b**) silicon-28, (**c**) chromium-52, (**d**) nickel-56, (**e**) krypton-84?

21.54 Which of the following statements best explains why alpha emission is relatively common, but proton emission is extremely rare?

(**a**) Alpha particles are very stable because of magic numbers of protons and neutrons.

(**b**) Alpha particles occur in the nucleus.

(**c**) Alpha particles are the nuclei of an inert gas.

(**d**) An alpha particle has a higher charge than a proton.

21.55 Which statement best explains why nuclear transmutations involving neutrons are generally easier to accomplish than those involving protons or alpha particles?

(**a**) Neutrons are not a magic number particle.

(**b**) Neutrons do not have an electrical charge.

(**c**) Neutrons are smaller than protons or alpha particles.

(**d**) Neutrons are attracted to the nucleus even at long distances, whereas protons and alpha particles are repelled.

21.56 Complete and balance the following nuclear equations by supplying the missing particle:

(**a**) $^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{0}_{-1}\text{e} + ?$

(**b**) $^{238}_{92}\text{U} + {}^{4}_{2}\text{He} \longrightarrow 3\,{}^{1}_{0}\text{n} + ?$

(**c**) $^{218}_{85}\text{At} \longrightarrow {}^{0}_{-1}\text{e} + ?$

(**d**) $^{146}_{62}\text{Sm} \longrightarrow {}^{142}_{60}\text{Nd} + ?$

(**e**) $^{118}_{53}\text{I} + {}^{0}_{-1}\text{e} \longrightarrow ?$

21.57 Write balanced equations for (**a**) $^{238}_{92}\text{U}(\alpha, \text{n})^{241}_{94}\text{Pu}$, (**b**) $^{14}_{7}\text{N}(\alpha, \text{p})^{17}_{8}\text{O}$, (**c**) $^{56}_{26}\text{Fe}(\alpha, \beta^{-})^{60}_{29}\text{Cu}$.

Rates of Radioactive Decay (Section 21.3)

21.58 Each statement that follows refers to a comparison between two radioisotopes, A and X. Indicate whether each of the following statements is true or false.

(**a**) If the half-life for A is shorter than the half-life for X, A has a larger decay rate constant.

(**b**) If X is "not radioactive," its half-life is essentially zero.

(**c**) If A has a half-life of 10 yr, and X has a half-life of 10,000 yr, A would be a more suitable radioisotope to measure processes occurring on the 40-yr time scale.

21.59 Some watch dials are coated with a phosphor, like ZnS, and a polymer in which some of the ^{1}H atoms have been replaced by ^{3}H atoms, tritium. The phosphor emits light when struck by the beta particle from the tritium decay, causing the dials to glow in the dark. The half-life of tritium is 12.3 yr. If the light given off is assumed to be directly proportional to the amount of tritium, by how much will a dial be dimmed in a watch that is 50 yr old?

21.60 Cobalt-60 is a strong gamma emitter that has a half-life of 5.26 yr. The cobalt-60 in a radiotherapy unit must

be replaced when its radioactivity falls to 75% of the original sample. If an original sample was purchased in June 2016, when will it be necessary to replace the cobalt-60?

21.61 Radium-226, which undergoes alpha decay, has a half-life of 1600 yr. (**a**) How many alpha particles are emitted in 5.0 min by a 10.0-mg sample of ^{226}Ra? (**b**) What is the activity of the sample in mCi?

21.62 A 10.00 g plant fossil from an archaeological site is found to have a ^{14}C activity of 3094 disintegrations over a period of ten hours. A living plant is found to have a ^{14}C activity of 9207 disintegrations over the same period of time for an equivalent amount of sample with respect to the total contents of carbon. Given that the half-life of ^{14}C is 5715 years, how old is the plant fossil?

21.63 Phosphorus-32 is commonly used in nuclear medicine for the identification of malignant tumors. It decays to sulphur-32 with a half-life of 14.29 days. If a patient is given 3.5 mg of phosphorus-32, how much phosphorus-32 will remain after 1 month (i.e. 30 days)?

Detection of Radioactivity (Section 21.4)

21.64 Why is it important that radioisotopes used as diagnostic tools in nuclear medicine produce gamma radiation when they decay? Why are alpha emitters not used as diagnostic tools?

Energy Changes in Nuclear Reactions (Section 21.5)

21.65 An analytical laboratory balance typically measures mass to the nearest 0.1 mg. What energy change would accompany the loss of 0.1 mg in mass?

21.66 The thermite reaction, $Fe_2O_3(s) + 2\,Al(s) \longrightarrow 2\,Fe(s) + Al_2O_3(s)$, $\Delta H° = -851.5$ kJ/mol, is one of the most exothermic reactions known. Because the heat released is sufficient to melt the iron product, the reaction is used to weld metal under the ocean. How much heat is released per mole of Al_2O_3 produced? How does this amount of thermal energy compare with the energy released when 2 mol of protons and 2 mol of neutrons combine to form 1 mol of alpha particles?

21.67 How much energy must be supplied to break a single aluminum-27 nucleus into separated protons and neutrons if an aluminum-27 atom has a mass of 26.9815386 u? How much energy is required for 100.0 g of aluminum-27? (The mass of an electron is given on the inside back cover.)

21.68 The atomic masses of hydrogen-2 (deuterium), helium-4, and lithium-6 are 2.014102 u, 4.002602 u, and 6.0151228 u, respectively. For each isotope, calculate (**a**) the nuclear mass, (**b**) the nuclear binding energy, (**c**) the nuclear binding energy per nucleon. (**d**) Which of these three isotopes has the largest nuclear binding energy per nucleon? Does this agree with the trends plotted in Figure 21.12?

21.69 Based on the following atomic mass values = ^{2}H, 2.01410 u; ^{3}H, 3.01605 u; ^{3}He, 3.01603 u; ^{4}He, 4.00260 u—and the mass of the neutron given in the text, calculate the energy released per mole in each of the following nuclear reactions, all of which are possibilities for a controlled fusion process.

(**a**) $^2_1H + {}^3_1H \longrightarrow {}^4_2He + {}^1_0n$

(**b**) $^2_1H + {}^2_1H \longrightarrow {}^3_2He + {}^1_0n$

21.70 The isotope $^{62}_{28}$Ni has the largest binding energy per nucleon of any isotope. Calculate this value from the atomic mass of nickel-62 (61.928345 u) and compare it with the value given for iron-56 in Table 21.7.

21.71 (**a**) Which of the following are required characteristics of an isotope to be used as a fuel in a nuclear power reactor? (i) It must emit gamma radiation. (ii) On decay, it must release two or more neutrons. (iii) It must have a half-life less than one hour. (iv) It must undergo fission upon the absorption of a neutron. (**b**) What is the most common fissionable isotope in a commercial nuclear power reactor?

21.72 What is the function of the control rods in a nuclear reactor? What substances are used to construct control rods? Why are these substances chosen?

21.73 Complete and balance the nuclear equations for the following fission or fusion reactions:

(**a**) $^{235}_{92}U + {}^1_0n \longrightarrow {}^{92}_{36}Kr + {}^{141}_{56}Zn + _$

(**b**) $^2_1H + {}^3_1H \longrightarrow {}^4_2He + _$

21.74 A portion of the Sun's energy comes from the reaction

$$4\,{}^1_1H \longrightarrow {}^4_2He + 2\,{}^0_1e$$

which requires a temperature of 10^6 to 10^7 K. Use the mass of the helium-4 nucleus given in Table 21.7 to determine how much energy is released per mol of hydrogen atoms.

21.75 The spent fuel elements from a fission reactor are much more intensely radioactive than the original fuel elements. (**a**) What does this tell you about the products of the fission process in relationship to the belt of stability, Figure 21.2? (**b**) Given that only two or three neutrons are released per fission event and knowing that the nucleus undergoing fission has a neutron-to-proton ratio characteristic of a heavy nucleus, what sorts of decay would you expect to be dominant among the fission products?

21.76 Which type or types of nuclear reactors have these characteristics?

(**a**) Does not use a secondary coolant

(**b**) Creates more fissionable material than it consumes

(**c**) Uses a gas, such as He or CO_2, as the primary coolant

21.77 Which are not classified as ionizing radiation: gamma rays, beta particles, radio waves used in radio and television, and infrared radiation from sun?

Radiation in the Environment (Sections 21.6)

21.78 A laboratory rat is exposed to an alpha-radiation source whose activity is 14.3 mCi. (**a**) What is the activity of the radiation in disintegrations per second? In becquerels? (**b**) The rat has a mass of 385 g and is exposed to the radiation for 14.0 s, absorbing 35% of the emitted alpha particles, each having an energy of 9.12×10^{-13} J. Calculate the absorbed dose in millirads and grays. (**c**) If the RBE of the radiation is 9.5, calculate the effective absorbed dose in mrem and Sv.

Additional Exercises

21.79 The table to the right gives the number of protons (p) and neutrons (n) for four nuclides. (**a**) Write the symbol for each of the isotopes based on the information given in the table. (**b**) Which of the isotopes is most likely to be unstable? (**c**) Which of the isotopes involves a magic number of protons and/or neutrons? (**d**) Which isotope will yield iron-58 following positron emission?

	(i)	(ii)	(iii)	(iv)
p	27	27	28	28
n	30	31	28	30

21.80 Assume that Bismuth-213 decays to a stable nucleus by a series of two alpha and two beta emissions. What is the stable nucleus that is formed?

21.81 Equation 21.28 is the nuclear reaction responsible for much of the helium-4 production in our Sun. How much energy is released in this reaction?

21.82 Chlorine has two stable nuclides, ^{35}Cl and ^{37}Cl. In contrast, ^{36}Cl is a radioactive nuclide that decays by beta emission. (**a**) What is the product of decay of ^{36}Cl? (**b**) Based on the empirical rules about nuclear stability, explain why the nucleus of ^{36}Cl is less stable than either ^{35}Cl or ^{37}Cl.

21.83 When two protons fuse in a star, the product is ^{2}H plus a positron. Write the nuclear equation for this process.

21.84 Nuclear scientists have synthesized new elements and isotopes, which are not known in nature using heavy-ion bombardment techniques in high-energy particle accelerators. Complete and balance the following reactions:

(**a**) $^{12}_{6}\text{C} + {}^{12}_{6}\text{C} \longrightarrow ? + {}^{4}_{2}\text{He}$

(**b**) $^{6}_{3}\text{Li} + {}^{63}_{28}\text{Ni} \longrightarrow ?$

(**c**) $^{252}_{98}\text{Cf} + {}^{10}_{5}\text{B} \longrightarrow ?$

(**d**) $^{238}_{92}\text{U} + {}^{12}_{6}\text{C} \longrightarrow ? + 4\,{}^{1}_{0}\text{n}$

21.85 In 2002, a team of scientists from Russia and the United States reported the creation of the first atom of element 118, which is named oganesson, and whose symbol is Og. The synthesis involved the collision of californium-249 atoms with accelerated ions of an atom which we will denote X. In the synthesis, an oganesson-294 is formed together with three neutrons.

$$^{249}_{98}\text{Cf} + \text{X} \longrightarrow {}^{294}_{118}\text{Og} + 3\,{}^{1}_{0}\text{n}$$

(**a**) What are the identities of isotopes X? (**b**) Isotope X is unusual in that it is very long-lived (its half-life is on the order of 10^{19} yr) in spite of having an unfavorable neutron-to-proton ratio (Figure 21.1). Can you propose a reason for its unusual stability? (**c**) Oganesson-294 decays into livermorium-290 by alpha decay. Write a balanced equation for this.

21.86 The synthetic radioisotope, phosphorus-32, which decays by beta emission, is used as radioactive labelled for DNA molecules. The following data were collected on a sample of phosphorus:

Ci	Time (days)
80	0
49	10
30	20
18	30
10.5	40
6.3	50
4.2	60

Using these data, make an appropriate graph and curve fit to determine the half-life.

21.87 According to current regulations, the maximum permissible dose of strontium-90 in the body of an adult is 1 μCi (1×10^{-6} Ci). Using the relationship rate = kN, calculate the number of atoms of strontium-90 to which this dose corresponds. To what mass of strontium-90 does this correspond? The half-life for strontium-90 is 28.8 yr.

21.88 Methyl acetate (CH_3COOCH_3) is formed by the reaction of acetic acid with methanol. If the methanol is labeled with oxygen-18, the oxygen-18 ends up in the methyl acetate:

$$\text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OH} + \text{H}^{18}\text{OCH}_3 \longrightarrow \text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}{}^{18}\text{OCH}_3 + \text{H}_2\text{O}$$

(**a**) Do the C—OH bond of the acid and the O—H bond of the alcohol break in the reaction, or do the O—H bond of the acid and the C—OH bond of the alcohol break? (**b**) Imagine a similar experiment using the radioisotope ^{3}H, which is called *tritium* and is usually denoted T. Would the reaction between CH_3COOH and $TOCH_3$ provide the same information about which bond is broken as does the experiment with $H^{18}OCH_3$?

21.89 Each of the following transmutations produces a radionuclide used in positron emission tomography (PET). (**a**) In equations (i) and (ii), identify the species signified as "X." (**b**) In equation (iii), one of the species is indicated as "d." What do you think it represents?

(i) $^{14}\text{N}(\text{p}, \alpha)\text{X}$

(ii) $^{18}\text{O}(\text{p}, \text{X})^{18}\text{F}$

(iii) $^{14}\text{N}(\text{d}, \text{n})^{15}\text{O}$

21.90 The nuclear masses of ^{7}Be, ^{9}Be, and ^{10}Be are 7.0147, 9.0100, and 10.0113 u, respectively. Which of these nuclei has the largest binding energy per nucleon?

21.91 A 26.00 g sample of water containing tritium, $^{3}_{1}$H, emits 1.50×10^{3} beta particles per second. Tritium is a weak beta emitter with a half-life of 12.3 yr. What fraction of all the hydrogen in the water sample is tritium?

21.92 The Sun radiates energy into space at the rate of 3.9×10^{26} J/s. (**a**) Calculate the rate of mass loss from the Sun in kg/s. (**b**) How does this mass loss arise? (**c**) It is estimated that the Sun contains 9×10^{56} free protons. How many protons per second are consumed in nuclear reactions in the Sun?

21.93 The average energy released in the fission of a single uranium-235 nucleus is about 3×10^{-11} J. If the conversion of this energy to electricity in a nuclear power plant is 40% efficient, what mass of uranium-235 undergoes fission in a year in a plant that produces 1000 megawatts? Recall that a watt is 1 J/s.

21.94 Tests on human subjects in Boston in 1965 and 1966, following the era of atomic bomb testing, revealed average quantities of about 2 pCi of plutonium radioactivity in the average person. How many disintegrations per second does this level of activity imply? If each alpha particle deposits 8×10^{-13} J of energy and if the average person weighs 75 kg, calculate the number of grays and sieverts of radiation in 1 yr from such a level of plutonium.

Integrative Exercises

21.95 A 0.53 g sample of fludeoxyglucose ($C_6H_{11}FO_5$) contains radioactive fluorine-18 (whose atomic mass is 18.0 u). If 68.3% of the fluorine atoms in the sample are fluorine-18 and the remainder are naturally occurring nonradioactive fluorine-19 atoms, how many disintegrations per second are produced by this sample? The half-life of fluorine-18 is 110 min.

21.96 Calculate the mass of methane, $CH_4(g)$, that must be burned in air to evolve the same quantity of energy as produced by the fusion of 1.0 g of deuterium and 1.5 g of tritium in the following fusion reaction:

$$^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$$

Assume that all the products of the combustion of methane are in their gas phases. Use data from Exercise 21.28, Appendix C, and the inside covers of the text. The standard enthalpy of formation of methane is −74.8 kJ/mol.

21.97 Naturally found uranium consists of 99.274% ^{238}U, 0.720% ^{235}U, and 0.006% ^{233}U. As we have seen, ^{235}U is the isotope that can undergo a nuclear chain reaction. Most of the ^{235}U used in the first atomic bomb was obtained by gaseous diffusion of uranium hexafluoride, $UF_6(g)$. (**a**) What is the mass of UF_6 in a 30.0 L vessel of UF_6 at a pressure of 92.7 kPa at 350 K? (**b**) What is the mass of ^{235}U in the sample described in part (a)? (**c**) Now suppose that the UF_6 is diffused through a porous barrier and that the change in the ratio of ^{238}U and ^{235}U in the diffused gas can be described by Equation 10.23. What is the mass of ^{235}U in a sample of the diffused gas analogous to that in part (a)? (**d**) After one more cycle of gaseous diffusion, what is the percentage of $^{235}UF_6$ in the sample?

21.98 Polonium-210 is a powerful alpha emitter. A sample of polonium-210 having an activity of 85.2 Ci is stored in a 25.0-mL sealed container at 30 °C for 15 hours. (**a**) How many alpha particles are formed during this time? (**b**) Assuming that each alpha particle is converted to a helium atom, what is the partial pressure, in kPa, of helium gas in the container after this 15-hour period?

21.99 Charcoal samples from Stonehenge in England were burned in O_2, and the resultant CO_2 gas bubbled into a solution of $Ca(OH)_2$ (limewater), resulting in the precipitation of $CaCO_3$. The $CaCO_3$ was removed by filtration and dried. A 788 mg sample of the $CaCO_3$ had a radioactivity of 1.5×10^{-2} Bq due to carbon-14. By comparison, living organisms undergo 15.3 disintegrations per minute per gram of carbon. Using the half-life of carbon-14, 5700 yr, calculate the age of the charcoal sample.

21.100 A 2.5 mL sample of 0.188 *M* silver nitrate solution was mixed with 2.5 mL of 0.188 *M* sodium chloride solution labeled with radioactive chlorine-36. The activity of the initial sodium chloride solution was 2.46×10^6 Bq/mL. After the resultant precipitate was removed by filtration, the remaining filtrate was found to have an activity of 175 Bq/mL. (**a**) Write a balanced chemical equation for the reaction that occurred. (**b**) Calculate the K_{sp} for the precipitate under the conditions of the experiment.

Design an Experiment

Because radioactivity can have harmful effects on human health, very stringent experimental procedures and precautions are required when undertaking experiments on radioactive materials. As such, we typically do not have experiments involving radioactive substances in general chemistry laboratories. We can nevertheless ponder the design of some hypothetical experiments that would allow us to explore some of the properties of radium, which was discovered by Marie and Pierre Curie in 1898.

(**a**) A key aspect of the discovery of radium was Marie Curie's observation that *pitchblende*, a natural ore of uranium, had greater radioactivity than pure uranium metal. Design an experiment to reproduce this observation and to obtain a ratio of the activity of pitchblende relative to that of pure uranium.

(**b**) Radium was first isolated as halide salts. Suppose you had pure samples of radium metal and radium bromide. The sample sizes are on the order of milligrams and are not amenable to the usual forms of elemental analysis. Could you use a device that measures radioactivity quantitatively to determine the empirical formula of radium bromide? What information must you use that the Curies may not have had at the time of their discovery?

(**c**) Suppose you had a 1-yr time period in order to measure the half-life of radium and related elements. You have some pure samples and a device that measures radioactivity quantitatively. Could you determine the half-life of the elements in the samples? Would you have different experimental constraints depending on whether the half-life were 10 yr or 1000 yr?

(**d**) Before its negative health effects were better understood, small amounts of radium salts were used in "glow in the dark" watches, such as the one shown here. The glow is not due to the radioactivity of radium directly; rather, the radium is combined with a luminescent substance, such as zinc sulfide, which glows when it is exposed to radiation. Suppose you had pure samples of radium and zinc sulfide. How could you determine whether the glow of zinc sulfide is due to alpha, beta, or gamma radiation? What type of device could you design to use the glow as a quantitative measure of the amount of radioactivity in a sample?



WHAT'S AHEAD

22.1 ▶ Periodic Trends and Chemical Reactions

22.2 ▶ Hydrogen

22.3 ▶ Group 18: The Noble Gases

22.4 ▶ Group 17: The Halogens

22.5 ▶ Oxygen

22.6 ▶ The Other Group 16 Elements: S, Se, Te, and Po

22.7 ▶ Nitrogen

22.8 ▶ The Other Group 15 Elements: P, As, Sb, and Bi

22.9 ▶ Carbon

22.10 ▶ The Other Group 14 Elements: Si, Ge, Sn, and Pb

22.11 ▶ Boron

22

CHEMISTRY OF THE NONMETALS

22.1 Periodic Trends and Chemical Reactions



A great number of chemical elements go into making up living spaces with all their paraphernalia. One of the first questions we might ask is:

What is the relative importance of metallic and nonmetallic elements? Some carpets or mats may be made of organic fibers derived from bamboo. Walls may be made of cellulososic material that is essentially nonmetallic. Objects such as chair coverings, chairs, and ceramic plant pots are all constructed from mainly nonmetallic elements as well. Metals are certainly important too, as they are necessary to manufacture the electrical wiring in the walls, perhaps steel girders in the building's frame, perhaps plumbing fixtures. Overall, however, the stuff of which such a living space is constructed is largely nonmetallic in origin.

Chemical innovation has resulted in a host of materials that form the stuff of modern life. We've learned in earlier chapters about a variety of chemical reaction types that allows chemists to purify materials and polymerize small mol ecules into much larger ones. We've also learned how the properties of pure substances and mixtures depend on underlying molecular properties. But what are the chemical and physical properties of the elements that make up all these materials? In this chapter and the next, we look at the properties of many elements and at how these properties determine the possibilities for useful applications.

In this chapter, we start by taking a panoramic view of the descriptive chemistry of the nonmetallic elements, starting with hydrogen and then progressing, group by group, from right to left across the periodic table. We emphasize hydrogen, oxygen, nitrogen, and carbon. These four nonmetals form many commercially important compounds and account for 99% of the atoms required by living cells.

At the end of this section, you should be able to

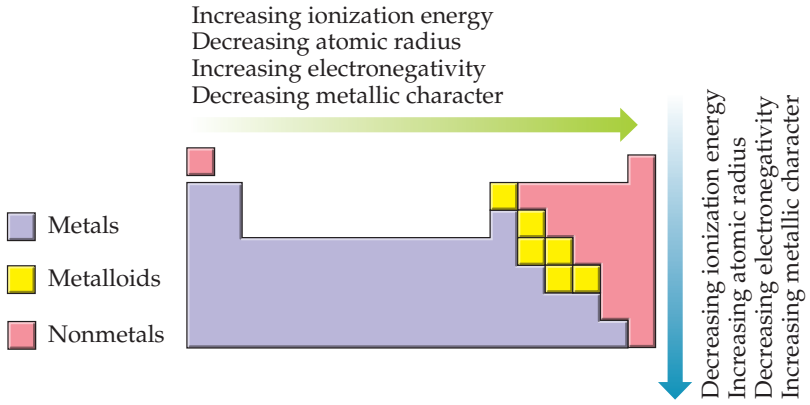
- Explain two ways in which the first element of the group differs from subsequent elements in the group

Recall that we can classify elements as metals, metalloids, and nonmetals. Except for hydrogen, which is a special case, the nonmetals occupy the upper right portion of the periodic table. This division of elements relates nicely to trends in their properties as summarized in **Figure 22.1**. Electronegativity, for example, increases as we move left to right across a period and decreases as we move down a group. The nonmetals thus have higher electronegativities than the metals. This difference leads to the formation of ionic solids in reactions between metals and nonmetals. In contrast, compounds formed between two or more nonmetals are usually molecular substances.

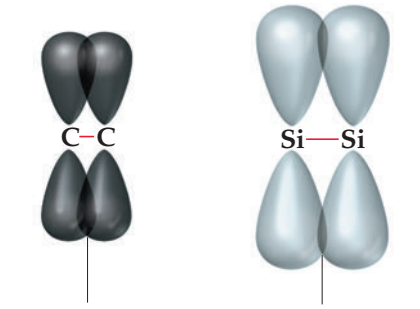
The chemistry exhibited by the first member of a nonmetal group can differ from that of subsequent members in important ways. Two differences are particularly notable:

- The first member is able to accommodate fewer bonded neighbors. For example, nitrogen is able to bond to a maximum of three Cl atoms, NCl_3, whereas phosphorus can bond to five, PCl_5. The small size of nitrogen is largely responsible for this difference.
- The first member can more readily form π bonds and hence double and triple bonds. This trend is also due, in part, to size because small atoms are able to approach each other more closely. As a result, the overlap of *p* orbitals, which results in the formation of π bonds, is more effective for the first element in each group (**Figure 22.2**). More effective overlap means stronger π bonds, reflected in bond enthalpies. For example, the difference between the enthalpies of the C—C bond and the C=C bond is about 270 kJ/mol (Table 8.3); this large value reflects the "strength" of a carbon–carbon π bond. On the other hand, the difference between Si—Si and Si=Si bonds is only about 100 kJ/mol, significantly lower than that for carbon, reflecting much weaker π bonding.

As we shall see, π bonds are particularly important in the chemistry of carbon, nitrogen, and oxygen, each the first member in its group. The heavier elements in these groups have a tendency to form only single bonds.



▲ **Figure 22.1** **Trends in elemental properties.**



▲ **Figure 22.2** **π Bonds in Period 2 and Period 3 elements.**

The ready ability of Period 2 elements to form π bonds is an important factor in determining the elemental forms of these elements. Compare, for example, carbon and silicon. Carbon has five major crystalline *allotropes*: diamond, graphite, buckminsterfullerene, graphene, and carbon nanotubes. Diamond is a covalent-network solid that has C—C σ bonds but no π bonds. Other allotropes of carbon have π bonds that result from the sideways overlap of *p* orbitals. Elemental silicon, however, exists only as a diamond-like covalent-network solid with σ bonds; it has no forms analogous to graphite, buckminsterfullerene, graphene, or carbon nanotubes, apparently because Si—Si π bonds are too weak.

We likewise see significant differences in the dioxides of carbon and silicon as a result of their relative abilities to form π bonds (**Figure 22.3**). CO_2 is a molecular substance containing C=O double bonds, whereas SiO_2 is a covalent-network solid in which four oxygen atoms are bonded to each silicon atom by single bonds, forming an extended structure that has the empirical formula SiO_2.

Sample Exercise 22.1

Identifying Elemental Properties

Of the elements Li, K, N, P, and Ne, which (**a**) is the most electronegative, (**b**) has the greatest metallic character, (**c**) can bond to more than four atoms in a molecule, and (**d**) forms π bonds most readily?

SOLUTION

Analyze We are given a list of elements and asked to predict several properties that can be related to periodic trends.

Plan We can use Figures 22.1 and 22.2 to guide us to the answers.

Solve

(**a**) Electronegativity increases as we proceed toward the upper right portion of the periodic table, excluding the noble gases. Thus, N is the most electronegative element of our choices.

(**b**) Metallic character correlates inversely with electronegativity—the less electronegative an element, the greater its metallic character. The element with the greatest metallic character is therefore K, which is closest to the lower left corner of the periodic table.

(**c**) Nonmetals tend to form molecular compounds, so we can narrow our choice to the three nonmetals on the list: N, P, and Ne. To form more than four bonds, an element must be able to expand its valence shell to allow more than an octet of electrons around it. Valence-shell expansion occurs for Period 3 elements and below; N and Ne are both in Period 2 and do not undergo valence-shell expansion. Thus, the answer is P.

(**d**) Period 2 nonmetals form π bonds more readily than elements in Period 3 and below. There are no compounds known that contain covalent bonds to Ne. Thus, N is the element from the list that forms π bonds most readily.

▶ Practice Exercise

Which description correctly describes a difference between the chemistry of oxygen and sulfur?
(**a**) Oxygen is a nonmetal and sulfur is a metalloid. (**b**) Oxygen can form more than four bonds, whereas sulfur cannot. (**c**) Sulfur has a higher electronegativity than oxygen. (**d**) Oxygen is better able to form π bonds than sulfur.

Chemical Reactions

Because O_2 and H_2O are abundant in our environment, it is particularly important to consider how these substances react with other compounds. About one-third of the reactions discussed in this chapter involve either O_2 (oxidation or combustion reactions) or H_2O (especially proton-transfer reactions).

In combustion reactions, hydrogen-containing compounds produce H_2O. Carbon-containing ones produce CO_2 (unless the amount of O_2 is insufficient, in which case CO or even C can form). Nitrogen-containing compounds tend to form N_2, although NO can form in special cases or in small amounts. A reaction illustrating these points is:

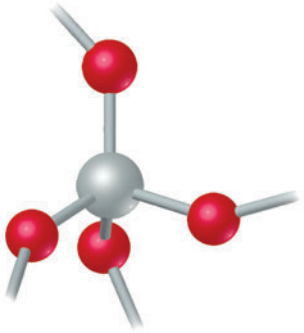
$$4\,CH_3NH_2(g) + 9\,O_2(g) \longrightarrow 4\,CO_2(g) + 10\,H_2O(g) + 2\,N_2(g) \qquad [22.1]$$

The formation of H_2O, CO_2, and N_2 reflects the high thermodynamic stability of these substances, indicated by the large bond energies for the O—H, C═O, and N≡N bonds (463, 799, and 941 kJ/mol, respectively).

When dealing with proton-transfer reactions, remember that the weaker a Brønsted–Lowry acid, the stronger its conjugate base. For example, H_2, OH^-, NH_3, and CH_4 are exceedingly weak proton donors that have *no* tendency to act as acids in water. Thus, the species formed by removing one or more protons from them are extremely strong bases. All of them react readily with water, removing protons from H_2O to form OH^-. Two representative reactions are:

$$CH_3^-(aq) + H_2O(l) \longrightarrow CH_4(g) + OH^-(aq) \qquad [22.2]$$

$$N^{3-}(aq) + 3\,H_2O(l) \longrightarrow NH_3(aq) + 3\,OH^-(aq) \qquad [22.3]$$



Fragment of extended SiO_2 lattice; Si forms only single bonds



CO_2; C forms double bonds

▲ **Figure 22.3 Comparison of the bonds in SiO_2 and CO_2.**

Sample Exercise 22.2

Predicting the Products of Chemical Reactions

Predict the products formed in each of the following reactions, and write a balanced equation:

(**a**) $CH_3NHNH_2(g) + O_2(g) \longrightarrow$? (**b**) $Mg_3P_2(s) + H_2O(l) \longrightarrow$?

SOLUTION

Analyze We are given the reactants for two chemical equations and asked to predict the products and then balance the equations.

Plan We need to examine the reactants to see if we might recognize a reaction type. In (**a**) the carbon compound is reacting with O_2, which suggests a combustion reaction. In (**b**) water reacts with an ionic compound. The anion P^{3-} is a strong base and H_2O is able to act as an acid, so the reactants suggest an acid–base (proton-transfer) reaction.

Solve

(**a**) Based on the elemental composition of the carbon compound, this combustion reaction should produce CO_2, H_2O, and N_2:

$$2\,CH_3NHNH_2(g) + 5\,O_2(g) \longrightarrow 2\,CO_2(g) + 6\,H_2O(g) + 2\,N_2(g)$$

(**b**) Mg_3P_2 is ionic, consisting of Mg^{2+} and P^{3-} ions. The P^{3-} ion, like N^{3-}, has a strong affinity for protons and reacts with H_2O to form OH^- and PH_3 (PH^{2-}, PH_2^-, and PH_3 are all exceedingly weak proton donors).

$$Mg_3P_2(s) + 6\,H_2O(l) \longrightarrow 2\,PH_3(g) + 3\,Mg(OH)_2(s)$$

$Mg(OH)_2$ has low solubility in water and will precipitate.

Practice Exercise

When CaC_2 reacts with water, what carbon-containing compound forms?

(**a**) CO (**b**) CO_2 (**c**) CH_4 (**d**) C_2H_2 (**e**) H_2CO_3

Self-Assessment Exercise

22.1 Carbon dioxide is found in nature as $CO_2(g)$. Would you expect silicon dioxide to be found in nature as $SiO_2(g)$?

(a) Yes

(b) No

Exercises

22.2 Identify each of the following elements as a metal, nonmetal, or metalloid: (**a**) germanium, (**b**) bismuth, (**c**) sulphur, (**d**) calcium, (**e**) rhenium, (**f**) tin.

22.3 Consider the elements Ba, Na, O, B, P, and Kr. From this list, select the element that (**a**) is most electronegative, (**b**) has the greatest metallic character, (**c**) most readily forms a positive ion, (**d**) exhibits a maximum oxidation sate of +5, (**e**) exists as monoatomic gas at room temperature, (**f**) has multiple allotropes.

22.4 Which of the following statements are true?

(**a**) Si can form an ion with six fluorine atoms, SiF_6^{2-}, whereas carbon cannot.

(**b**) Si can form three stable compounds containing two Si atoms each, Si_2H_2, Si_2H_4, and Si_2H_6.

(**c**) In HNO_3 and H_3PO_4 the central atoms, N and P, have different oxidation states.

(**d**) S is more electronegative than Se.

22.5 Complete and balance the following equations:

(**a**) $Mg_3N_2(s) + H_2O(l) \longrightarrow$

(**b**) $C_3H_7OH(l) + O_2(g) \longrightarrow$

(**c**) $MnO_2(s) + C(s) \xrightarrow{\Delta}$

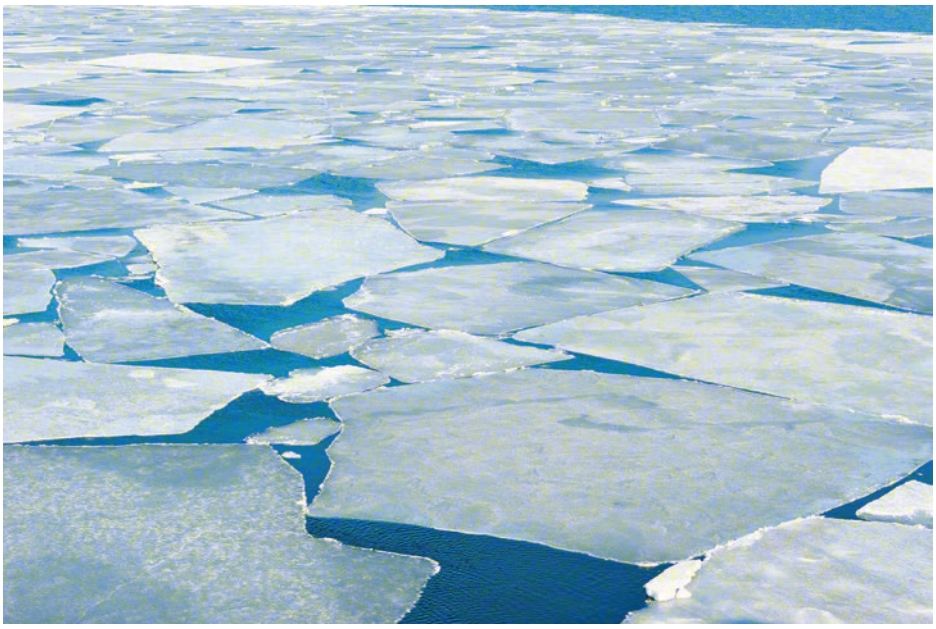
(**d**) $AlP(s) + H_2O(l) \longrightarrow$

(**e**) $Na_2S(s) + HCl(aq) \longrightarrow$

Answers to Self-Assessment Exercise

22.1 (b)

22.2 | Hydrogen



The mass percent of hydrogen in water changes from 11% to 20% as the isotope of hydrogen is changed from ^1H to ^2H. This dramatic change effects both the physical and chemical properties of the material; for example, the density of ice made from ^2H_2O is greater than water made from ^1H_2O, and so ice cubes sink, unlike ice made from ^1H_2O, which floats, as pictured here.

In this section, we review some of the properties and chemistry of hydrogen. By the end of the section, you should be able to

- Appreciate the unique nature of hydrogen.

Because hydrogen produces water when burned in air, the French chemist Antoine Lavoisier gave it the name *hydrogen*, which means "water producer" (Greek: *hydro*, water; *gennao*, to produce).

Hydrogen is the most abundant element in the universe. It is the nuclear fuel consumed by our Sun and other stars to produce energy. Although about 75% of the known mass of the universe is hydrogen, it constitutes only 0.87% of Earth's mass. Most of the hydrogen on our planet is found associated with oxygen. Water, which is 11% hydrogen by mass, is the most abundant hydrogen compound.

Isotopes of Hydrogen

The most common isotope of hydrogen, $^{1}_{1}H$, has a nucleus consisting of a single proton. This isotope, sometimes referred to as **protium**,* makes up 99.9844% of naturally occurring hydrogen.

Two other isotopes are known: $^{2}_{1}H$, whose nucleus contains a proton and a neutron, and $^{3}_{1}H$, whose nucleus contains a proton and two neutrons. The $^{2}_{1}H$ isotope, **deuterium**, makes up 0.0156% of naturally occurring hydrogen. It is not radioactive, and it is often given the symbol D in chemical formulas, as in D_2O (deuterium oxide), which is known as *heavy water*.

Because an atom of deuterium is about twice as massive as an atom of protium, the properties of deuterium-containing substances vary somewhat from those of the protium-containing analogs. For example, the normal melting and boiling points of D_2O are 3.81 °C and 101.42 °C, respectively, versus 0.00 °C and 100.00 °C for H_2O. Not surprisingly, the density of D_2O at 25 °C (1.104 g/mL) is greater than that of H_2O (0.997 g/mL). Replacing protium with deuterium (a process called *deuteration*) can also have a profound effect on reaction rates, a phenomenon called a *kinetic-isotope effect*. For example, heavy water can be obtained from the electrolysis $[2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)]$ of ordinary water because the small amount of naturally occurring D_2O in the sample undergoes electrolysis more slowly than H_2O and, therefore, becomes concentrated during the reaction.

The third isotope, $^{3}_{1}H$, **tritium**, is radioactive, with a half-life of 12.3 yr:

$$^{3}_{1}H \longrightarrow {}^{3}_{2}He + {}^{0}_{-1}e \quad t_{1/2} = 12.3\,\text{yr} \qquad [22.4]$$

Because of its short half-life, only trace quantities of tritium exist naturally. The isotope can be synthesized in nuclear reactors by neutron bombardment of lithium-6:

$$^{6}_{3}Li + {}^{1}_{0}n \longrightarrow {}^{3}_{1}H + {}^{4}_{2}He \qquad [22.5]$$

Deuterium and tritium are useful in studying reactions of compounds containing hydrogen. A compound is "labeled" by replacing one or more ordinary hydrogen atoms with deuterium or tritium at specific locations in a molecule. By comparing the locations of the label atoms in reactants and products, the reaction mechanism can often be inferred. When methanol (CH_3OH) is placed in D_2O, for example, the H atom of the O—H bond exchanges rapidly with the D atoms, forming CH_3OD. The H atoms of the CH_3 group do not exchange. This experiment demonstrates the kinetic stability of C—H bonds and reveals the speed at which the O—H bond in the molecule breaks and re-forms.

Properties of Hydrogen

Hydrogen is the only element that is not a member of any family in the periodic table. Because of its $1s^1$ electron configuration, it is generally placed above lithium in the table. However, it is definitely *not* an alkali metal. It forms a positive ion much less readily than any alkali metal. The ionization energy of the hydrogen atom is 1312 kJ/mol, whereas that of lithium is 520 kJ/mol.

Hydrogen is sometimes placed above the halogens in the periodic table because the hydrogen atom can pick up one electron to form the *hydride ion*, H^-, which has the same electron configuration as helium. However, the electron affinity of hydrogen, $EA = -73$ kJ/mol, is not as large as that of any halogen. In general, hydrogen shows no closer resemblance to the halogens than it does to the alkali metals.

*Giving unique names to isotopes is limited to hydrogen. Because of the proportionally large differences in their masses, the isotopes of H show appreciably more differences in their properties than isotopes of heavier elements.

Elemental hydrogen exists at room temperature as a colorless, odorless, tasteless gas composed of diatomic molecules. We can call H_2 *dihydrogen*, but it is more commonly referred to as either *molecular hydrogen* or simply hydrogen. Because H_2 is nonpolar and has only two electrons, attractive forces between molecules are extremely weak. As a result, its melting point (−259 °C) and boiling point (−253 °C) are very low.

The H—H bond enthalpy (436 kJ/mol) is high for a single bond. (Table 8.3) By comparison, the Cl—Cl bond enthalpy is only 242 kJ/mol. Because H_2 has a strong bond, most reactions involving H_2 are slow at room temperature. However, the molecule is readily activated by heat, irradiation, or catalysis. The activation generally produces hydrogen atoms, which are very reactive. Once H_2 is activated, it reacts rapidly and exothermically with a wide variety of substances.

Hydrogen forms strong covalent bonds with many other elements, including oxygen; the O—H bond enthalpy is 463 kJ/mol. The formation of the strong O—H bond makes hydrogen an effective reducing agent for many metal oxides. When H_2 is passed over heated CuO, for example, copper is produced:

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g) \qquad [22.6]$$

When H_2 is ignited in air, a vigorous reaction occurs, forming H_2O. Air containing as little as 4% H_2 by volume is potentially explosive. Combustion of hydrogen–oxygen mixtures is used in liquid-fuel rocket engines such as those of the Space Shuttle. The hydrogen and oxygen are stored at low temperatures in liquid form.

Production of Hydrogen

When a small quantity of H_2 is needed in the laboratory, it is usually obtained by the reaction between an active metal such as zinc and a dilute strong acid such as HCl or H_2SO_4:

$$Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \qquad [22.7]$$

Large quantities of H_2 are produced by reacting methane with steam at 1100 °C. We can view this process as involving two reactions:

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\,H_2(g) \qquad [22.8]$$

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g) \qquad [22.9]$$

Carbon heated with water to about 1000 °C is another source of H_2:

$$C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g) \qquad [22.10]$$

This mixture, known as *water gas*, is used as an industrial fuel.

A CLOSER LOOK The Hydrogen Economy

The reaction of hydrogen with oxygen is highly exothermic:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \quad \Delta H = -483.6\ \text{kJ} \qquad [22.12]$$

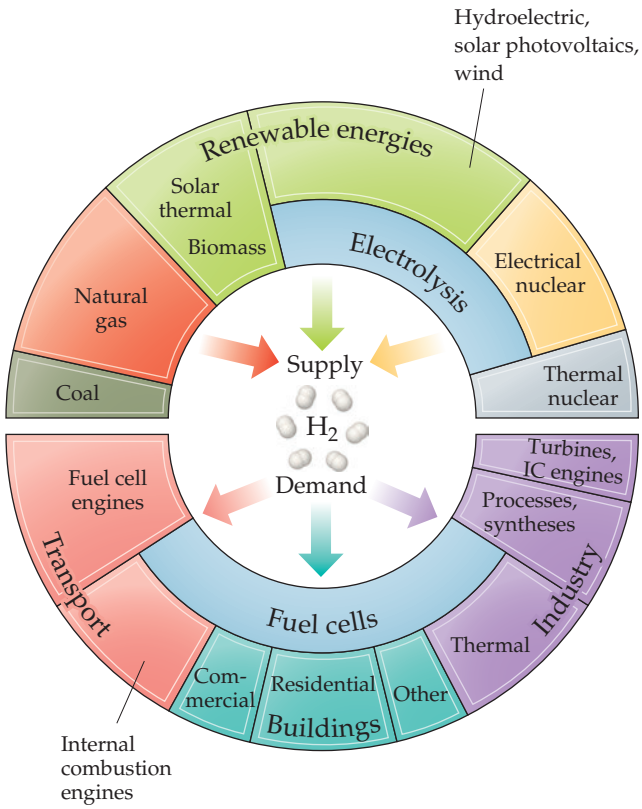
Because H_2 has a low molar mass and a high enthalpy of combustion, it has a high energy density by mass. (That is, its combustion produces high energy per gram.) The only product of the reaction is water vapor, which means that hydrogen is environmentally cleaner than fossil fuels. Thus, the prospect of using hydrogen widely as a fuel is attractive. Furthermore, the hydrogen can be utilized as a fuel in hydrogen fuel cells, enhancing the efficiency of its use.

The term *hydrogen economy* is used to describe the concept of delivering and using hydrogen as a fuel in place of fossil fuels. In order to develop a hydrogen economy, it would be necessary to generate elemental hydrogen on a large scale and arrange for its transport and storage. These matters provide significant technical challenges.

Figure 22.4 illustrates various sources and uses of H_2 fuel. The generation of H_2 through electrolysis of water is in principle the cleanest route, because this process produces only hydrogen and oxygen. (Figure 1.7) However, the energy required to electrolyze water must come from somewhere. If we burn fossil fuels to generate this energy, we have not advanced very far toward a true hydrogen economy. If the energy for electrolysis came instead from a hydroelectric or nuclear power plant, solar cells, or wind generators, consumption of nonrenewable energy sources and undesired production of CO_2 could be avoided.

The storage of hydrogen is another technical obstacle that must be overcome in developing a hydrogen economy. Although $H_2(g)$ has a high energy density by mass, it has a low energy density by volume. Thus, storing hydrogen as a gas requires a large volume compared to the energy it delivers. There are also safety issues associated with handling and storing the gas because its combustion can be explosive. Storing hydrogen in the form of various hydride compounds such as $LiAlH_4$ is being investigated as a means of reducing the volume and increasing the safety. One problem with this approach, however, is that such compounds have high energy density by volume but low energy density by mass.

Related Exercises: 22.11, 22.64, 22.104



▲ **Figure 22.4** **The hydrogen economy would require hydrogen to be produced from various sources and would use hydrogen in energy-related applications.**

Electrolysis of water consumes too much energy and is consequently too costly to be used commercially to produce H_2. However, H_2 is produced as a by-product in the electrolysis of brine (NaCl) solutions in the course of commercial Cl_2 and NaOH manufacture:

$$2\,NaCl(aq) + 2\,H_2O(l) \xrightarrow{\text{electrolysis}} H_2(g) + Cl_2(g) + 2\,NaOH(aq) \qquad [22.11]$$

Uses of Hydrogen

Hydrogen is commercially important. About half of the H_2 produced is used to synthesize ammonia by the Haber process. Much of the remaining hydrogen is used to convert high-molecular-weight hydrocarbons from petroleum into lower-molecular-weight hydrocarbons suitable for fuel (petrol, diesel, and others) in a process known as *cracking*. Hydrogen is also used to manufacture methanol via the catalytic reaction of CO and H_2 at high pressure and temperature:

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g) \qquad [22.13]$$

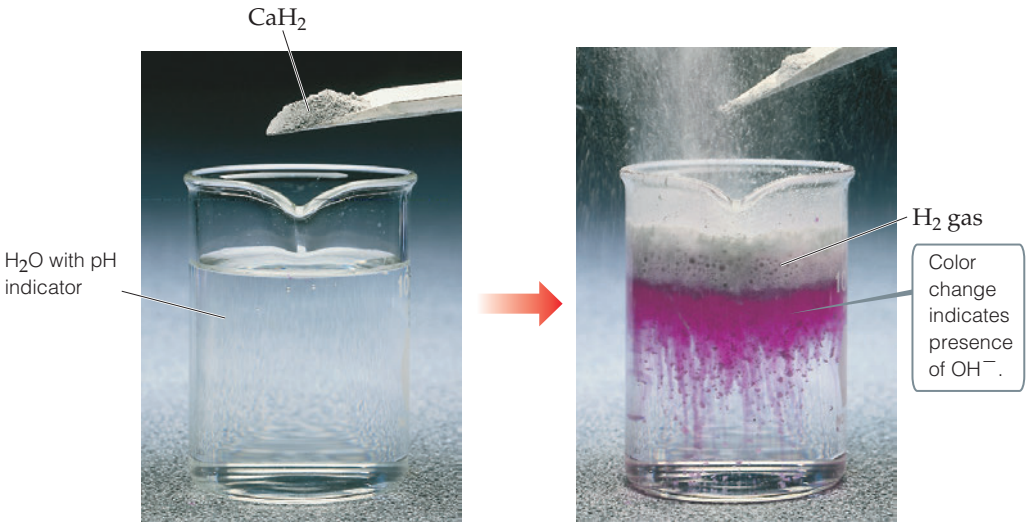
Binary Hydrogen Compounds

Hydrogen reacts with other elements to form three types of compounds: (1) ionic hydrides, (2) metallic hydrides, and (3) molecular hydrides.

The **ionic hydrides** are formed by the alkali metals and by the heavier alkaline earths (Ca, Sr, and Ba). These active metals are much less electronegative than hydrogen. (Figure 8.8) Consequently, hydrogen acquires electrons from them to form hydride ions (H^-):

$$Ca(s) + H_2(g) \longrightarrow CaH_2(s) \qquad [22.14]$$

Go Figure This reaction is exothermic. Is the beaker on the right warmer or colder than the beaker on the left?



▲ **Figure 22.5 The reaction of CaH_2 with water.**

Go Figure Which is the most thermodynamically stable hydride? Which is the least thermodynamically stable?

14	15	16	17
$CH_4(g)$ −50.8	$NH_3(g)$ −16.7	$H_2O(l)$ −237	$HF(g)$ −271
$SiH_4(g)$ +56.9	$PH_3(g)$ +18.2	$H_2S(g)$ −33.0	$HCl(g)$ −95.3
$GeH_4(g)$ +117	$AsH_3(g)$ +111	$H_2Se(g)$ +71	$HBr(g)$ −53.2
	$SbH_3(g)$ +187	$H_2Te(g)$ +138	$HI(g)$ +1.30

▲ **Figure 22.6 Standard free energies of formation of molecular hydrides.** All values are kilojoules per mole of hydride.

The hydride ion is very basic and reacts readily with compounds having even weakly acidic protons to form H_2 as shown in Figure 22.5 and summarized by the following equation:

$$H^-(aq) + H_2O(l) \longrightarrow H_2(g) + OH^-(aq) \qquad [22.15]$$

Ionic hydrides can therefore be used as convenient (although expensive) sources of H_2.

Calcium hydride (CaH_2) is used to inflate life rafts, weather balloons, and the like where a simple, compact means of generating H_2 is desired (Figure 22.5).

Metallic hydrides are formed when hydrogen reacts with transition metals. These compounds are so named because they retain their metallic properties. In many metallic hydrides, the ratio of metal atoms to hydrogen atoms is not fixed or in small whole numbers. The composition can vary within a range, depending on reaction conditions. TiH_2 can be produced, for example, but preparations usually yield $TiH_{1.8}$. These nonstoichiometric metallic hydrides are sometimes called *interstitial hydrides*. Because hydrogen atoms are small enough to fit between the sites occupied by the metal atoms, many metal hydrides behave like interstitial alloys.

The **molecular hydrides**, formed by nonmetals and metalloids, are either gases or liquids under standard conditions. The simple molecular hydrides are listed in Figure 22.6, together with their standard free energies of formation, ΔG_f°. In each family, the thermal stability (measured as ΔG_f°) decreases as we move down the family. (Recall that the more stable a compound is with respect to its elements under standard conditions, the more negative ΔG_f° is.)

Self-Assessment Exercise

22.6 What is the oxidation state of H in $LiAlH_4$?

(a) −1
(b) 0
(c) +1

Exercises

22.7 (**a**) Give the names and chemical symbols for the three isotopes of hydrogen. (**b**) List the isotopes in order of decreasing natural abundance. (**c**) Which hydrogen isotope is radioactive? (**d**) Write the nuclear equation for the radioactive decay of this isotope.

22.8 What does hydrogen have in common with the halogens? Explain.

22.9 Write balanced equations for each of the following reactions (some of these are analogous to reactions shown in the chapter). (**a**) Aluminum metal reacts with acids to form hydrogen gas. (**b**) Steam reacts with magnesium metal to give magnesium oxide and hydrogen. (**c**) Manganese(IV) oxide is reduced to manganese(II) oxide by hydrogen gas. (**d**) Calcium hydride reacts with water to generate hydrogen gas.

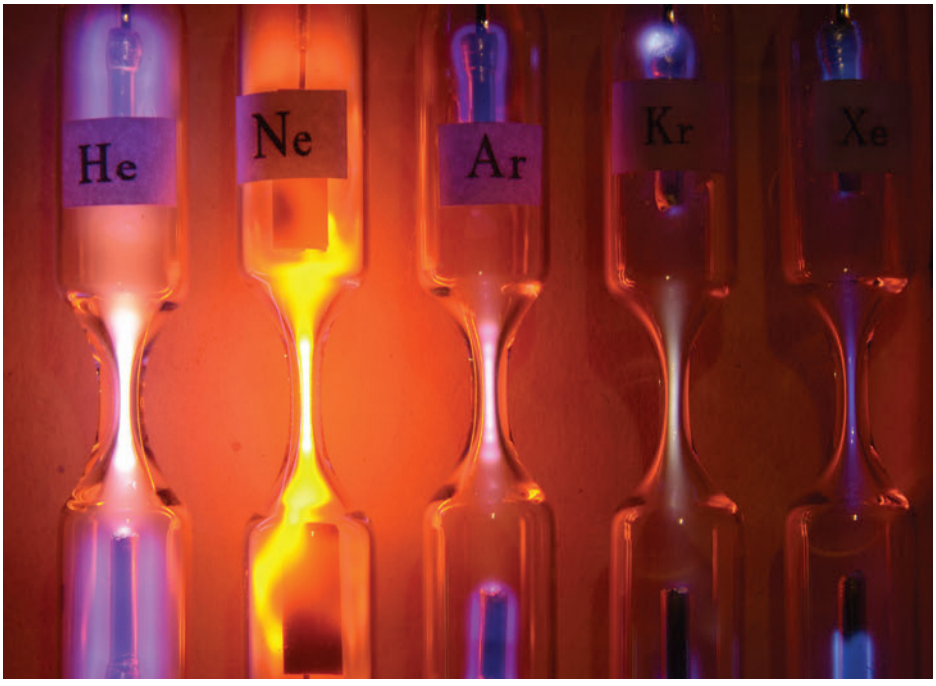
22.10 Identify the following hydrides as ionic, metallic, or molecular: (**a**) MgH_2, (**b**) HI, (**c**) $LaNi_{4.7}Al_{0.3}H_6$.

22.11 The H_2/O_2 fuel cell converts elemental hydrogen and oxygen into water, producing, theoretically, 1.23 V. What is the most sustainable way to obtain hydrogen to run a large number of fuel cells? Explain.

Answers to Self-Assessment Exercise

22.6 (a)

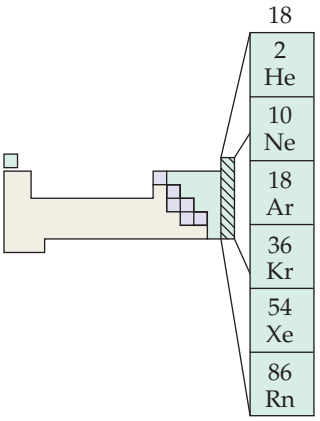
22.3 | Group 18: The Noble Gases



In this section, we review some of the properties of the noble gasses. By the end of this section, you should be able to

- Understand that some Group 18 elements form compounds

The elements of Group 18 are chemically unreactive. Indeed, most of our references to these elements have been in relation to their physical properties, as when we discussed intermolecular forces. The relative inertness of these elements is due to the presence of



a completed octet of valence-shell electrons (except He, which only has a filled 1*s* shell). The stability of such an arrangement is reflected in the high ionization energies of the Group 18 elements.

The Group 18 elements are all gases at room temperature. They are components of Earth's atmosphere, except for radon, which exists only as a short-lived radioisotope. Only argon is relatively abundant. (Table 18.1)

Neon, argon, krypton, and xenon are used in lighting, display, and laser applications in which the atoms are excited electrically and electrons that are in a higher energy state emit light as they return to the ground state. Argon is also used as a protective atmosphere to prevent oxidation in welding and certain high-temperature metallurgical processes.

Helium is in many ways the most important noble gas. Liquid helium is used as a coolant to conduct experiments at very low temperatures. Helium boils at 4.2 K and 101.3 kPa, the lowest boiling point of any substance. It is found in relatively high concentrations in many natural-gas wells from which it is isolated.

Noble Gas Compounds

Because the noble gases are exceedingly stable, they react only under rigorous conditions. We expect the heavier ones to be most likely to form compounds because their ionization energies are lower. (Figure 7.10) A lower ionization energy suggests the possibility of sharing an electron with another atom, leading to a chemical bond. In addition, because the Group 18 elements (except helium) already contain eight electrons in their valence shell, formation of covalent bonds will require an expanded valence shell. Valence-shell expansion occurs most readily with larger atoms.

The first noble gas compound was reported in 1962. This discovery caused a sensation because it undercut the belief that the noble gas elements were inert. The initial study involved xenon in combination with fluorine, the element we would expect to be most reactive in pulling electron density from another atom. Since that time chemists have prepared several xenon compounds of fluorine and oxygen (**Table 22.1**). The fluorides XeF_2, XeF_4, and XeF_6 are made by direct reaction of the elements. By varying the ratio of reactants and altering reaction conditions, each of the three compounds can be obtained. The oxygen containing compounds are formed when the fluorides react with water as, for example,

$$XeF_6(s) + 3\,H_2O(l) \longrightarrow XeO_3(aq) + 6\,HF(aq) \qquad [22.16]$$

TABLE 22.1 Properties of Xenon Compounds

Compound	Oxidation State of Xe	Melting Point (°C)	ΔH°_f (kJ/mol)[a]
XeF_2	+2	129	−109(*g*)
XeF_4	+4	117	−218(*g*)
XeF_6	+6	49	−298(*g*)
$XeOF_4$	+6	−41 to −28	+146(*l*)
XeO_3	+6	−[b]	+402(*s*)
XeO_2F_2	+6	31	+145(*s*)
XeO_4	+8	−[c]	–

[a]At 25 °C, for the compound in the state indicated.
[b]A solid; decomposes at 40 °C.
[c]A solid; decomposes at −40 °C.

Sample Exercise 22.3

Predicting a Molecular Structure

Use the VSEPR model to predict the structure of XeF_4.

SOLUTION

Analyze We must predict the geometrical structure given only the molecular formula.

Plan We must first write the Lewis structure for the molecule. We then count the number of electron pairs (domains) around the Xe atom and use that number and the number of bonds to predict the geometry.

Solve There are 36 valence-shell electrons (8 from xenon and 7 from each fluorine). If we make four single Xe—F bonds, each fluorine has its octet satisfied. Xe then has 12 electrons in its valence shell, so we expect an octahedral arrangement of six electron pairs. Two of these are nonbonded pairs. Because nonbonded pairs require more volume than bonded pairs, it is reasonable to expect these nonbonded pairs to be opposite each other. The expected structure is square planar, as shown in Figure 22.7.



▲ **Figure 22.7** Xenon tetrafluoride.

Comment The experimentally determined structure agrees with this prediction.

Practice Exercise

Compounds containing the XeF_3^+ ion have been characterized. Describe the electron-domain geometry and molecular geometry of this ion.
(**a**) trigonal planar, trigonal planar (**b**) tetrahedral, trigonal pyramidal (**c**) trigonal bipyramidal, T shaped (**d**) tetrahedral, tetrahedral (**e**) octahedral, square planar

The other noble gas elements form compounds much less readily than xenon. For many years, only one binary krypton compound, KrF_2, was known with certainty, and it decomposes to its elements at −10 °C. Other compounds of krypton have been isolated at very low temperatures (40 K). In 2000, a compound of argon, HArF, was discovered, but it can exist only in argon matrices at very low temperatures.

Self-Assessment Exercise

22.12 Predict the molecular geometry of XeO_3.

(a) Trigonal planar
(b) Trigonal pyramidal
(c) T-shaped

Exercises

22.13 A friend tells you that the "neon" in neon signs is a compound of neon and aluminum. Can your friend be correct? Explain.

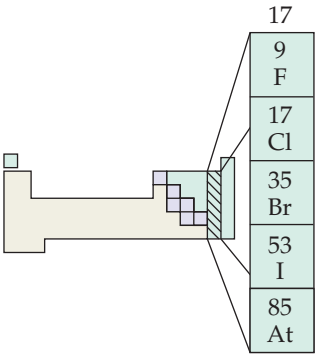
22.14 Write the chemical formula for each of the following, and indicate the oxidation state of the halogen or noble-gas atom in each: (**a**) krypton tetrafluoride, (**b**) hexafluoroantimonate ion, (**c**) sodium hypoiodite, (**d**) perbromic acid, (**e**) aluminum perchlorate, (**f**) iron(II) iodite.

Answers to Self-Assessment Exercise

22.12 (b)

22.4 | Group 17: The Halogens





Fluorite is a mineral composed of calcium fluoride and is found in colors ranging from yellow to green to purple. It is a commercial source of fluorine in the form of hydrogen fluoride. In contrast chlorine, bromine and iodine may all be obtained from sea water.

By the end of this section, which reviews the halogens, you should be able to

- Understand the trends in selected physical and chemical properties of the halogens

The elements of Group 17, the halogens, have the outer-electron configuration ns^2np^5, where n ranges from 2 through 6. The halogens have large negative electron affinities, and they most often achieve a noble-gas configuration by gaining an electron, which results in a -1 oxidation state. Fluorine, being the most electronegative element, exists in compounds only in the -1 state. The other halogens exhibit positive oxidation states up to $+7$ in combination with more electronegative atoms such as O. In the positive oxidation states, the halogens tend to be good oxidizing agents, readily accepting electrons.

Chlorine, bromine, and iodine are found as the halides in seawater and in salt deposits. Fluorine occurs in the minerals fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluorapatite [$Ca_5(PO_4)_3F$].* Only fluorspar is an important commercial source of fluorine.

All isotopes of astatine are radioactive. The longest-lived isotope is astatine-210, which has a half-life of 8.1 h and decays mainly by electron capture. Because astatine is so unstable, very little is known about its chemistry.

Properties and Production of the Halogens

Most properties of the halogens vary in a regular fashion as we go from fluorine to iodine (**Table 22.2**).

Under ordinary conditions the halogens exist as diatomic molecules. The molecules are held together in the solid and liquid states by dispersion forces. Because I_2 is the largest and most polarizable halogen molecule, the intermolecular forces between I_2 molecules

*Minerals are solid substances that occur in nature. They are usually known by their common names rather than by their chemical names. What we know as rock is merely an aggregate of different minerals.

TABLE 22.2 Some Properties of the Halogens

Property	F	Cl	Br	I
Atomic radius (pm)	57	102	120	139
Ionic radius, X^- (pm)	133	181	196	220
First ionization energy (kJ/mol)	1681	1251	1140	1008
Electron affinity (kJ/mol)	−328	−349	−325	−295
Electronegativity	4.0	3.0	2.8	2.5
X—X single-bond enthalpy (kJ/mol)	155	242	193	151
Reduction potential (V):				
$\frac{1}{2}X_2(aq) + e^- \longrightarrow X^-(aq)$	2.87	1.36	1.07	0.54

are the strongest. Thus, I_2 has the highest melting point and boiling point. At room temperature and 101.3 kPa, I_2 is a purple solid, Br_2 is a red-brown liquid, and Cl_2 and F_2 are gases. (Figure 7.28) Chlorine readily liquefies upon compression at room temperature and is normally stored and handled in liquid form under pressure in steel containers.

The comparatively low bond enthalpy of F_2 (155 kJ/mol) accounts in part for the extreme reactivity of elemental fluorine. Because of its high reactivity, F_2 is difficult to work with. Certain metals, such as copper and nickel, can be used to contain F_2 because their surfaces form a protective coating of metal fluoride. Chlorine and the heavier halogens are also reactive, though less so than fluorine.

Because of their high electronegativities, the halogens tend to gain electrons from other substances and thereby serve as oxidizing agents. The oxidizing ability of the halogens, indicated by their standard reduction potentials, decreases going down the group. As a result, a given halogen is able to oxidize the halide anions below it. For example, Cl_2 oxidizes Br^- and I^- but not F^-, as seen in **Figure 22.8**.

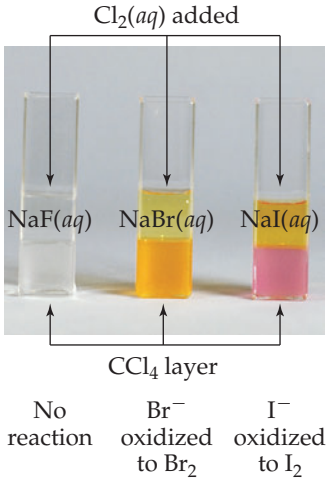
Notice in Table 22.2 that the standard reduction potential of F_2 is exceptionally high. As a result, fluorine gas readily oxidizes water:

$$F_2(aq) + H_2O(l) \longrightarrow 2\,HF(aq) + \tfrac{1}{2}\,O_2(g) \qquad E^\circ = 1.80\,V \qquad [22.17]$$

Fluorine cannot be prepared by electrolytic oxidation of aqueous solutions of fluoride salts because water is oxidized more readily than F^-. In practice, the element is formed by electrolytic oxidation of a solution of KF in anhydrous HF.

Go Figure

Do Br_2 and I_2 appear to be more or less soluble in CCl_4 than in H_2O?



▲ Figure 22.8 Reaction of Cl_2 with aqueous solutions of NaF, NaBr, and NaI in the presence of tetrachloromethane. The top liquid layer in each vial is water; the bottom liquid layer is tetrachloromethane. The $Cl_2(aq)$, which has been added to each vial, is colorless. The brown color in the carbon tetrachloride layer indicates the presence of Br_2, whereas purple indicates the presence of I_2.

Sample Exercise 22.4

Predicting Chemical Reactions among the Halogens

Write the balanced equation for the reaction, if any, between (**a**) $I^-(aq)$ and $Br_2(l)$, (**b**) $Cl^-(aq)$ and $I_2(s)$.

SOLUTION

Analyze We are asked to determine whether a reaction occurs when a particular halide and halogen are combined.

Plan A given halogen is able to oxidize anions of the halogens below it in the periodic table. Thus, in each pair the halogen having the smaller atomic number ends up as the halide ion. If the halogen with the smaller atomic number is already the halide ion, there is no reaction. Thus, the key to determining whether a reaction occurs is locating the elements in the periodic table.

Solve

(**a**) Br_2 can oxidize (remove electrons from) the anions of the halogens below it in the periodic table. Thus, it oxidizes I^-:

$$2\,I^-(aq) + Br_2(aq) \longrightarrow I_2(s) + 2\,Br^-(aq)$$

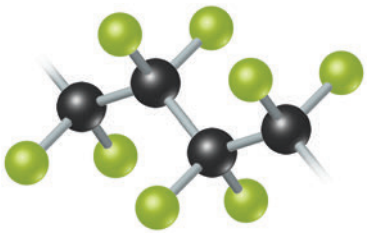
(**b**) Cl^- is the anion of a halogen above iodine in the periodic table. Thus, I_2 cannot oxidize Cl^-; there is no reaction.

Practice Exercise

Which is (are) able to oxidize Cl^-?
(**a**) F_2
(**b**) F^-
(**c**) Both Br_2 and I_2
(**d**) Both Br^- and I^-

Go Figure

What is the repeating unit in this polymer?



▲ **Figure 22.9** **Structure of Teflon®, a fluorocarbon polymer.**

Chlorine is produced mainly by electrolysis of either molten or aqueous sodium chloride. Both bromine and iodine are obtained commercially from brines containing the halide ions; the reaction used is oxidation with Cl_2.

Uses of the Halogens

Fluorine is used to prepare fluorocarbons—very stable carbon–fluorine compounds used as refrigerants, lubricants, and plastics. Teflon® (**Figure 22.9**) is a polymeric fluorocarbon noted for its high thermal stability and lack of chemical reactivity.

Chlorine is by far the most commercially important halogen. About half of the chlorine is used to manufacture chlorine-containing organic compounds, such as the vinyl chloride (C_2H_3Cl) used in making polyvinyl chloride (PVC) plastics. Much of the remainder is used as a bleaching agent in the paper and textile industries.

When Cl_2 dissolves in cold dilute base, it converts into Cl^- and hypochlorite, ClO^-:

$$Cl_2(aq) + 2\,OH^-(aq) \rightleftharpoons Cl^-(aq) + ClO^-(aq) + H_2O(l) \qquad [22.18]$$

Sodium hypochlorite (NaClO) is the active ingredient in many liquid bleaches. Chlorine is also used in water treatment to oxidize and thereby destroy bacteria.

A common use of iodine is as KI in table salt. Iodized salt provides the small amount of iodine necessary in our diets; it is essential for the formation of thyroxin, a hormone secreted by the thyroid gland. Lack of iodine in the diet results in an enlarged thyroid gland, a condition called *goiter*.

The Hydrogen Halides

All the halogens form stable diatomic molecules with hydrogen. The hydrogen halides can be formed by direct reaction of the elements.

The hydrogen halides form hydrohalic acid solutions when dissolved in water. These solutions have the characteristic properties of acids, such as reactions with active metals to produce hydrogen gas. Hydrofluoric acid also reacts readily with **silica** (SiO_2) and with silicates to form hexafluorosilicic acid (H_2SiF_6):

$$SiO_2(s) + 6\,HF(aq) \longrightarrow H_2SiF_6(aq) + 2\,H_2O(l) \qquad [22.19]$$

Interhalogen Compounds

Because the halogens exist as diatomic molecules, diatomic molecules made up of two different halogen atoms exist. These compounds are the simplest examples of **interhalogens**, compounds, such as ClF and IF_5, formed between two halogen elements.

The vast majority of the higher interhalogen compounds have a central Cl, Br, or I atom surrounded by fluorine atoms. The large size of the iodine atom allows the formation of IF_3, IF_5, and IF_7, in which the oxidation state of I is +3, +5, and +7, respectively. With the smaller bromine and chlorine atoms, only compounds with three or five fluorines form. The only higher interhalogen compounds that do not have outer F atoms are ICl_3 and ICl_5; the large size of the I atom can accommodate five Cl atoms, whereas Br is not large enough to allow even $BrCl_3$ to form. All of the interhalogen compounds are powerful oxidizing agents.

Oxyacids and Oxyanions

Table 22.3 summarizes the formulas of the known oxyacids of the halogens and the way they are named.* The acid strengths of the oxyacids increase with the increasing oxidation state of the central halogen atom. All the oxyacids are strong oxidizing agents. The

*Fluorine forms one oxyacid, HOF. Because the electronegativity of fluorine is greater than that of oxygen, we must consider fluorine to be in a −1 oxidation state and oxygen to be in the 0 oxidation state in this compound.

TABLE 22.3 The Stable Oxyacids of the Halogens

	Formula of Acid			
Oxidation State of Halogen	Cl	Br	I	Acid Name
+1	HClO	HBrO	HIO	*Hypo*halous acid
+3	$HClO_2$	—	—	Hal*ous* acid
+5	$HClO_3$	$HBrO_3$	HIO_3	Hal*ic* acid
+7	$HClO_4$	$HBrO_4$	HIO_4	*Perhalic* acid

oxyanions, formed on removal of H^+ from the oxyacids, are generally more stable than the oxyacids. Hypochlorite salts are used as bleaches and disinfectants because of the powerful oxidizing capabilities of the ClO^- ion. Chlorate salts are similarly very reactive. For example, potassium chlorate is used to make matches and fireworks.

Perchloric acid and its salts are the most stable oxyacids and oxyanions. Dilute solutions of perchloric acid are quite safe, and many perchlorate salts are stable except when heated with organic materials. When heated, however, perchlorates can become vigorous, even violent, oxidizers. Considerable caution should be exercised, therefore, when handling these substances, and it is crucial to avoid contact between perchlorates and readily oxidized material. The use of ammonium perchlorate (NH_4ClO_4) as the oxidizer in the solid booster rockets for the Space Shuttle demonstrates the oxidizing power of perchlorates. The solid propellant contains a mixture of NH_4ClO_4 and powdered aluminum, the reducing agent. Each shuttle launch requires about 6×10^5 kg of NH_4ClO_4 (Figure 22.10).



▲ **Figure 22.10 Launch of the Space Shuttle *Columbia* from the Kennedy Space Center.**

Self-Assessment Exercise

22.15 What is the oxidation state of Cl in each Cl species in Equation 22.18?

(a) Cl_2 0; Cl^- −1; ClO^- −1
(b) Cl_2 0; Cl^- −1; ClO^- +1
(c) Cl_2 0; Cl^- +1; ClO^- +1

Exercises

22.16 Name the following compounds and assign oxidation states to the halogens in them: (**a**) BCl_3, (**b**) $Sr(IO_4)_2$, (**c**) LiOCl, (**d**) HClO, (**e**) CuClO, (**f**) $Mg(IO_2)$.

22.17 Explain the following observations: (**a**) For a given oxidation state, the acid strength of the oxyacid in aqueous solution decreases in the order chlorine > bromine > iodine. (**b**) Hydrofluoric acid cannot be stored in glass bottles. (**c**) HI cannot be prepared by treating NaI with sulfuric acid. (**d**) The interhalogen ICl_3 is known, but $BrCl_3$ is not.

Answers to Self-Assessment Exercise

22.15 (b)

22.5 | Oxygen



Oxygen is one of the most reactive nonmetals, and as a consequence of this, and its abundant supply, we live in a world dominated by oxidation products. Considerable effort is put into extracting metals from their oxides and preventing oxidation of food stuffs or the rusting of iron used in construction. On the other side it is essential to the respiration of all aerobic organisms. In this overview, we look at the different forms (oxidation states) that oxygen can adopt. By the end of this section, you should be able to

- Identify the different oxides that occur and their reactions with water

Oxygen is found in combination with other elements in a great variety of compounds—water (H_2O), silica (SiO_2), alumina (Al_2O_3), and the iron oxides (Fe_2O_3, Fe_3O_4) are obvious examples. Indeed, oxygen is the most abundant element by mass both in Earth's crust and in the human body. It is the oxidizing agent for the metabolism of our foods and is crucial to human life.

Properties of Oxygen

Oxygen has two allotropes, O_2 and O_3. When we speak of molecular oxygen or simply oxygen, it is usually understood that we are speaking of *dioxygen* (O_2), the normal form of the element; O_3 is ozone.

At room temperature, dioxygen is a colorless and odorless gas. Dioxygen is only slightly soluble in water (0.04 g/L, or 0.001 *M* at 25 °C), but its presence in water is essential to marine life.

The electron configuration of the oxygen atom is $[He]2s^22p^4$. Thus, oxygen can complete its octet of valence electrons either by picking up two electrons to form the oxide ion (O^{2-}) or by sharing two electrons. In its covalent compounds, it tends to form either two single bonds, as in H_2O, or a double bond, as in formaldehyde ($H_2C{=}O$). The O_2 molecule contains a double bond. The bond in O_2 is very strong (bond enthalpy 495 kJ/mol). Oxygen also forms strong bonds with many other elements. Consequently, many oxygen-containing compounds are thermodynamically more stable than O_2. In the absence of a catalyst, however, most reactions of O_2 have high activation energies and thus require

high temperatures to proceed at a suitable rate. Once a sufficiently exothermic reaction begins, it may accelerate rapidly, producing a reaction of explosive violence.

Production of Oxygen

Nearly all commercial oxygen is obtained from air. The normal boiling point of O_2 is −183 °C, whereas that of N_2, the other principal component of air, is −196 °C. Thus, when air is liquefied and then allowed to warm, the N_2 boils off, leaving liquid O_2 contaminated mainly by small amounts of N_2 and Ar.

Much of the O_2 in the atmosphere is replenished through photosynthesis, in which green plants use the energy of sunlight to generate O_2 (along with glucose, $C_6H_{12}O_6$) from atmospheric CO_2:

$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6\,O_2(g) \qquad [22.20]$$

Uses of Oxygen

In industrial use, oxygen ranks behind only sulfuric acid (H_2SO_4) and nitrogen (N_2). Oxygen is by far the most widely used oxidizing agent in industry. Over half of the O_2 produced is used in the steel industry, mainly to remove impurities from steel. It is also used to bleach pulp and paper. (Oxidation of colored compounds often gives colorless products.) Oxygen is used together with acetylene (C_2H_2) in oxyacetylene welding (**Figure 22.11**). The reaction between C_2H_2 and O_2 is highly exothermic, producing temperatures in excess of 3000 °C.



▲ **Figure 22.11** **Welding with an oxyacetylene torch.**

Ozone

Ozone is a pale blue, poisonous gas with a sharp, irritating odor. Many people can detect as little as 0.01 ppm in air. Exposure to 0.1 to 1 ppm produces headaches, burning eyes, and irritation to the respiratory passages.

The O_3 molecule possesses π electrons that are delocalized over the three oxygen atoms. The molecule dissociates readily, forming reactive oxygen atoms:

$$O_3(g) \longrightarrow O_2(g) + O(g) \quad \Delta H^\circ = 105\ \text{kJ} \qquad [22.21]$$

Ozone is a stronger oxidizing agent than dioxygen. Ozone forms oxides with many elements under conditions where O_2 will not react; indeed, it oxidizes all the common metals except gold and platinum.

Ozone can be prepared by passing electricity through dry O_2. During thunderstorms, ozone is generated (and can be smelled, if you are too close) from lightning strikes:

$$3\,O_2(g) \xrightarrow{\text{electricity}} 2\,O_3(g) \quad \Delta H^\circ = 285\ \text{kJ} \qquad [22.22]$$

Ozone is sometimes used to treat drinking water. Like Cl_2, ozone kills bacteria and oxidizes organic compounds. The largest use of ozone, however, is in the preparation of pharmaceuticals, synthetic lubricants, and other commercially useful organic compounds, where O_3 is used to sever carbon–carbon double bonds.

Ozone is an important component of the upper atmosphere, where it screens out ultraviolet radiation and so protects us from the effects of these high-energy rays. For this reason, depletion of stratospheric ozone is a major scientific concern. In the lower atmosphere, ozone is considered an air pollutant and is a major constituent of smog. Because of its oxidizing power, ozone damages living systems and structural materials, especially rubber.

Oxides

The electronegativity of oxygen is second only to that of fluorine. As a result, oxygen has negative oxidation states in all compounds except OF_2 and O_2F_2. The −2 oxidation state is by far the most common. Compounds that contain oxygen in this oxidation state are called *oxides*.

Nonmetals form covalent oxides, most of which are simple molecules with low melting and boiling points. Both SiO_2 and B_2O_3, however, have extended structures. Most nonmetal oxides combine with water to give oxyacids. Sulfur dioxide (SO_2), for example, dissolves in water to give sulfurous acid (H_2SO_3):

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq) \qquad [22.23]$$

This reaction and that of SO_3 with H_2O to form H_2SO_4 are largely responsible for acid rain. The analogous reaction of CO_2 with H_2O to form carbonic acid (H_2CO_3) causes the acidity of carbonated water.

Oxides that form acids when they react with water are called either **acidic anhydrides** (anhydride means "without water") or **acidic oxides**. A few nonmetal oxides, especially ones with the nonmetal in a low oxidation state—such as N_2O, NO, and CO—do not react with water and are not acidic anhydrides.

Most metal oxides are ionic compounds. The ionic oxides that dissolve in water form hydroxides and, consequently, are called either **basic anhydrides** or **basic oxides**. Barium oxide, for example, reacts with water to form barium hydroxide (**Figure 22.12**). These kinds of reactions are due to the high basicity of the O^{2-} ion and its virtually complete hydrolysis in water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq) \qquad [22.24]$$

Even those ionic oxides that are insoluble in water tend to dissolve in strong acids. Iron(III) oxide, for example, dissolves in acids:

$$Fe_2O_3(s) + 6\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + 3\,H_2O(l) \qquad [22.25]$$

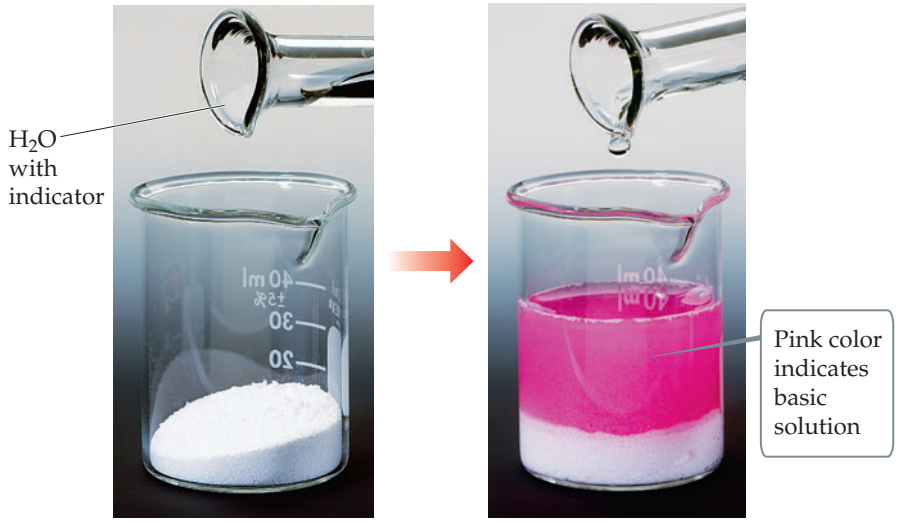
This reaction is used to remove rust ($Fe_2O_3 \cdot nH_2O$) from iron or steel before a protective coat of zinc or tin is applied.

Oxides that can exhibit both acidic and basic characters are said to be *amphoteric*. If a metal forms more than one oxide, the basic character of the oxide decreases as the oxidation state of the metal increases (**Table 22.4**).

Peroxides and Superoxides

Compounds containing O—O bonds and oxygen in the −1 oxidation state are *peroxides*. Oxygen has an oxidation state of $-\frac{1}{2}$ in O_2^-, which is called the *superoxide* ion. The

Go Figure Is this reaction a redox reaction?



▲ **Figure 22.12** Reaction of a basic oxide with water.

TABLE 22.4 Acid–Base Character of Chromium Oxides

Oxide	Oxidation State of Cr	Nature of Oxide
CrO	+2	Basic
Cr_2O_3	+3	Amphoteric
CrO_3	+6	Acidic

most active (easily oxidized) metals (K, Rb, and Cs) react with O_2 to give superoxides (KO_2, RbO_2, and CsO_2). Their active neighbors in the periodic table (Na, Ca, Sr, and Ba) react with O_2, producing peroxides (Na_2O_2, CaO_2, SrO_2, and BaO_2). Less active metals and nonmetals produce normal oxides.

When superoxides dissolve in water, O_2 is produced:

$$4\,KO_2(s) + 2\,H_2O(l) \longrightarrow 4\,K^+(aq) + 4\,OH^-(aq) + 3\,O_2(g) \qquad [22.26]$$

Because of this reaction, potassium superoxide is used as an oxygen source in masks worn by rescue workers (**Figure 22.13**). For proper breathing in toxic environments, oxygen must be generated in the mask and exhaled carbon dioxide in the mask must be eliminated. Moisture in the breath causes the KO_2 to decompose to O_2 and KOH, and the KOH removes CO_2 from the exhaled breath:

$$2\,OH^-(aq) + CO_2(g) \longrightarrow H_2O(l) + CO_3^{2-}(aq) \qquad [22.27]$$

Hydrogen peroxide (**Figure 22.14**) is the most familiar and commercially important peroxide. Pure hydrogen peroxide is a clear, syrupy liquid that melts at −0.4 °C. Concentrated hydrogen peroxide is dangerously reactive because the decomposition to water and oxygen is very exothermic:

$$2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g) \quad \Delta H^\circ = -196.1\ \text{kJ} \qquad [22.28]$$

This is an example of a **disproportionation** reaction, in which an element is simultaneously oxidized and reduced. The oxidation number of oxygen changes from −1 to −2 and 0.

Hydrogen peroxide is marketed as a chemical reagent in aqueous solutions of up to about 30% by mass. A solution containing about 3% H_2O_2 by mass is sold in drugstores and used as a mild antiseptic. Somewhat more concentrated solutions are used to bleach fabrics.

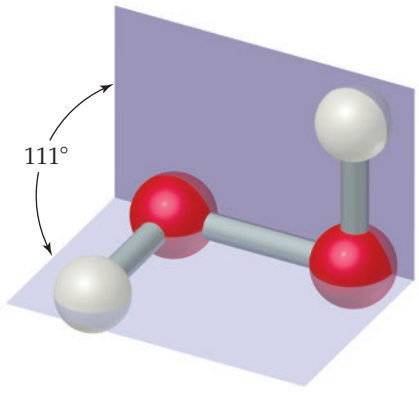
The peroxide ion is a by-product of metabolism that results from the reduction of O_2. The body disposes of this reactive ion with enzymes such as peroxidase and catalase.



▲ **Figure 22.13 A self-contained breathing apparatus.**

Go Figure

Does H_2O_2 have a dipole moment?



◀ **Figure 22.14 Molecular structure of hydrogen peroxide in the gas phase.** The repulsive interaction of the O—H bonds with the lone pairs of electrons on each O atom restricts the free rotation around the O—O single bond.

Self-Assessment Exercise

22.18 What acid is produced by the reaction of N_2O_5 with water?

(a) HNO
(b) HNO_2
(c) HNO_3

Exercises

22.19 Complete and balance the following equations:

(a) $CaO(s) + H_2O(l) \longrightarrow$
(b) $Al_2O_3(s) + H^+(aq) \longrightarrow$
(c) $Na_2O_2(s) + H_2O(l) \longrightarrow$
(d) $N_2O_3(g) + H_2O(l) \longrightarrow$
(e) $KO_2(s) + H_2O(l) \longrightarrow$
(f) $NO(g) + O_3(g) \longrightarrow$

22.20 Select the more acidic member of each of the following pairs: **(a)** V_2O_5 and VO, **(b)** PbO and PbO_2, **(c)** N_2O_3 and N_2O_2, **(d)** SO_2 and SeO_2, **(e)** Al_2O_3 and SeO_2, **(f)** CO_2 and B_2O_3.

Answers to Self-Assessment Exercise

22.18 (c)

22.6 The Other Group 16 Elements: S, Se, Te, and Po



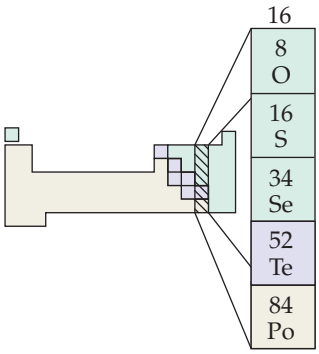
Deep in the ocean, there is no light and little food. Nevertheless, there can be thriving ecosystems centered around hydrothermal vents associated with tectonic activity. Here, bacteria have evolved to convert the heat and sulfur compounds (usually H_2S) emitted by the vent into food and energy. They are the bottom of a small, but important, food chain! In this section, we review the other elements of Group 16, the most important of which is sulfur. By the end of this section, you should be able to

- Name the most important types of sulfur compound

TABLE 22.5 Some Properties of the Group 16 Elements

Property	O	S	Se	Te
Atomic radius (pm)	66	105	121	138
X^{2-} ionic radius (pm)	140	184	198	221
First ionization energy (kJ/mol)	1314	1000	941	869
Electron affinity (kJ/mol)	−141	−200	−195	−190
Electronegativity	3.5	2.5	2.4	2.1
X—X single-bond enthalpy (kJ/mol)	146*	266	172	126
Reduction potential to H_2X in acidic solution (V)	1.23	0.14	−0.40	−0.72

*Based on O—O bond enthalpy in H_2O_2.



The other Group 16 elements are sulfur, selenium, tellurium, and polonium. Of these, sulfur is the most important, and polonium, which has no stable isotopes and is found only in minute quantities in radium-containing minerals, is least important.

The Group 16 elements possess the general outer-electron configuration ns^2np^4 with n ranging from 2 to 6. Thus, these elements attain a noble-gas electron configuration by adding two electrons, which results in a −2 oxidation state. Except for oxygen, the Group 16 elements are also commonly found in positive oxidation states up to +6, and they can have expanded valence shells. Thus, we have such compounds as SF_6, SeF_6, and TeF_6 with the central atom in the +6 oxidation state.

Table 22.5 summarizes some properties of the Group 16 elements.

Occurrence and Production of S, Se, and Te

Sulfur, selenium, and tellurium can all be mined from the earth. Large underground deposits are the principal source of elemental sulfur (Figure 22.15). Sulfur also occurs widely as sulfide (S^{2-}) and sulfate (SO_4^{2-}) minerals. Its presence as a minor component of coal and petroleum poses a major problem. Combustion of these "unclean" fuels leads to serious pollution by sulfur oxides. Much effort has been directed at removing this sulfur, and these efforts have increased the availability of sulfur.

Selenium and tellurium occur in rare minerals, such as Cu_2Se, PbSe, Cu_2Te, and PbTe, and as minor constituents in sulfide ores of copper, iron, nickel, and lead.



▲ Figure 22.15 Massive amounts of sulfur are extracted every year from the earth.

Properties and Uses of Sulfur, Selenium, and Tellurium

Elemental sulfur is yellow, tasteless, and nearly odorless. It is insoluble in water and exists in several allotropic forms. The thermodynamically stable form at room temperature is rhombic sulfur, which consists of puckered S_8 rings with each sulfur atom forming two bonds (Figure 7.26).

Most of the sulfur produced world wide each year is used to manufacture sulfuric acid. Sulfur is also used to vulcanize rubber, a process that toughens rubber by introducing cross-linking between polymer chains.

Selenium is used in photoelectric cells and light meters because its electrical conductivity increases greatly upon exposure to light. Photocopiers also depend on the photoconductivity of selenium. Photocopy machines contain a belt or drum coated with a film of selenium. This drum is electrostatically charged and then exposed to light reflected from the image being photocopied. The charge drains from the regions where the selenium film has been made conductive by exposure to light. A black powder (the toner) sticks only to the areas that remain charged. The photocopy is made when the toner is transferred to a sheet of plain paper.



▲ Figure 22.16 Iron pyrite (FeS_2, on the right) with gold for comparison.

Sulfides

When an element is less electronegative than sulfur, *sulfides* that contain S^{2-} form. Many metallic elements are found in the form of sulfide ores, such as PbS (galena) and HgS (cinnabar). A series of related ores containing the disulfide ion, S_2^{2-} (analogous to the peroxide ion), are known as *pyrites*. Iron pyrite, FeS_2, occurs as golden yellow cubic crystals (Figure 22.16). Because it has been occasionally mistaken for gold by miners, iron pyrite is often called fool's gold.

One of the most important sulfides is hydrogen sulfide (H_2S). One of hydrogen sulfide's most readily recognized properties is its odor, which is most frequently encountered as the offensive odor of rotten eggs. Hydrogen sulfide is toxic, but our noses can detect H_2S in extremely low, nontoxic concentrations. A sulfur-containing organic molecule, such as dimethyl sulfide, $(CH_3)_2S$, which is similarly odoriferous and can be detected by smell at a level of one part per trillion, is added to natural gas as a safety factor to give it a detectable odor.

Oxides, Oxyacids, and Oxyanions of Sulfur



▲ Figure 22.17 Food label warning of sulfites.

Sulfur dioxide, formed when sulfur burns in air, has a choking odor and is poisonous. The gas is particularly toxic to lower organisms, such as fungi, so it is used to sterilize dried fruit and wine. At 101.3 kPa and room temperature, SO_2 dissolves in water to produce a 1.6 *M* solution. The SO_2 solution is acidic, and we describe it as sulfurous acid (H_2SO_3).

Salts of SO_3^{2-} (sulfites) and HSO_3^- (hydrogen sulfites or bisulfites) are well known. Small quantities of Na_2SO_3 or $NaHSO_3$ are used as food additives to prevent bacterial spoilage. However, they are known to increase asthma symptoms in approximately 5% of asthmatics. Thus, all food products with sulfites must now carry a warning label disclosing their presence (Figure 22.17).

Although combustion of sulfur in air produces mainly SO_2, small amounts of SO_3 are also formed. The reaction produces chiefly SO_2 because the activation-energy barrier for oxidation to SO_3 is very high unless the reaction is catalyzed. Interestingly, the SO_3 by-product is used industrially to make H_2SO_4, which is the ultimate product of the reaction between SO_3 and water. In the manufacture of sulfuric acid, SO_2 is obtained by burning sulfur and then is oxidized to SO_3, using a catalyst such as V_2O_5 or platinum. The SO_3 is dissolved in H_2SO_4 because it does not dissolve quickly in water, and then the $H_2S_2O_7$ formed in this reaction, called pyrosulfuric acid, is added to water to form H_2SO_4:

$$SO_3(g) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l) \qquad [22.29]$$

$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2\,H_2SO_4(l) \qquad [22.30]$$

Commercial sulfuric acid is 98% H_2SO_4. It is a dense, colorless, oily liquid. It is a strong acid, a good dehydrating agent (Figure 22.18), and a moderately good oxidizing agent.

Year after year, the production of sulfuric acid is the largest of any chemical produced in the world. It is employed in some way in almost all manufacturing.

Sulfuric acid is a strong acid, but only the first hydrogen is completely ionized in aqueous solution:

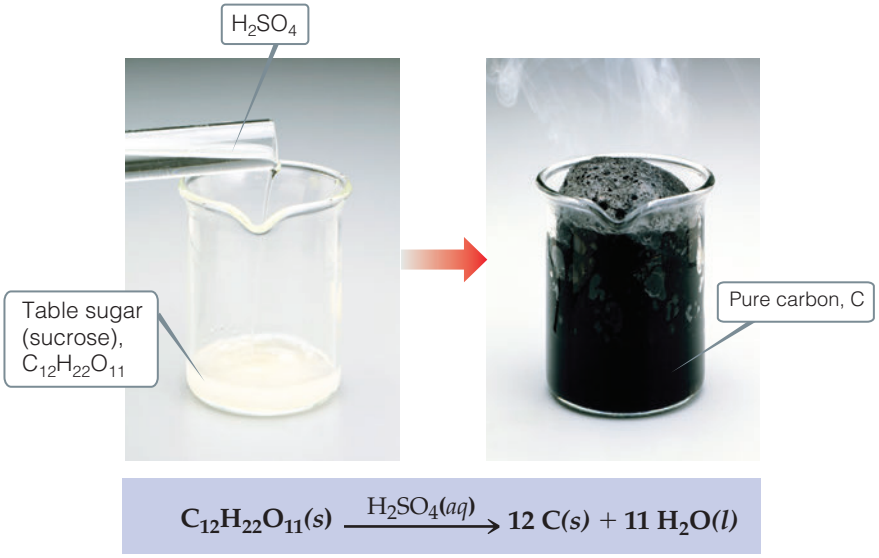
$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \qquad [22.31]$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.1 \times 10^{-2} \qquad [22.32]$$

Consequently, sulfuric acid forms both sulfates (SO_4^{2-} salts) and bisulfates (or hydrogen sulfates, HSO_4^- salts). Hydrogen sulfate salts are common components of the "dry acids" used for adjusting the pH of swimming pools and hot tubs; they are also components of many toilet bowl cleaners.

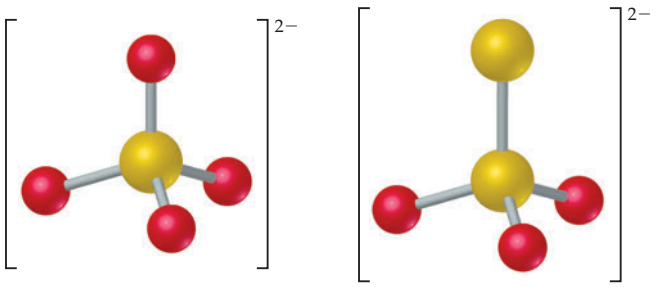
Another important sulfur-containing ion is thiosulfate ion ($S_2O_3^{2-}$). The term *thio* indicates substitution of sulfur for oxygen. The structures of the sulfate and thiosulfate ions are compared in Figure 22.19.

Thiols, organic compounds with a —SH group bonded to carbon, play important roles in biology. When thiols are oxidized under mild conditions, they form disulfides, organic compounds with S—S bonds between carbon atoms. In the

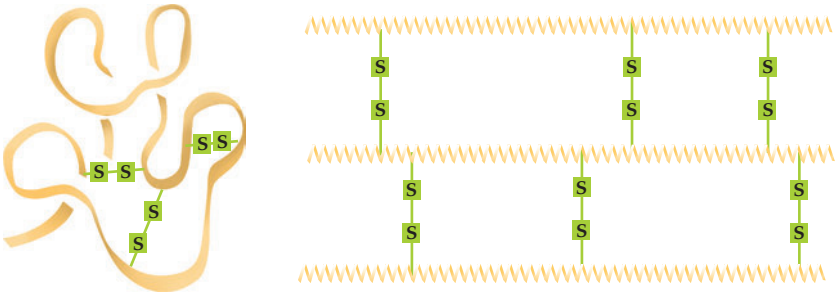


▲ **Figure 22.18** **Sulfuric acid dehydrates table sugar to produce elemental carbon.**

Go Figure What are the oxidation states of the sulfur atoms in the $S_2O_3^{2-}$ ion?



▲ **Figure 22.19** **Structures of the sulfate (left) and thiosulfate (right) ions.**



▲ **Figure 22.20** **Hair straightening and curling.** People can alter the shape of their hair by first applying a reducing agent that breaks the disulfide bonds between protein strands. The hair is given its desired shape, and then an oxidizing agent is added to form new disulfide bonds to maintain the shape.

opposite fashion, disulfide bonds can be broken by reducing them to thiols. The shape and function of proteins can be modified by forming or breaking disulfide bonds between protein strands. Hair-straightening and curling technologies rely on the breaking and re-forming of disulfide bonds between the protein molecules of hair (**Figure 22.20**).

Self-Assessment Exercise

22.21 The structure of the thiosulfate ion is shown in figure 22.19. The oxidation state of one sulfur atom is –2, what is the oxidation state of the other sulfur atom?

(a) –2

(b) 0

(c) +4

(d) +6

Exercises

22.22 Write the chemical formula for each of the following compounds, and indicate the oxidation state of the Group 16 elements in each: (**a**) selenious acid, (**b**) sulphur trioxide, (**c**) selenium dichloride, (**d**) aluminium selenide, (**e**) iron(II) sulfate, (**f**) tellurium trioxide.

22.23 An aqueous solution of SO_2 reduces (**a**) aqueous $KMnO_4$ to $MnSO_4(aq)$, (**b**) acidic aqueous $K_2Cr_2O_7$ to aqueous Cr^{3+}, (**c**) aqueous $Hg_2(NO_3)_2$ to mercury metal. Write balanced equations for these reactions.

22.24 The SF_5^- ion is formed when $SF_4(g)$ reacts with fluoride salts containing large cations, such as $CsF(s)$. Draw the Lewis structures for SF_4 and SF_5^-, and predict the molecular structure of each.

22.25 Write a balanced equation for each of the following reactions. (You may have to guess at one or more of the reaction products, but you should be able to make a reasonable guess, based on your study of this chapter.) (**a**) Hydrogen selenide can be prepared by reaction of an aqueous acid solution on aluminum selenide. (**b**) Sodium thiosulfate is used to remove excess Cl_2 from chlorine-bleached fabrics. The thiosulfate ion forms SO_4^{2-} and elemental sulfur, while Cl_2 is reduced to Cl^-.

Answers to Self-Assessment Exercise

22.21 (d)

22.7 | Nitrogen



On 4 August 2020, a massive explosion of almost 3000 tons of ammonium nitrate devastated the port of Beirut, killing at least 220 people, injuring more than 5000, and making an estimated 300,000 homeless. The blast was so powerful that it could be heard in Cyprus, some 200 km away. Ammonium nitrate is a commonly used fertilizer.

It is usually manufactured as small pellets that are reasonably safe to handle but, when stored, can absorb moisture and form a solid, rock like mass. Heat, such as from a fire, can cause the mass to ignite and explode.

Nitrogen and its compounds display a staggering nine different oxidation states, and we revise some of its chemistry in this section. By the end, you should be able to

- Appreciate the wide variety of bonding arrangements that nitrogen can adopt

Nitrogen constitutes 78% by volume of Earth's atmosphere, where it occurs as N_2 molecules. Although nitrogen is a key element in living organisms, compounds of nitrogen are not abundant in Earth's crust. The major natural deposits of nitrogen compounds are those of KNO_3 (saltpeter) in India and $NaNO_3$ (Chile saltpeter) in Chile and other desert regions of South America.

Properties of Nitrogen

Nitrogen is a colorless, odorless, tasteless gas composed of N_2 molecules. The N_2 molecule is very unreactive because of the strong triple bond between nitrogen atoms (the N≡N bond enthalpy is 941 kJ/mol, nearly twice that for the bond in O_2. (Table 8.3) When substances burn in air, they normally react with O_2 but not with N_2.

The electron configuration of the nitrogen atom is $[He]2s^2 2p^3$. The element exhibits all formal oxidation states from +5 to −3 (**Table 22.6**). The +5, 0, and −3 oxidation states are the most common and generally the most stable of these. Because nitrogen is more electronegative than all other elements except fluorine, oxygen, and chlorine, it exhibits positive oxidation states only in combination with these three elements.

TABLE 22.6 Oxidation States of Nitrogen

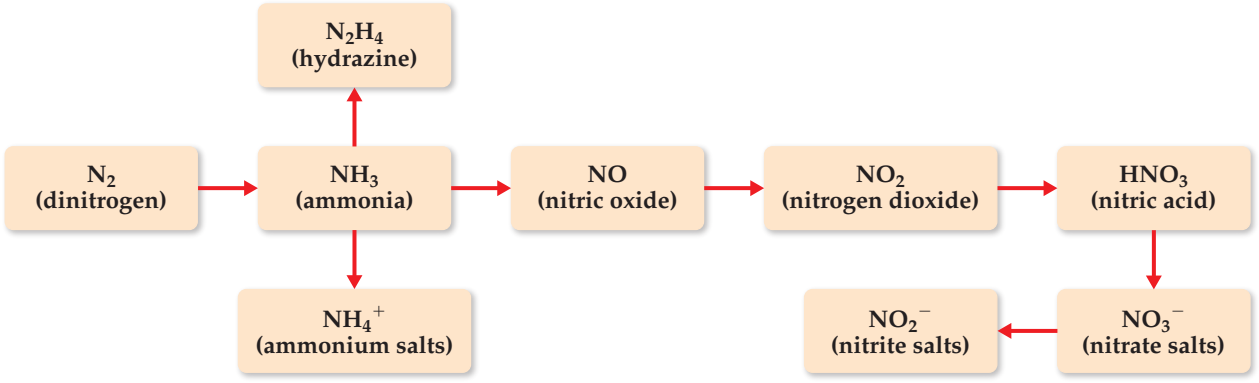
Oxidation State	Examples
+5	N_2O_5, HNO_3, NO_3^-
+4	NO_2, N_2O_4
+3	HNO_2, NO_2^-, NF_3
+2	NO
+1	N_2O, $H_2N_2O_2$, $N_2O_2^{2-}$, HNF_2
0	N_2
−1	NH_2OH, NH_2F
−2	N_2H_4
−3	NH_3, NH_4^+, NH_2^-

Production and Uses of Nitrogen

Elemental nitrogen is obtained in commercial quantities by fractional distillation of liquid air. Because of its low reactivity, large quantities of N_2 are used as an inert gaseous blanket to exclude O_2 in food processing, manufacture of chemicals, metal fabrication, and production of electronic devices. Liquid N_2 is employed as a coolant to freeze foods rapidly.

The largest use of N_2 is in the manufacture of nitrogen-containing fertilizers. These fertilizers provide a source of *fixed* nitrogen—nitrogen that has been incorporated into compounds. We have previously discussed nitrogen fixation in the "Chemistry Put to Work" box in Section 14.7 and in the "Chemistry Put to Work" box in Section 15.2. Our starting point in fixing nitrogen is the manufacture of ammonia via the Haber process. The ammonia can then be converted into a variety of useful, simple nitrogen-containing species (**Figure 22.21**).

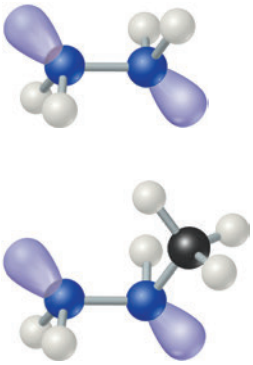
Go Figure In which of these species is the oxidation number of nitrogen +3?



▲ **Figure 22.21** Sequence of conversion of N_2 into common nitrogen compounds.

Go Figure

Is the N—N bond length in these molecules shorter or longer than the N—N bond length in N_2?



▲ **Figure 22.22** **Hydrazine (top, N_2H_4) and methylhydrazine (bottom, CH_3NHNH_2).**

Hydrogen Compounds of Nitrogen

Ammonia is one of the most important compounds of nitrogen. It is a colorless, toxic gas that has a characteristic irritating odor. As noted in previous discussions, the NH_3 molecule is basic ($K_b = 1.8 \times 10^{-5}$).

In the laboratory, NH_3 can be prepared by the action of NaOH on an ammonium salt. The NH_4^+ ion, which is the conjugate acid of NH_3, transfers a proton to OH^-. The resultant NH_3 is volatile and is driven from the solution by mild heating:

$$NH_4Cl(aq) + NaOH(aq) \longrightarrow NH_3(g) + H_2O(l) + NaCl(aq) \qquad [22.33]$$

Commercial production of NH_3 is achieved by the Haber process:

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \qquad [22.34]$$

About 75% is used for fertilizer.

Hydrazine (N_2H_4) is another important hydride of nitrogen. The hydrazine molecule contains an N—N single bond (**Figure 22.22**). It can be prepared by the reaction of ammonia with hypochlorite ion (OCl^-) in aqueous solution:

$$2\,NH_3(aq) + OCl^-(aq) \longrightarrow N_2H_4(aq) + Cl^-(aq) + H_2O(l) \qquad [22.35]$$

The reaction involves several intermediates, including chloramine (NH_2Cl). The poisonous NH_2Cl bubbles out of solution when household ammonia and chlorine bleach (which contains OCl^-) are mixed. This reaction is one reason for the frequently cited warning not to mix bleach and household ammonia.

Pure hydrazine is a strong and versatile reducing agent. The major use of hydrazine and compounds related to it, such as methylhydrazine (Figure 22.22), is as rocket fuel.

Sample Exercise 22.5

Writing a Balanced Equation

Hydroxylamine (NH_2OH) reduces copper(II) to the free metal in acid solutions. Write a balanced equation for the reaction, assuming that N_2 is the oxidation product.

SOLUTION

Analyze We are asked to write a balanced oxidation–reduction equation in which NH_2OH is converted to N_2 and Cu^{2+} is converted to Cu.

Plan Because this is a redox reaction, the equation can be balanced by the method of half-reactions discussed in Section 20.2. Thus, we begin with two half-reactions, one involving the NH_2OH and N_2 and the other involving Cu^{2+} and Cu.

Solve

The unbalanced and incomplete half-reactions are

$$Cu^{2+}(aq) \longrightarrow Cu(s)$$

$$NH_2OH(aq) \longrightarrow N_2(g)$$

Balancing these equations as described in Section 20.2 gives

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$

$$2\,NH_2OH(aq) \longrightarrow N_2(g) + 2\,H_2O(l) + 2\,H^+(aq) + 2\,e^-$$

Adding these half-reactions gives the balanced equation:

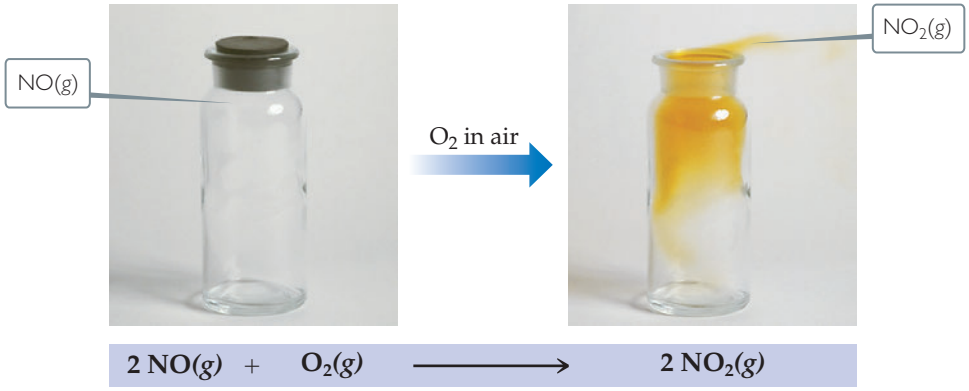
$$Cu^{2+}(aq) + 2\,NH_2OH(aq) \longrightarrow Cu(s) + N_2(g) + 2\,H_2O(l) + 2\,H^+(aq)$$

Practice Exercise

In power plants, hydrazine is used to prevent corrosion of the metal parts of steam boilers by the O_2 dissolved in the water. The hydrazine reacts with O_2 in water to give N_2 and H_2O. Write a balanced equation for this reaction.

Oxides and Oxyacids of Nitrogen

Nitrogen forms three common oxides: N_2O (nitrous oxide), NO (nitric oxide), and NO_2 (nitrogen dioxide). It also forms two unstable oxides that we will not discuss, N_2O_3 (dinitrogen trioxide) and N_2O_5 (dinitrogen pentoxide).



▲ **Figure 22.23** **Formation of $NO_2(g)$ as $NO(g)$ combines with $O_2(g)$ in the air.**

Nitrous oxide (N_2O) is also known as laughing gas because a person becomes giddy after inhaling a small amount. This colorless gas was the first substance used as a general anesthetic. It is used as the compressed gas propellant in several aerosols and foams, such as in whipped cream.

Nitric oxide (NO) is also a colorless gas but, unlike N_2O, it is slightly toxic. It can be prepared in the laboratory by reduction of dilute nitric acid, using copper or iron as a reducing agent:

$$3\,Cu(s) + 2\,NO_3^-(aq) + 8\,H^+(aq) \longrightarrow 3\,Cu^{2+}(aq) + 2\,NO(g) + 4\,H_2O(l) \quad [22.36]$$

Nitric oxide is also produced by direct reaction of N_2 and O_2 at high temperatures. This reaction is a significant source of nitrogen oxide air pollutants. The direct combination of N_2 and O_2 is not used for commercial production of NO, however, because the yield is low, the equilibrium constant K_p at 2400 K being only 0.05. ("Chemistry Put to Work: Controlling Nitric Oxide Emissions")

The commercial route to NO (and hence to other oxygen-containing compounds of nitrogen) is via the catalytic oxidation of NH_3:

$$4\,NH_3(g) + 5\,O_2(g) \xrightarrow[850\,^\circ C]{\text{Pt catalyst}} 4\,NO(g) + 6\,H_2O(g) \quad [22.37]$$

This reaction is the first step in the **Ostwald process**, by which NH_3 is converted commercially into nitric acid (HNO_3).

When exposed to air, nitric oxide reacts readily with O_2 (**Figure 22.23**):

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \quad [22.38]$$

When dissolved in water, NO_2 forms nitric acid:

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,H^+(aq) + 2\,NO_3^-(aq) + NO(g) \quad [22.39]$$

Nitrogen is both oxidized and reduced in this reaction, which means it disproportionates. The NO can be converted back into NO_2 by exposure to air (Equation 22.38) and thereafter dissolved in water to prepare more HNO_3.

NO is an important neurotransmitter in the human body. It causes the muscles that line blood vessels to relax, thus allowing an increased passage of blood (see "Chemistry and Life: Nitroglycerin, Nitric Oxide, and Heart Disease").

Nitrogen dioxide (NO_2) is a yellow-brown gas (Figure 22.23). Like NO, it is a major constituent of smog. It is poisonous and has a choking odor. As discussed in Section 15.1, NO_2 and N_2O_4 exist in equilibrium:

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H^\circ = -58\ kJ \quad [22.40]$$

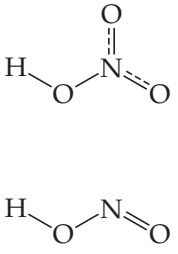
The two common oxyacids of nitrogen are nitric acid (HNO_3) and nitrous acid (HNO_2) (**Figure 22.24**). *Nitric acid* is a strong acid. It is also a powerful oxidizing agent, as indicated by the standard reduction potential in the reaction

$$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l) \quad E^\circ = +0.96\ V \quad [22.41]$$

Concentrated nitric acid attacks and oxidizes most metals except Au, Pt, Rh, and Ir.

Go Figure

Which is the shortest NO bond in these two molecules?



▲ **Figure 22.24** **Structures of nitric acid (top) and nitrous acid (bottom).**

Its largest use is in the manufacture of NH_4NO_3 for fertilizers. It is also used in the production of plastics, drugs, and explosives. Among the explosives made from nitric acid are nitroglycerin, trinitrotoluene (TNT), and nitrocellulose. The following reaction occurs when nitroglycerin explodes:

$$4\,C_3H_5N_3O_9(l) \longrightarrow 6\,N_2(g) + 12\,CO_2(g) + 10\,H_2O(g) + O_2(g) \qquad [22.42]$$

All the products of this reaction contain very strong bonds and are gases. As a result, the reaction is very exothermic, and the volume of the products is far larger than the volume occupied by the reactant. Thus, the expansion resulting from the heat generated by the reaction produces the explosion.

CHEMISTRY AND LIFE Nitroglycerin, Nitric Oxide, and Heart Disease

During the 1870s, an interesting observation was made in Alfred Nobel's dynamite factories. Workers who suffered from heart disease that caused chest pains when they exerted themselves found relief from the pains during the workweek. It quickly became apparent that nitroglycerin, present in the air of the factory, acted to enlarge blood vessels. Thus, this powerfully explosive chemical became a standard treatment for angina pectoris, the chest pains accompanying heart failure. It took more than 100 years to discover that nitroglycerin was converted in the vascular smooth muscle into NO, which is the chemical agent actually causing dilation of the blood vessels. In 1998, the Nobel Prize in Physiology or Medicine was awarded to Robert F. Furchgott, Louis J. Ignarro, and Ferid Murad for their discoveries of the detailed pathways by which NO acts in the cardiovascular system. It was a sensation that this simple, common air pollutant could exert important functions in mammals, including humans.

As useful as nitroglycerin is to this day in treating angina pectoris, it has a limitation in that prolonged administration results in development of tolerance, or desensitization, of the vascular muscle to further vasorelaxation by nitroglycerin. The bioactivation of nitroglycerin is the subject of active research in the hope that a means of circumventing desensitization can be found.

Self-Assessment Exercise

22.26 Which of the following reactions is a disproportionation reaction?

(a) $2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$

(b) $2NH_3(aq) + OCl^-(aq) \rightarrow N_2H_4(aq) + Cl^-(aq) + H_2O(l)$

(c) $2NO_2 \rightleftharpoons N_2O_4(g)$

Exercises

22.27 Write the chemical formula for each of the following compounds, and indicate the oxidation state of nitrogen in each: (**a**) dinitrogen trioxide, (**b**) dinitrogen pentoxide, (**c**) hydrogen cyanide, (**d**) ammonium nitrate, (**e**) iron(III) nitrite, (**f**) nitrogen trichloride.

22.28 Write the Lewis structure for each of the following species, describe its geometry, and indicate the oxidation state of the nitrogen: (**a**) N_2O_3, (**b**) NOCl, (**c**) NO_2Cl, (**d**) N_2O_4.

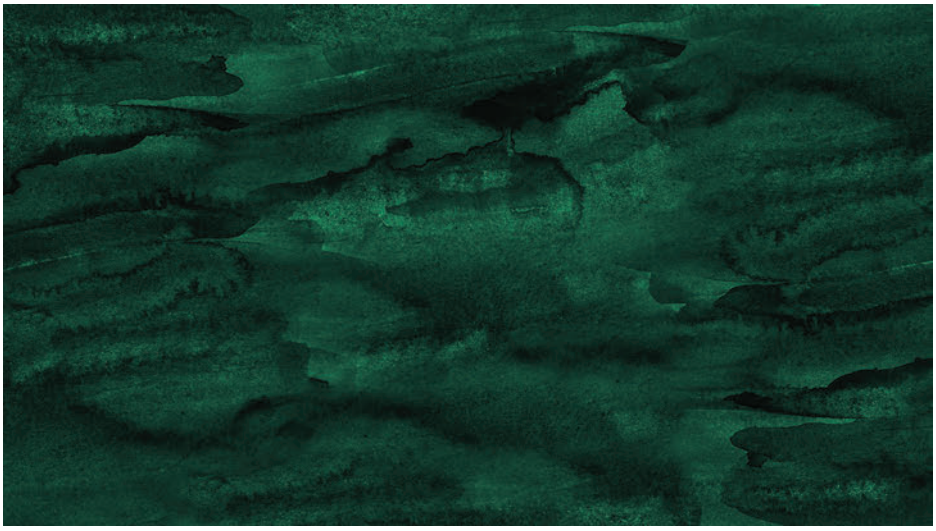
22.29 Write a balanced net ionic equation for each of the following reactions: (**a**) Dilute nitric acid reacts with zinc metal with formation of nitrous oxide. (**b**) Concentrated nitric acid reacts with sulfur with formation of nitrogen dioxide. (**c**) Concentrated nitric acid oxidizes sulfur dioxide with formation of nitric oxide. (**d**) Hydrazine is burned in excess fluorine gas, forming NF_3. (**e**) Hydrazine reduces CrO_4^{2-} to $Cr(OH)_4^-$ in base (hydrazine is oxidized to N_2).

22.30 Write complete balanced half-reactions for (**a**) reduction of nitrate ion to NO in acidic solution, (**b**) oxidation of HNO_2 to NO_2 in acidic solution.

Answers to Self-Assessment Exercise

22.26 (a)

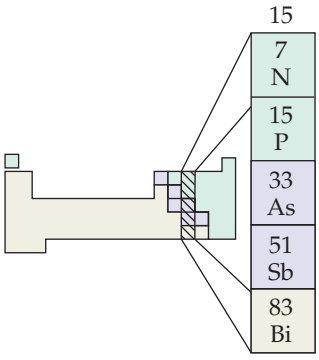
22.8 The Other Group 15 Elements: P, As, Sb, and Bi



Paris green is an arsenic compound that shows a pale blue green color when finely ground and darker emerald green if the particle size is larger. While its toxicity was realized from the start, it was a popular pigment with artists such as Turner, Monet, Gauguin, and van Gogh.

In this section, we review the other Group 15 elements focusing our attention on phosphorus—one that is essential to life. By the end of this section, you should be able to

- Understand the structure and properties of phosphorus compounds



Of the other Group 15 elements—phosphorus, arsenic, antimony, and bismuth—phosphorus has a central role in several aspects of biochemistry and environmental chemistry.

The Group 15 elements have the outer-shell electron configuration ns^2np^3, with n ranging from 2 to 6. A noble-gas configuration is achieved by adding three electrons to form the −3 oxidation state. Ionic compounds containing X^{3-} ions are not common, however. More commonly, the Group 15 element acquires an octet of electrons via covalent bonding and oxidation numbers ranging from −3 to +5.

Because of its lower electronegativity, phosphorus is found more frequently in positive oxidation states than is nitrogen. Furthermore, compounds in which phosphorus has the +5 oxidation state are not as strongly oxidizing as the corresponding compounds of nitrogen. Compounds in which phosphorus has a −3 oxidation state are much stronger reducing agents than are the corresponding nitrogen compounds.

Some properties of the Group 15 elements are listed in **Table 22.7**. The variation in properties among Group 15 elements is more striking than that seen in Groups 16 and 17. Nitrogen at the one extreme exists as a gaseous diatomic molecule, clearly nonmetallic. At the other extreme, bismuth is a reddish white, metallic-looking substance that has most of the characteristics of a metal.

The values listed for X—X single-bond enthalpies are not reliable because it is difficult to obtain such data from thermochemical experiments. However, there is no doubt

TABLE 22.7 Properties of the Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic radius (pm)	71	107	119	139	148
First ionization energy (kJ/mol)	1402	1012	947	834	703
Electron affinity (kJ/mol)	> 0	−72	−78	−103	−91
Electronegativity	3.0	2.1	2.0	1.9	1.9
X—X single-bond enthalpy (kJ/mol)*	163	200	150	120	—
X≡X triple-bond enthalpy (kJ/mol)	941	490	380	295	192

*Approximate values only.

about the general trend: a low value for the N—N single bond, an increase at phosphorus, and then a gradual decline to arsenic and antimony. From observations of the elements in the gas phase, it is possible to estimate the X≡X triple-bond enthalpies. Here, we see a trend that is different from that for the X—X single bond. Nitrogen forms a much stronger triple bond than the other elements, and there is a steady decline in the triple-bond enthalpy down through the group. These data help us to appreciate why nitrogen alone of the Group 15 elements exists as a diatomic molecule in its stable state at 25 °C. All the other elements exist in structural forms with single bonds between the atoms.

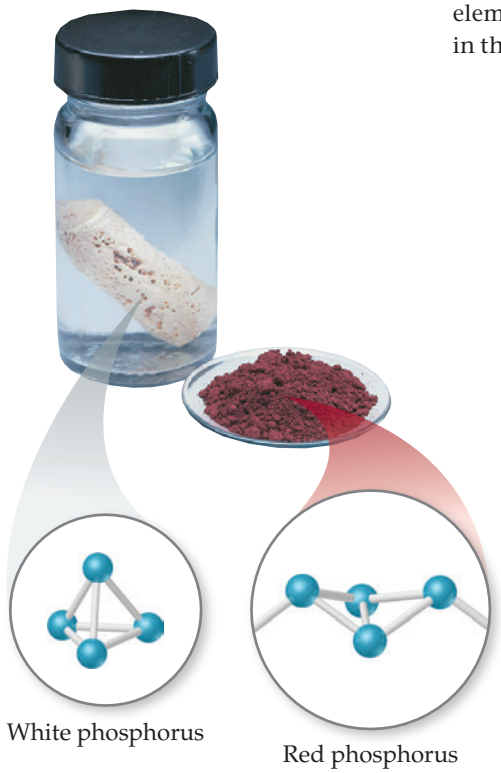
Occurrence, Isolation, and Properties of Phosphorus

Phosphorus occurs mainly in the form of phosphate minerals. The principal source of phosphorus is phosphate rock, which contains phosphate principally as $Ca_3(PO_4)_2$. The element is produced commercially by the reduction of calcium phosphate with carbon in the presence of SiO_2:

$$2\,Ca_3(PO_4)_2(s) + 6\,SiO_2(s) + 10\,C(s) \xrightarrow{1500\,^\circ C} P_4(g) + 6\,CaSiO_3(l) + 10\,CO(g) \quad [22.43]$$

The phosphorus produced in this fashion is the allotrope known as white phosphorus. This form distills from the reaction mixture as the reaction proceeds.

Phosphorus exists in several allotropic forms. White phosphorus consists of P_4 tetrahedra (Figure 22.25). The bond angles in this molecule, 60°, are unusually small, so there is much strain in the bonding, which is consistent with the high reactivity of white phosphorus. This allotrope bursts spontaneously into flames if exposed to air. When heated in the absence of air to about 400 °C, white phosphorus is converted to a more stable allotrope known as red phosphorus, which does not ignite on contact with air. Red phosphorus is also considerably less poisonous than the white form. We will denote elemental phosphorus as simply P(*s*).



▲ **Figure 22.25 White and red phosphorus.** Despite the fact that both contain only phosphorus atoms, these two forms of phosphorus differ greatly in reactivity. The white allotrope, which reacts violently with oxygen, must be stored under water so that it is not exposed to air. The much less reactive red form does not need to be stored this way.

Phosphorus Halides

Phosphorus forms a wide range of compounds with the halogens, the most important of which are the trihalides and pentahalides. Phosphorus trichloride (PCl_3) is commercially the most significant of these compounds and is used to prepare a wide variety of products, including soaps, detergents, plastics, and insecticides.

Phosphorus chlorides, bromides, and iodides can be made by direct oxidation of elemental phosphorus with the elemental halogen. PCl_3, for example, which is a liquid at room temperature, is made by passing a stream of dry chlorine gas over white or red phosphorus:

$$2\,P(s) + 3\,Cl_2(g) \longrightarrow 2\,PCl_3(l) \quad [22.44]$$

If excess chlorine gas is present, an equilibrium is established between PCl_3 and PCl_5.

$$PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s) \qquad [22.45]$$

The phosphorus halides react readily with water, and most fume in air because of reaction with water vapor. In the presence of excess water, the products are the corresponding phosphorus oxyacid and hydrogen halide:

$$PBr_3(l) + 3\,H_2O(l) \longrightarrow H_3PO_3(aq) + 3\,HBr(aq) \qquad [22.46]$$

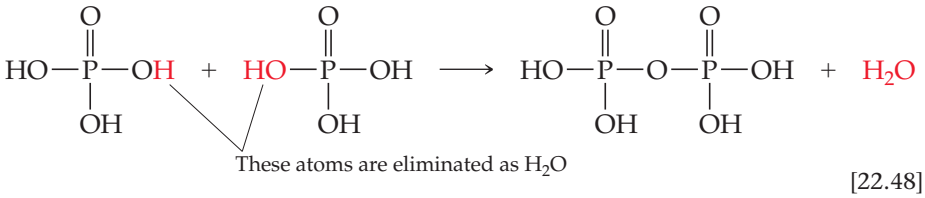
$$PCl_5(l) + 4\,H_2O(l) \longrightarrow H_3PO_4(aq) + 5\,HCl(aq) \qquad [22.47]$$

Oxy Compounds of Phosphorus

Probably the most significant phosphorus compounds are those in which the element is combined with oxygen. Phosphorus(III) oxide (P_4O_6) is obtained by allowing white phosphorus to oxidize in a limited supply of oxygen. When oxidation takes place in the presence of excess oxygen, phosphorus(V) oxide (P_4O_{10}) forms. This compound is also readily formed by oxidation of P_4O_6. These two oxides represent the two most common oxidation states for phosphorus, +3 and +5. The structural relationship between P_4O_6 and P_4O_{10} is shown in **Figure 22.26**. Notice the resemblance these molecules have to the P_4 molecule (Figure 22.26); all three substances have a P_4 core.

Phosphorus(V) oxide is the anhydride of phosphoric acid (H_3PO_4), a weak triprotic acid. In fact, P_4O_{10} has a very high affinity for water and is consequently used as a drying agent. Phosphorus(III) oxide is the anhydride of phosphorous acid (H_3PO_3), a weak diprotic acid (**Figure 22.27**).*

One characteristic of phosphoric and phosphorous acids is their tendency to undergo *condensation reactions* when heated. For example, two H_3PO_4 molecules are joined by the elimination of one H_2O molecule to form $H_4P_2O_7$:



[22.48]

Phosphoric acid and its salts find their most important uses in detergents and fertilizers. The phosphates in detergents are often in the form of sodium triphosphate ($Na_5P_3O_{10}$). The phosphate ions "soften" water by binding their oxygen groups to the metal ions that contribute to the hardness of water. This keeps the metal ions from interfering with the action of the detergent. The phosphates also keep the pH above 7 and thus prevent the detergent molecules from becoming protonated.

Most mined phosphate rock is converted to fertilizers. The $Ca_3(PO_4)_2$ in phosphate rock is insoluble ($K_{sp} = 2.0 \times 10^{-29}$). It is converted to a soluble form for use in fertilizers by treatment with sulfuric or phosphoric acid. The reaction with phosphoric acid yields $Ca(H_2PO_4)_2$:

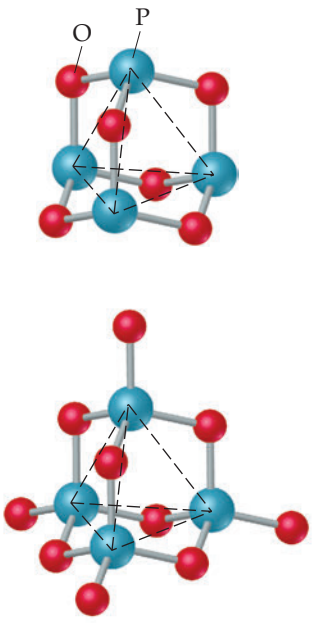
$$Ca_3(PO_4)_2(s) + 4\,H_3PO_4(aq) \longrightarrow 3\,Ca^{2+}(aq) + 6\,H_2PO_4^-(aq) \qquad [22.49]$$

Although the solubility of $Ca(H_2PO_4)_2$ allows it to be assimilated by plants, it also allows it to be washed from the soil and into bodies of water, thereby contributing to water pollution.

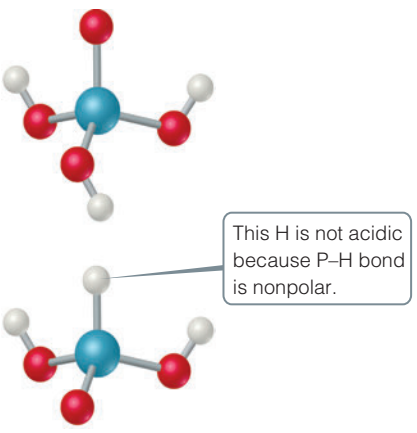
*Note that the element phosphorus (*FOS · for · us*) has a *-us* suffix, whereas the first word in the name phosphorous (*fos · FOR · us*) acid has an *-ous* suffix.

Go Figure

How do the electron domains about P in P_4O_6 differ from those about P in P_4O_{10}?

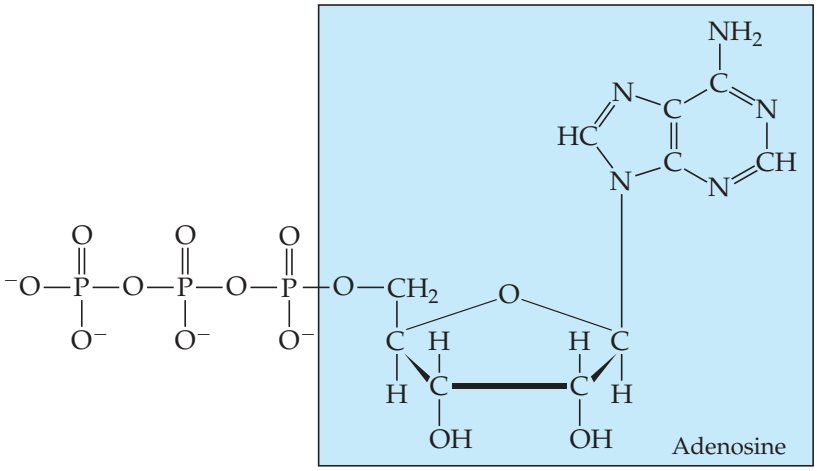


▲ **Figure 22.26** **Structures of P_4O_6 (top) and P_4O_{10} (bottom).**

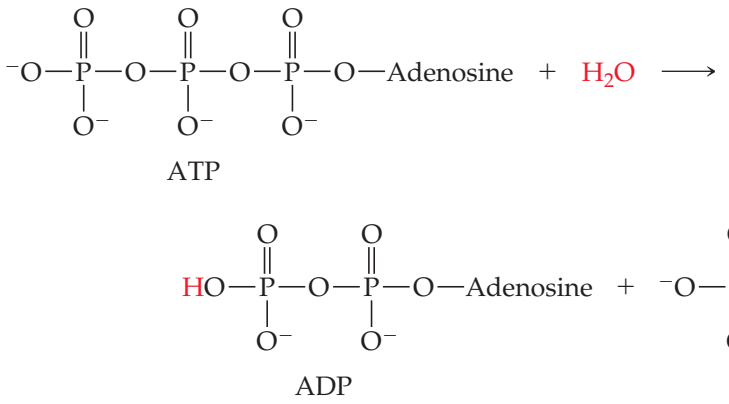


▲ **Figure 22.27** **Structures of H_3PO_4 (top) and H_3PO_3 (bottom).**

Phosphorus compounds are important in biological systems. The element occurs in phosphate groups in RNA and DNA, the molecules responsible for the control of protein biosynthesis and transmission of genetic information. It also occurs in adenosine triphosphate (ATP), which stores energy in biological cells and has the following structure:



The P—O—P bond of the end phosphate group is broken by hydrolysis with water, forming adenosine diphosphate (ADP):



[22.50]

This reaction releases 33 kJ of energy under standard conditions, but in the living cell, the Gibbs free energy change for the reaction is closer to −57 kJ/mol. The concentration of ATP inside a living cell is in the range of 1–10 m*M*, and a typical human metabolizes her or his body mass of ATP in one day! ATP is continually made from ADP and continually converted back to ADP, releasing energy that can be harnessed by other cellular reactions.

CHEMISTRY AND LIFE Arsenic in Drinking Water

Arsenic, in the form of its oxides, has been known as a poison for centuries.

When it contaminates drinking water, this can cause widespread poisoning, as has occurred in Bangladesh. Historically, surface water sources in that country have been contaminated with microorganisms, causing significant health problems. During the 1970s, international agencies, headed by the United Nations Children's Fund (UNICEF), began investing millions of dollars of aid money in Bangladesh for wells to provide "clean" drinking water. Unfortunately, no one tested the well water for the presence of arsenic; the problem was not discovered until the 1980s. The result has been the biggest outbreak of mass poisoning in history. Up to half of the country's estimated 10 million wells have arsenic concentrations above 50 ppb.

In water, the most common forms of arsenic are the arsenate ion and its protonated hydrogen anions (AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_4^-$) and the arsenite ion and its protonated forms (AsO_3^{3-}, $HAsO_3^{2-}$, $H_2AsO_3^-$, and H_3AsO_3). These species are collectively referred to by the oxidation number of the arsenic as arsenic(V) and arsenic(III), respectively. Arsenic(V) is more prevalent in oxygen-rich (aerobic) surface waters, whereas arsenic(III) is more likely to occur in oxygen-poor (anaerobic) groundwaters.

One of the challenges in determining the health effects of arsenic in drinking waters is the different chemistry of arsenic(V) and arsenic(III), as well as the different concentrations required for physiological responses in different individuals. In Bangladesh, skin lesions were the first sign of the arsenic problem. Statistical studies correlating arsenic levels with the occurrence of disease indicate a lung and bladder cancer risk arising from even low levels of arsenic.

The current technologies for removing arsenic perform most effectively when treating arsenic in the form of arsenic(V), so water treatment strategies require preoxidation of the drinking water. Once in the form of arsenic(V), there are a number of possible removal strategies. For example, Fe^{3+} can be added to precipitate $FeAsO_4$, which is then removed by filtration.

Self-Assessment Exercise

22.31 Which oxyacid is produced when PF_3 reacts with water?

(a) H_3PO_3
(b) H_3PO_4
(c) $H_4P_2O_7$

Exercises

22.32 Write a chemical formula for each compound or ion, and indicate the oxidation state of the Group 15 element in each formula: (**a**) diarsenic trisulfide, (**b**) arsenic pentoxide, (**c**) phosphorus trichloride, (**d**) phosphonium ion, (**e**) indium antimonide, (**f**) sodium arsenite.

22.33 Account for the following observations: (**a**) H_3PO_3 is a diprotic acid. (**b**) Nitric acid is a strong acid, whereas phosphoric acid is weak. (**c**) Phosphate rock is ineffective as a phosphate fertilizer. (**d**) Phosphorus does not exist at room temperature as diatomic molecules, but nitrogen does. (**e**) Solutions of Na_3PO_4 are quite basic.

22.34 Write a balanced equation for each of the following reactions: (**a**) hydrolysis of PCl_5, (**b**) dehydration of phosphoric acid (also called orthophosphoric acid) to form pyrophosphoric acid, (**c**) reaction of P_4O_{10} with water.

Answers to Self-Assessment Exercise

22.32 (a)

22.9 | Carbon



Carbon constitutes only 0.027% of Earth's crust. Although some carbon occurs in elemental form as graphite and diamond, most is found in combined form. Over half occurs in carbonate compounds. Carbon is also found in coal, petroleum, and natural gas. The importance of the element stems in large part from its occurrence in all living organisms: Life as we know it is based on carbon compounds. In this section, we focus on inorganic carbon, and by the end, you should be able to

- Recognize the main reactions involving oxides of carbon, carbonates, and carbides

Elemental Forms of Carbon

We have seen that carbon exists in several allotropic crystalline forms: graphite, diamond, fullerenes, carbon nanotubes, and graphene. Fullerenes, nanotubes, and graphene are discussed in Chapter 12; here we focus on graphite and diamond.

Graphite is a soft, black, slippery solid that has a metallic luster and conducts electricity. It consists of parallel sheets of sp^2 hybridized carbon atoms held together by dispersion forces. *Diamond* is a clear, hard solid in which the carbon atoms form an sp^3 hybridized covalent network. Diamond is denser than graphite ($d = 2.25\ g/cm^3$ for graphite; $d = 3.51\ g/cm^3$ for diamond). At approximately 10 GPa at 3000 °C, graphite converts to diamond. In fact, almost any carbon-containing substance, if put under sufficiently high pressure, forms diamonds; scientists at General Electric in the 1950s used peanut butter to make diamonds. About 3×10^4 kg of industrial grade diamonds are synthesized each year, mainly for use in cutting, grinding, and polishing tools.

Graphite has a well-defined crystalline structure, but it also exists in two common amorphous forms: **carbon black** and **charcoal**. Carbon black is formed when hydrocarbons are heated in a very limited supply of oxygen, such as in this methane reaction:

$$CH_4(g) + O_2(g) \longrightarrow C(s) + 2\,H_2O(g) \qquad [22.51]$$

Carbon black is used as a pigment in black inks; large amounts are also used in making vehicle tires.

Charcoal is formed when wood is heated strongly in the absence of air. Charcoal has an open structure, giving it an enormous surface area per unit mass. "Activated charcoal," a pulverized form of charcoal whose surface is cleaned by heating with steam, is widely used to adsorb molecules. It is used in filters to remove offensive odors from air and colored or bad-tasting impurities from water.

Oxides of Carbon

Carbon forms two principal oxides: carbon monoxide (CO) and carbon dioxide (CO_2). *Carbon monoxide* is formed when carbon or hydrocarbons are burned in a limited supply of oxygen:

$$2\,C(s) + O_2(g) \longrightarrow 2\,CO(g) \qquad [22.52]$$

CO is a colorless, odorless, tasteless gas that is toxic because it binds to hemoglobin in the blood and thus interferes with oxygen transport. Low-level poisoning results in headaches and drowsiness; high-level poisoning can cause death.

Carbon monoxide is unusual in that it has a nonbonding pair of electrons on carbon: $:C{\equiv}O:$. It is isoelectronic with N_2, so you might expect CO to be equally unreactive. Moreover, both substances have high bond energies (1072 kJ/mol for $C{\equiv}O$ and 941 kJ/mol for $N{\equiv}N$). Because of the lower nuclear charge on carbon (compared with either N or O), however, the carbon nonbonding pair is not held as strongly as that on N or O. Consequently, CO is better able to function as a Lewis base than is N_2; for example, CO can coordinate its nonbonding pair to the iron of hemoglobin, displacing O_2, but N_2 cannot.

Carbon monoxide has several commercial uses. Because it burns readily, forming CO_2, it is employed as a fuel:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) \qquad \Delta H^\circ = -566\ kJ \qquad [22.53]$$

Carbon monoxide is an important reducing agent, widely used in metallurgical operations to reduce metal oxides, such as the iron oxides:

$$Fe_3O_4(s) + 4\,CO(g) \longrightarrow 3\,Fe(s) + 4\,CO_2(g) \qquad [22.54]$$

Carbon dioxide is produced when carbon-containing substances are burned in excess oxygen, such as in this reaction involving ethanol:

$$C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(g) \qquad [22.55]$$

It is also produced when many carbonates are heated:

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \qquad [22.56]$$

CHEMISTRY PUT TO WORK Carbon Fibers and Composites

The properties of graphite are anisotropic; that is, they differ in different directions through the solid. Along the carbon planes, graphite possesses great strength because of the number and strength of the carbon–carbon bonds in this direction. The bonds between planes are relatively weak, however, making graphite weak in that direction.

Fibers of graphite can be prepared in which the carbon planes are aligned to varying extents parallel to the fiber axis. These fibers are lightweight (density of about 2 g/cm^3) and chemically quite unreactive. The oriented fibers are made by first slowly pyrolyzing (decomposing by action of heat) organic fibers at about 150 to 300 °C. These fibers are then heated to about 2500 °C to graphitize them (convert amorphous carbon to graphite). Stretching the fiber during pyrolysis helps orient the graphite planes parallel to the fiber axis. More amorphous carbon fibers are formed by pyrolysis of organic fibers at lower temperatures (1200 to 400 °C). These amorphous materials, commonly called *carbon fibers*, are the type most often used in commercial materials.

Composite materials that take advantage of the strength, stability, and low density of carbon fibers are widely used. Composites are combinations of two or more materials. These materials are present as separate phases and are combined to form structures that take advantage of certain desirable properties of each component. In carbon composites, the graphite fibers are often woven into a fabric that is embedded in a matrix that binds them into a solid structure. The fibers transmit loads evenly throughout the matrix. The finished composite is thus stronger than any one of its components.

Carbon composite materials are used widely in a number of applications, including high-performance graphite sports equipment such as tennis racquets, golf clubs, and bicycle wheels (**Figure 22.28**). Heat-resistant composites are required for many aerospace applications, where carbon composites now find wide use.



▲ **Figure 22.28** **Carbon composites in commercial products.**

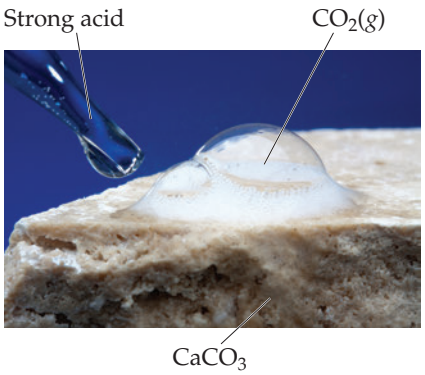
In the laboratory, CO_2 can be produced by the action of acids on carbonates (**Figure 22.29**):

$$CO_3^{2-}(aq) + 2\,H^+(aq) \longrightarrow CO_2(g) + H_2O(l) \qquad [22.57]$$

Carbon dioxide is a colorless, odorless gas. It is a minor component of Earth's atmosphere but a major contributor to the greenhouse effect. Although it is not toxic, high concentrations of CO_2 increase respiration rate and can cause suffocation. It is readily liquefied by compression. When cooled at atmospheric pressure, however, CO_2 forms a solid rather than liquefying. The solid sublimes at atmospheric pressure at −78 °C. This property makes solid CO_2, known as *dry ice*, valuable as a refrigerant. About half of the CO_2 consumed annually is used for refrigeration. The other major use of CO_2 is in the production of carbonated beverages. Large quantities are also used to manufacture *washing soda* ($Na_2CO_3 \cdot 10\,H_2O$), used to precipitate metal ions that interfere with the cleansing action of soap, and *baking soda* ($NaHCO_3$). Baking soda is so named because this reaction occurs during baking:

$$NaHCO_3(s) + H^+(aq) \longrightarrow Na^+(aq) + CO_2(g) + H_2O(l) \qquad [22.58]$$

The $H^+(aq)$ is provided by vinegar, sour milk, or the hydrolysis of certain salts. The bubbles of CO_2 that form are trapped in the baking dough, causing it to rise.



▲ **Figure 22.29** **CO_2 formation from the reaction between an acid and calcium carbonate in rock.**

Carbonic Acid and Carbonates

Carbon dioxide is moderately soluble in H_2O at atmospheric pressure. The resulting solution is moderately acidic because of the formation of carbonic acid (H_2CO_3):

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad [22.59]$$

Carbonic acid is a weak diprotic acid. Its acidic character causes carbonated beverages to have a sharp, slightly acidic taste.

Although carbonic acid cannot be isolated, hydrogen carbonates (bicarbonates) and carbonates can be obtained by neutralizing carbonic acid solutions. Partial neutralization produces HCO_3^-, and complete neutralization gives CO_3^{2-}. The HCO_3^- ion is a stronger base than acid ($K_b = 2.3 \times 10^{-8}$; $K_a = 5.6 \times 10^{-11}$). The carbonate ion is much more strongly basic ($K_b = 1.8 \times 10^{-4}$).

The principal carbonate minerals are calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite [$MgCa(CO_3)_2$], and siderite ($FeCO_3$). Calcite is the principal mineral in limestone and the main constituent of marble, chalk, pearls, coral reefs, and the shells of marine animals such as clams and oysters. Although $CaCO_3$ has low solubility in pure water, it dissolves readily in acidic solutions with evolution of CO_2:

$$CaCO_3(s) + 2\,H^+(aq) \rightleftharpoons Ca^{2+}(aq) + H_2O(l) + CO_2(g) \qquad [22.60]$$

Because water containing CO_2 is slightly acidic (Equation 22.59), $CaCO_3$ dissolves slowly in this medium:

$$CaCO_3(s) + H_2O(l) + CO_2(g) \longrightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq) \qquad [22.61]$$

This reaction occurs when surface waters move underground through limestone deposits. It is the principal way Ca^{2+} enters groundwater, producing *hard water*, (water with a high mineral content, containing especially Ca^{2+} and Mg^{2+} ions). If the limestone deposit is deep enough underground, dissolution of the limestone produces a cave.

One of the most important reactions of $CaCO_3$ is its decomposition into CaO and CO_2 at elevated temperatures (Equation 22.56). Because calcium oxide, known as lime or quicklime, reacts with water to form $Ca(OH)_2$, it is an important commercial base. It is also important in making mortar, the mixture of sand, water, and CaO used to bind bricks, blocks, or rocks together. Calcium oxide reacts with water and CO_2 to form $CaCO_3$, which binds the sand in the mortar:

$$CaO(s) + H_2O(l) \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq) \qquad [22.62]$$

$$Ca^{2+}(aq) + 2\,OH^-(aq) + CO_2(aq) \longrightarrow CaCO_3(s) + H_2O(l) \qquad [22.63]$$

Carbides

The binary compounds of carbon with metals, metalloids, and certain nonmetals are called **carbides**. The more active metals form *ionic carbides*, and the most common of these contain the *acetylide* ion (C_2^{2-}). This ion is isoelectronic with N_2, and its Lewis structure, $[:C{\equiv}C:]^{2-}$, has a carbon–carbon triple bond. The most important ionic carbide is calcium carbide (CaC_2), produced by the reduction of CaO with carbon at high temperature:

$$2\,CaO(s) + 5\,C(s) \longrightarrow 2\,CaC_2(s) + CO_2(g) \qquad [22.64]$$

The carbide ion is a very strong base that reacts with water to form acetylene (H—C≡C—H):

$$CaC_2(s) + 2\,H_2O(l) \longrightarrow Ca(OH)_2(aq) + C_2H_2(g) \qquad [22.65]$$

Calcium carbide is therefore a convenient solid source of acetylene, which is used in welding (Figure 22.11).

Interstitial carbides are formed by many transition metals. The carbon atoms occupy open spaces (interstices) between the metal atoms in a manner analogous to the interstitial hydrides. This process generally makes the metal harder. Tungsten carbide (WC), for example, is very hard and very heat-resistant and, thus, used to make cutting tools.

Covalent carbides are formed by boron and silicon. Silicon carbide (SiC), known as Carborundum®, is used as an abrasive and in cutting tools. Almost as hard as diamond, SiC has a diamond-like structure with alternating Si and C atoms.

Self-Assessment Exercise

22.35 The hydrogen carbonate ion is amphiprotic. Will the pH of a solution of $NaHCO_3$ be acidic, neutral, or basic?

(a) Acidic
(b) Neutral
(c) Basic

Exercises

22.36 Give the chemical formula for (**a**) fullerene, (**b**) potassium cyanide, (**c**) zinc carbide, (**d**) zinc acetylide, (**e**) carbon disulfide.

22.37 Complete and balance the following equations:

(**a**) $CO_2(g) + OH^-(aq) \longrightarrow$

(**b**) $NaHCO_3(s) + H^+(aq) \longrightarrow$

(**c**) $CaO(s) + C(s) \xrightarrow{\Delta}$

(**d**) $C(s) + H_2O(g) \xrightarrow{\Delta}$

(**e**) $CuO(s) + CO(g) \longrightarrow$

22.38 Write a balanced equation for each of the following reactions: (**a**) Burning magnesium metal in a carbon dioxide atmosphere reduces the CO_2 to carbon. (**b**) In photosynthesis, solar energy is used to produce glucose ($C_6H_{12}O_6$) and O_2 from carbon dioxide and water. (**c**) When carbonate salts dissolve in water, they produce basic solutions.

Answers to Self-Assessment Exercise

22.35 (c)

22.10 The Other Group 14 Elements: Si, Ge, Sn, and Pb

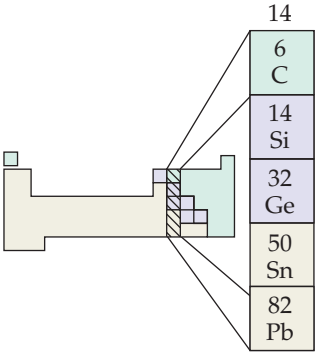


Asbestos is a general term applied to a group of fibrous silicate minerals. The structure of these minerals is either chains of silicate tetrahedra or sheets formed into rolls. The result is that the minerals have a fibrous character. Asbestos minerals were once widely used as thermal insulation, especially in high-temperature applications, because of the great chemical stability of the silicate structure. In addition, the fibers can be woven into asbestos cloth, which was once used for fireproof curtains and other applications.

However, the fibrous structure of asbestos minerals poses a health risk, because the fibers readily penetrate soft tissues, such as the lungs, where they can cause diseases, including cancer. The use of asbestos as a common building material has, therefore, been discontinued.

By the end of this section, you should be able to

- Understand the occurrence of silicates and some uses of silicon



The trend from nonmetallic to metallic character as we go down a family is strikingly evident in Group 14. Carbon is a nonmetal; silicon and germanium are metalloids; tin and lead are metals. In this section, we consider a few general characteristics of Group 14 and then look more thoroughly at silicon.

General Characteristics of the Group 14 Elements

The Group 14 elements possess the outer-shell electron configuration ns^2np^2. The electronegativities of the elements are generally low (**Table 22.8**); carbides that formally contain C^{4-} ions are observed only in the case of a few compounds of carbon with very active metals. Tin is unusual as it can form the Sn^{4+} ion, however the +4 oxidation state is common and is found in the vast majority of the compounds of the Group 14 elements. The +2 oxidation state is also found in the chemistry of germanium, tin, and lead and it is the principal oxidation state for lead. Carbon usually forms a maximum of four bonds. The other members of the family are able to form more than four bonds.

Table 22.8 shows that the strength of a bond between two atoms of a given element decreases as we go down Group 14. Carbon–carbon bonds are quite strong. Carbon, therefore, has a striking ability to form compounds in which carbon atoms are bonded to one another in extended chains and rings, which accounts for the large number of organic compounds that exist. Other elements can form chains and rings, but these bonds are far less important in the chemistries of these other elements. The Si—Si bond strength (226 kJ/mol), for example, is much lower than the Si—O bond strength (386 kJ/mol). As a result, the chemistry of silicon is dominated by the formation of Si—O bonds, and Si—Si bonds play a minor role.

Occurrence and Preparation of Silicon

Silicon is the second most abundant element, after oxygen, in Earth's crust. It occurs in SiO_2 and in an enormous variety of silicate minerals. The element is obtained by the reduction of molten silicon dioxide with carbon at high temperature:

$$SiO_2(l) + 2\,C(s) \longrightarrow Si(l) + 2\,CO(g) \qquad [22.66]$$

Elemental silicon has a diamond-like structure. Crystalline silicon is a gray metallic-looking solid that melts at 1410 °C. The element is a semiconductor, as we saw in Chapters 7 and 12, and is used to make solar cells and transistors for computer chips. To be used as a semiconductor, it must be extremely pure, possessing less than 10^{-7}% (1 ppb) impurities. One method of purification is to treat the element with Cl_2 to form $SiCl_4$, a volatile liquid that is purified by fractional distillation and then converted back to elemental silicon by reduction with H_2:

$$SiCl_4(g) + 2\,H_2(g) \longrightarrow Si(s) + 4\,HCl(g) \qquad [22.67]$$

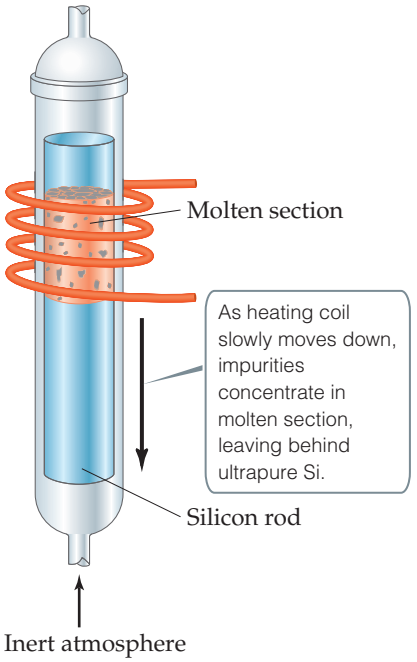
TABLE 22.8 Some Properties of the Group 14 Elements

Property	C	Si	Ge	Sn	Pb
Atomic radius (pm)	76	111	120	139	146
First ionization energy (kJ/mol)	1086	786	762	709	716
Electronegativity	2.5	1.8	1.8	1.8	1.9
X—X single-bond enthalpy (kJ/mol)	348	226	188	151	—

The process known as *zone refining* can further purify the element (Figure 22.30). As a heated coil is passed slowly along a silicon rod, a narrow band of the element is melted. As the molten section is swept slowly along the length of the rod, the impurities concentrate in this section, following it to the end of the rod. The purified top portion of the rod crystallizes as 99.999999999% pure silicon.

Go Figure

What limits the range of temperatures you can use for zone refining of silicon?



▲ **Figure 22.30** **Zone-refining apparatus for the production of ultrapure silicon.**

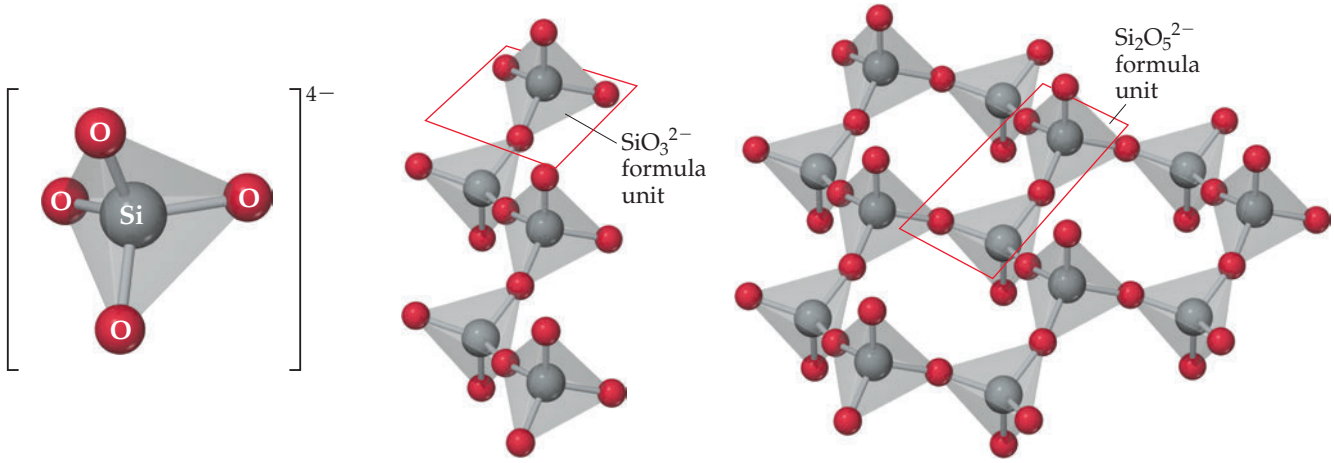
Silicates

Silicon dioxide and other compounds that contain silicon and oxygen make up over 90% of Earth's crust. In **silicates**, a silicon atom is surrounded by four oxygens and silicon is found in its most common oxidation state, +4. The orthosilicate ion, SiO_4^{4-}, is found in very few silicate minerals, but we can view it as the "building block" for many mineral structures. As Figure 22.31 shows, adjacent tetrahedra can be linked by a common oxygen atom. Two tetrahedra joined in this way, called the *disilicate* ion, contain two Si atoms and seven O atoms. Silicon and oxygen are in the +4 and −2 oxidation states, respectively, in all silicates, so the overall charge of any silicate ion must be consistent with these oxidation states. For example, the charge on Si_2O_7 is $(2)(+4) + (7)(-2) = -6$; it is the $Si_2O_7^{6-}$ ion.

In most silicate minerals, silicate tetrahedra are linked together to form chains, sheets, or three-dimensional structures. We can connect two vertices of each tetrahedron to two other tetrahedra, for example, leading to an infinite chain with an $\cdots$ O—Si—O—Si $\cdots$ backbone as shown in Figure 22.31(**b**). Notice that each silicon in this structure has two unshared (terminal) oxygens and two shared (bridging) oxygens. The stoichiometry is then $2(1) + 2(1/2) = 3$ oxygens per silicon. Thus, the formula unit for this chain is SiO_3^{2-}. The mineral *enstatite* ($MgSiO_3$) has this kind of structure, consisting of rows of single-strand silicate chains with Mg^{2+} ions between the strands to balance charge.

In Figure 22.31(**c**), each silicate tetrahedron is linked to three others, forming an infinite sheet structure. Each silicon in this structure has one unshared oxygen and three shared oxygens. The stoichiometry is then $1(1) + 3(\frac{1}{2}) = 2\frac{1}{2}$ oxygens per silicon. The simplest formula of this sheet is $Si_2O_5^{2-}$. The mineral *talc*, also known as talcum powder, has the formula $Mg_3(Si_2O_5)_2(OH)_2$ and is based on this sheet structure. The Mg^{2+} and OH^- ions lie between the silicate sheets. The slippery feel of talcum powder is due to the silicate sheets sliding relative to one another.

When all four vertices of each SiO_4 tetrahedron are linked to other tetrahedra, the structure extends in three dimensions. This linking of the tetrahedra forms quartz (SiO_2). Because the structure is locked together in a three-dimensional array much like diamond, quartz is harder than strand- or sheet-type silicates.



Silicate ion (a) Fragment of silicate chain (b) Fragment of silicate sheet (c)

▲ **Figure 22.31** **Silicate chains and sheets.**

Sample Exercise 22.6

Determining an Empirical Formula

The mineral *chrysotile* is a noncarcinogenic asbestos mineral that is based on the sheet structure shown in Figure 22.31(c). In addition to silicate tetrahedra, the mineral contains Mg^{2+} and OH^- ions. Analysis of the mineral shows that there are 1.5 Mg atoms per Si atom. What is the empirical formula for chrysotile?

SOLUTION

Analyze A mineral is described that has a sheet silicate structure with Mg^{2+} and OH^- ions to balance charge and 1.5 Mg for each 1 Si. We are asked to write the empirical formula for the mineral.

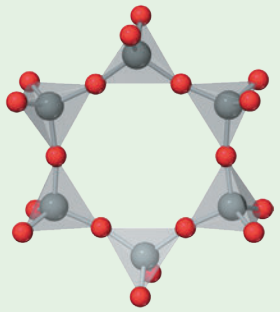
Plan As shown in Figure 22.31(c), the silicate sheet structure has the simplest formula $Si_2O_5^{2-}$. We first add Mg^{2+} to give the proper Mg:Si ratio. We then add OH^- ions to obtain a neutral compound.

Solve

The observation that the Mg:Si ratio equals 1.5 is consistent with three Mg^{2+} ions per $Si_2O_5^{2-}$ unit. The addition of three Mg^{2+} ions would make $Mg_3(Si_2O_5)^{4+}$. In order to achieve charge balance in the mineral, there must be four OH^- per $Si_2O_5^{2-}$. Thus, the formula of chrysotile is $Mg_3(Si_2O_5)(OH)_4$. Since this is not reducible to a simpler formula, this is the empirical formula.

Practice Exercise

In the mineral beryl, six silicate tetrahedra are connected to form a ring as shown here. The negative charge of this polyanion is balanced by Be^{2+} and Al^{3+} cations. If elemental analysis gives a Be:Si ratio of 1:2 and an Al:Si ratio of 1:3 what is the empirical formula of beryl: (**a**) $Be_2Al_3Si_6O_{19}$, (**b**) $Be_3Al_2(SiO_4)_6$, (**c**) $Be_3Al_2Si_6O_{18}$, (**d**) $BeAl_2Si_6O_{15}$?



Beryl

Glass

Quartz melts at approximately 1600 °C, forming a tacky liquid. In the course of melting, many silicon–oxygen bonds are broken. When the liquid cools rapidly, silicon–oxygen bonds are re-formed before the atoms are able to arrange themselves in a regular fashion. An amorphous solid, known as quartz glass or silica glass, results. Many substances can be added to SiO_2 to cause it to melt at a lower temperature. The common **glass** used in windows and bottles, known as soda-lime glass, contains CaO and Na_2O in addition to SiO_2 from sand. The CaO and Na_2O are produced by heating two inexpensive chemicals, limestone ($CaCO_3$) and soda ash (Na_2CO_3), which decompose at high temperatures:

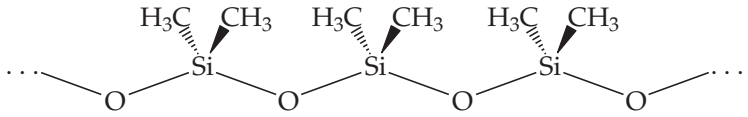
$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad [22.68]$$

$$Na_2CO_3(s) \longrightarrow Na_2O(s) + CO_2(g) \qquad [22.69]$$

Other substances can be added to soda-lime glass to produce color or to change the properties of the glass in various ways. The addition of CoO, for example, produces the deep blue color of "cobalt glass." Replacing Na_2O with K_2O results in a harder glass that has a higher melting point. Replacing CaO with PbO results in a denser "lead crystal" glass with a higher refractive index. Lead crystal is used for decorative glassware; the higher refractive index gives this glass a particularly sparkling appearance. Addition of nonmetal oxides, such as B_2O_3 and P_4O_{10}, which form network structures related to the silicates, also changes the properties of the glass. Adding B_2O_3 creates a "borosilicate" glass with a higher melting point and a greater ability to withstand temperature changes. Such glasses, sold commercially under trade names such as Pyrex® and Kimax®, are used where resistance to thermal shock is important, such as in laboratory glassware or coffeemakers.

Silicones

Silicones consist of O—Si—O chains in which the two remaining bonding positions on each silicon are occupied by organic groups such as CH_3:



Depending on chain length and degree of cross-linking, silicones can be either oils or rubber-like materials. Silicones are nontoxic and have good stability toward heat, light, oxygen, and water. They are used commercially in a wide variety of products, including lubricants, car polishes, sealants, and gaskets. They are also used for waterproofing fabrics. When applied to a fabric, the oxygen atoms form hydrogen bonds with the molecules on the surface of the fabric. The hydrophobic (water-repelling) organic groups of the silicone are then left pointing away from the surface as a barrier.

Self-Assessment Exercise

22.39 Sodium metasilicate has the formula Na_2SiO_3. What structure do you expect for the silicate ions?

(a) Individual units

(b) Chains

(c) Sheets

(d) 3-D network

Exercises

22.40 Select the member of Group 14 that best fits each description: (**a**) has the greatest tendency to form multiple bonds with itself, (**b**) forms polymeric structures with oxygen, (**c**) is a metal with +2 and +4 oxidation states.

22.41 Speculate as to why carbon forms carbonate rather than silicate analogs.

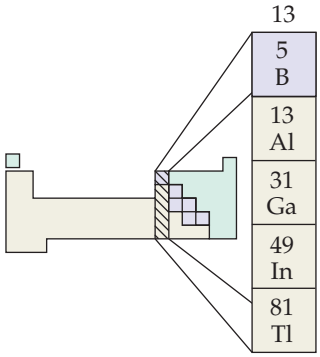
22.42 (**a**) Determine the number of sodium ions in the chemical formula of albite, $Na_xAlSi_3O_8$. (**b**) Determine the number of hydroxide ions in the chemical formula of tremolite, $Ca_2Mg_5(Si_4O_{11})_2(OH)_x$.

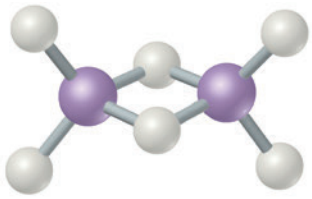
Answers to Self-Assessment Exercise

22.39 (b)

22.11 Boron







▲ **Figure 22.32** **The structure of diborane (B_2H_6).**

Boron is the only Group 13 element that can be considered nonmetallic and thus is our final element in this chapter. The element has an extended network structure with a melting point (2300 °C) that is intermediate between the melting points of carbon (3550 °C) and silicon (1410 °C). The electron configuration of boron is $[He]2s^2 2p^1$.

In the family of compounds called **boranes**, the molecules contain only boron and hydrogen. Because B is less electronegative than H, the B—H bond in these compounds is polarized, with H having the higher electron density. The simplest borane is BH_3. This molecule contains only six valence electrons and is therefore an exception to the octet rule. As a result, BH_3 reacts with itself to form *diborane* (B_2H_6). This reaction can be viewed as a Lewis acid–base reaction in which one B—H bonding pair of electrons in each BH_3 molecule is donated to the other. As a result, diborane is an unusual molecule in which hydrogen atoms form a bridge between two B atoms (**Figure 22.32**). Such hydrogens are called *bridging hydrogens*.

Sharing hydrogen atoms between the two boron atoms compensates somewhat for the deficiency in valence electrons around each boron. Nevertheless, diborane is an extremely reactive molecule, spontaneously flammable in air in a highly exothermic reaction:

$$B_2H_6(g) + 3\,O_2(g) \longrightarrow B_2O_3(s) + 3\,H_2O(g) \qquad \Delta H^\circ = -2030\ \text{kJ} \qquad [22.70]$$

Boron and hydrogen form a series of anions called *borane anions*. Salts of the borohydride ion (BH_4^-) are widely used as reducing agents. For example, sodium borohydride ($NaBH_4$) is a commonly used reducing agent for certain organic compounds.

The only important oxide of boron is boric oxide (B_2O_3). This substance is the anhydride of boric acid, which we may write as H_3BO_3 or $B(OH)_3$. Boric acid is so weak an acid ($K_a = 5.8 \times 10^{-10}$) that solutions of H_3BO_3 are used as an eyewash. Upon heating, boric acid loses water by a condensation reaction similar to that described for phosphorus in Section 22.8:

$$4\,H_3BO_3(s) \longrightarrow H_2B_4O_7(s) + 5\,H_2O(g) \qquad [22.71]$$

The diprotic acid $H_2B_4O_7$ is tetraboric acid. The hydrated sodium salt $Na_2B_4O_7 \cdot 10\,H_2O$, called borax, is used in various laundry and cleaning products.

Sample Integrative Exercise

Putting Concepts Together

The interhalogen compound BrF_3 is a volatile, straw-colored liquid. The compound exhibits appreciable electrical conductivity because of autoionization ("solv" refers to BrF_3 as the solvent):

$$2\,BrF_3(l) \rightleftharpoons BrF_2^+(solv) + BrF_4^-(solv)$$

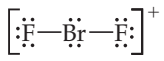
(**a**) What are the molecular structures of the BrF_2^+ and BrF_4^- ions?

(**b**) The electrical conductivity of BrF_3 decreases with increasing temperature. Is the autoionization process exothermic or endothermic?

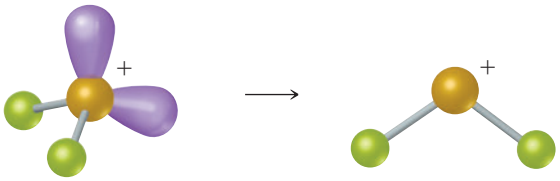
(**c**) One chemical characteristic of BrF_3 is that it acts as a Lewis acid toward fluoride ions. What do we expect will happen when KF is dissolved in BrF_3?

SOLUTION

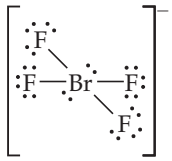
(**a**) The BrF_2^+ ion has $7 + 2(7) - 1 = 20$ valence-shell electrons. The Lewis structure for the ion is



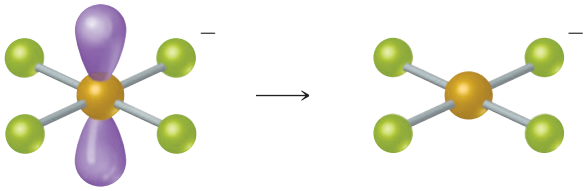
Because there are four electron domains around the central Br atom, the resulting electron domain geometry is tetrahedral. Because bonding pairs of electrons occupy two of these domains, the molecular geometry is bent:



The BrF_4^- ion has 7 + 4(7) + 1 = 36 electrons, leading to the Lewis structure:

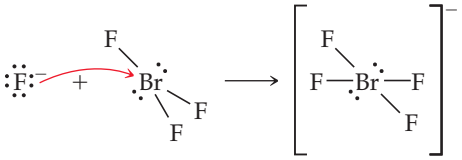


Because there are six electron domains around the central Br atom in this ion, the electron-domain geometry is octahedral. The two nonbonding pairs of electrons are located opposite each other on the octahedron, leading to a square-planar molecular geometry:



(**b**) The observation that conductivity decreases as temperature increases indicates that there are fewer ions present in the solution at the higher temperature. Thus, increasing the temperature causes the equilibrium to shift to the left. According to Le Châtelier's principle, this shift indicates that the reaction is exothermic as it proceeds from left to right.

(**c**) A Lewis acid is an electron-pair acceptor. The fluoride ion has four valence-shell electron pairs and can act as a Lewis base (an electron-pair donor). Thus, we can envision the following reaction occurring:



$$F^- + BrF_3 \longrightarrow BrF_4^-$$

Self-Assessment Exercise

22.43 Recall that the hydride ion is H^-. What is the oxidation state of boron in sodium borohydride?

(a) −1
(b) +1
(c) +3

Exercises

22.44 Write the formulas for the following compounds, and indicate the oxidation state of the Group 14 element or of boron in each: (**a**) stannous fluoride, (**b**) germane, (**c**) diborane, (**d**) tin(II) sulfate, (**e**) tin selenide, (**f**) zinc carbonate.

22.45 Write a balanced equation for each of the following reactions: (**a**) Diborane reacts with water to form boric acid and molecular hydrogen. (**b**) Upon heating, boric acid undergoes a condensation reaction to form tetraboric acid. (**c**) Boron oxide dissolves in water to give a solution of boric acid.

Answers to Self-Assessment Exercise

22.43 (c)

Chapter Summary and Key Terms

THE PERIODIC TABLE AND CHEMICAL REACTIONS (SECTION 22.1) The periodic table is useful for organizing and remembering the descriptive chemistry of the elements. Among elements of a given group, size increases with increasing atomic number, and electronegativity and ionization energy decrease. The most nonmetallic elements are found in the upper right portion of the periodic table.

Among the nonmetallic elements, the first member of each group differs dramatically from the other members; it forms a maximum of four bonds to other atoms and exhibits a much greater tendency to form π bonds than the heavier elements in its group.

Because O_2 and H_2O are abundant in our world, we focus on two important and general reaction types as we discuss the nonmetals: oxidation by O_2 and proton-transfer reactions involving H_2O or aqueous solutions.

HYDROGEN (SECTION 22.2) Hydrogen has three isotopes: **protium** (^1_1H), **deuterium** (^2_1H), and **tritium** (^3_1H). Hydrogen is not a member of any particular periodic group, although it is usually placed above lithium. The hydrogen atom can either lose an electron, forming H^+, or gain one, forming H^- (the hydride ion). Because the H—H bond is relatively strong, H_2 is fairly unreactive unless activated by heat or a catalyst. Hydrogen forms a very strong bond to oxygen, so the reactions of H_2 with oxygen-containing compounds usually lead to the formation of H_2O. The $H^+(aq)$ ion is able to oxidize many metals, forming $H_2(g)$. The electrolysis of water also forms $H_2(g)$.

The binary compounds of hydrogen are of three general types: **ionic hydrides** (formed by active metals), **metallic hydrides** (formed by transition metals), and **molecular hydrides** (formed by nonmetals). The ionic hydrides contain the H^- ion; because this ion is extremely basic, ionic hydrides react with H_2O to form H_2 and OH^-.

GROUP 18: THE NOBLE GASES AND GROUP 17: HALOGENS (SECTIONS 22.3 AND 22.4) The noble gases (Group 18) exhibit a very limited chemical reactivity because of the exceptional stability of their electron configurations. The xenon fluorides and oxides and KrF_2 are the best-established compounds of the noble gases.

The halogens (Group 17) occur as diatomic molecules. All except fluorine exhibit oxidation states varying from -1 to $+7$. Fluorine is the most electronegative element, so it is restricted to the oxidation states 0 and -1. The oxidizing power of the element (the tendency to form the -1 oxidation state) decreases as we proceed down the group.

The hydrogen halides are among the most useful compounds of these elements; these gases dissolve in water to form the hydrohalic acids, such as $HCl(aq)$. Hydrofluoric acid reacts with **silica**. The **interhalogens** are compounds formed between two different halogen elements. Chlorine, bromine, and iodine form a series of oxyacids, in which the halogen atom is in a positive oxidation state. These compounds and their associated oxyanions are strong oxidizing agents.

OXYGEN AND THE OTHER GROUP 16 ELEMENTS (SECTIONS 22.5 AND 22.6) Oxygen has two allotropes, O_2 and O_3 (ozone). Ozone is unstable compared to O_2, and it is a stronger oxidizing agent than O_2. Most reactions of O_2 lead to oxides, compounds in which oxygen is in the -2 oxidation state. The soluble oxides of nonmetals generally produce acidic aqueous solutions; they are called **acidic anhydrides** or **acidic oxides**. In contrast, soluble metal oxides produce basic solutions and are called **basic anhydrides** or **basic oxides**. Many metal oxides that are insoluble in water dissolve in acid, accompanied by the formation of H_2O.

Peroxides contain O—O bonds and oxygen in the -1 oxidation state. Peroxides are unstable, decomposing to O_2 and oxides. In such reactions peroxides are simultaneously oxidized and reduced, a process called **disproportionation**. Superoxides contain the O_2^- ion in which oxygen is in the $-\frac{1}{2}$ oxidation state.

Sulfur is the most important of the other Group 16 elements. It has several allotropic forms; the most stable one at room temperature consists of S_8 rings. Sulfur forms two oxides, SO_2 and SO_3, and both are important atmospheric pollutants. Sulfur trioxide is the anhydride of sulfuric acid, the most important sulfur compound and the most-produced industrial chemical. Sulfuric acid is a strong acid and a good dehydrating agent. Sulfur forms several oxyanions as well, including the SO_3^{2-} (sulfite), SO_4^{2-} (sulfate), and $S_2O_3^{2-}$ (thiosulfate) ions. Sulfur is found combined with many metals as a sulfide, in which sulfur is in the -2 oxidation state. These compounds often react with acids to form hydrogen sulfide (H_2S), which smells like rotten eggs.

NITROGEN AND THE OTHER GROUP 15 ELEMENTS (SECTIONS 22.7 AND 22.8) Nitrogen is found in the atmosphere as N_2 molecules. Molecular nitrogen is chemically very stable because of the strong N≡N bond. Molecular nitrogen can be converted into ammonia via the Haber process. Once the ammonia is made, it can be converted into a variety of different compounds that exhibit nitrogen oxidation states ranging from -3 to $+5$. The most important industrial conversion of ammonia is the **Ostwald process**, in which ammonia is oxidized to nitric acid (HNO_3).

Nitrogen has three important oxides: nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Nitrous acid (HNO_2) is a weak acid; its conjugate base is the nitrite ion (NO_2^-). Another important nitrogen compound is hydrazine (N_2H_4).

Phosphorus is the most important of the remaining Group 15 elements. It occurs in nature as phosphate minerals. Phosphorus has several allotropes, including white phosphorus, which consists of P_4 tetrahedra. In reaction with the halogens, phosphorus forms trihalides PX_3 and pentahalides PX_5. These compounds undergo hydrolysis to produce an oxyacid of phosphorus and HX.

Phosphorus forms two oxides, P_4O_6 and P_4O_{10}. Their corresponding acids, phosphorous acid and phosphoric acid, undergo condensation reactions when heated. Phosphorus compounds are important in biochemistry and as fertilizers.

CARBON AND THE OTHER GROUP 14 ELEMENTS (SECTIONS 22.9 AND 22.10) The allotropes of carbon include diamond, graphite, fullerenes, carbon nanotubes, and graphene. Amorphous forms of graphite include **charcoal** and **carbon black**. Carbon forms two common oxides, CO and CO_2. Aqueous solutions of CO_2 produce the weak diprotic acid carbonic acid (H_2CO_3), which is the parent acid of hydrogen carbonate and carbonate salts. Binary compounds of carbon are called **carbides**. Carbides may be ionic, interstitial, or covalent. Calcium carbide (CaC_2) contains the strongly basic acetylide ion (C_2^{2-}), which reacts with water to form acetylene.

The other Group 14 elements show great diversity in physical and chemical properties. Silicon, the second most abundant element, is a semiconductor. It reacts with Cl_2 to form $SiCl_4$, a liquid at room temperature, a reaction that is used to help purify silicon from its native minerals. Silicon forms strong Si—O bonds and therefore occurs in a variety of silicate minerals. Silica is SiO_2; **silicates** consist of SiO_4 tetrahedra, linked together at their vertices to form chains, sheets, or three-dimensional structures. The most common three-dimensional silicate is quartz (SiO_2). **Glass** is an amorphous (noncrystalline) form of SiO_2. Silicones contain O—Si—O chains with organic groups bonded to the Si atoms. Like silicon, germanium is a metalloid; tin and lead are metallic.

BORON (SECTION 22.11) Boron is the only Group 13 element that is a nonmetal. It forms a variety of compounds with hydrogen called boron hydrides, or **boranes**. Diborane (B_2H_6) has an unusual structure with two hydrogen atoms that bridge between the two boron atoms. Boranes react with oxygen to form boric oxide (B_2O_3), in which boron is in the +3 oxidation state. Boric oxide is the anhydride of boric acid (H_3BO_3). Boric acid readily undergoes condensation reactions.

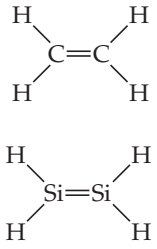
Learning Outcomes After studying this chapter, you should be able to:

- Use periodic trends to explain the basic differences between the elements of a group or period. (Section 22.1)
  Related Exercises: 22.57, 22.58, 22.59
- Explain two ways in which the first element in a group differs from subsequent elements in the group. (Section 22.1)
  Related Exercises: 22.46, 22.58
- Be able to determine electron configurations, oxidation numbers, and molecular shapes of elements and compounds. (Sections 22.2–22.11) *Related Exercises: 22.48, 22.67, 22.77*
- Complete and balance chemical equations for common reactions of the nonmetals. (Sections 22.1–22.11)
  Related Exercises: 22.20, 22.63, 22.84
- Understand how phosphoric and phosphorous acids undergo condensation reactions. (Section 22.8) *Related Exercise: 22.98*
- Explain how the bonding and structures of silicates relate to their chemical formulas and properties. (Section 22.10)
  Related Exercises: 22.87, 22.89, 22.102

Exercises

Visualizing Concepts

22.46 Which statement identifies which of these two compounds is more stable and explains why? [Section 22.1]



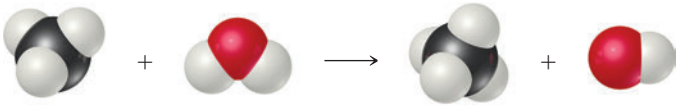
(**a**) The carbon compound because C is less electronegative than Si

(**b**) The silicon compound because Si forms stronger sigma bonds than C

(**c**) The carbon compound because C forms stronger multiple bonds than Si

(**d**) The silicon compound because Si forms stronger pi bonds than C

22.47 (**a**) Identify the *type* of chemical reaction represented by the following diagram. (**b**) Place appropriate charges on the species on both sides of the equation. (**c**) Write the chemical equation for the reaction. [Section 22.1]

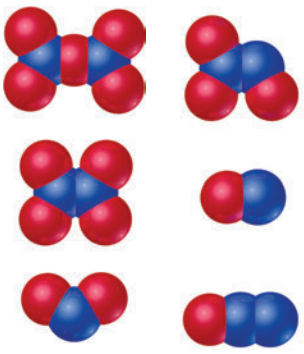


22.48 Which of the following species (there may be more than one) is/are likely to have the structure shown here: (**a**) XeF_4, (**b**) BrF_4^+, (**c**) SiF_4, (**d**) $TeCl_4$, (**e**) $HClO_4$? (The colors do not reflect atom identities.) [Sections 22.3, 22.4, 22.6, and 22.10]

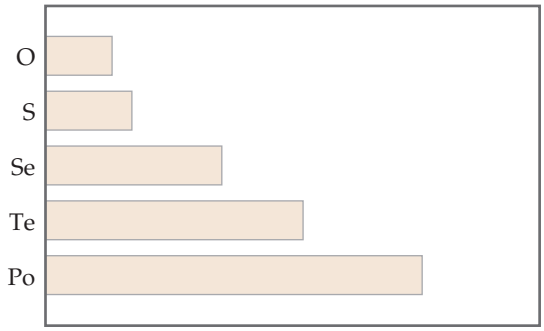


22.49 You have two glass bottles, one containing oxygen and one filled with nitrogen. How could you determine which one is which? [Sections 22.5 and 22.7]

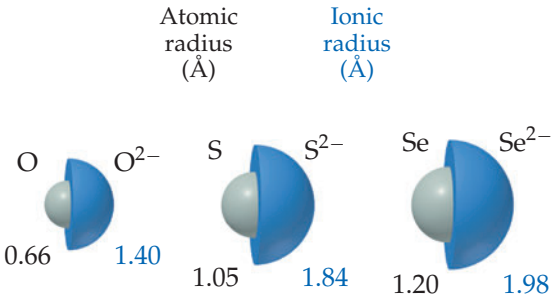
22.50 Write the molecular formula and Lewis structure for each of the following oxides of nitrogen: [Section 22.7]



22.51 Which property of the Group 16 elements might be the one depicted in the graph shown here: (**a**) electronegativity, (**b**) first ionization energy, (**c**) density, (**d**) X—X single-bond enthalpy, (**e**) electron affinity? [Sections 22.5 and 22.6]



22.52 Identify the true statements concerning the atoms and ions of the Group 16 elements. [Sections 22.5 and 22.6]



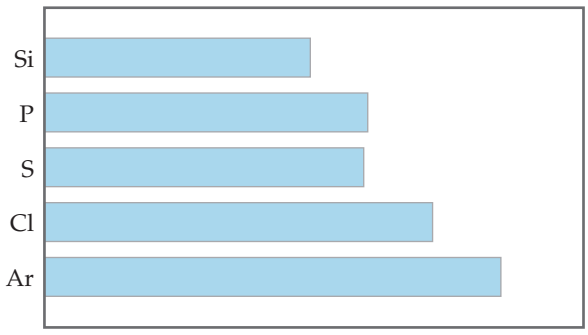
(a) The ionic radii are larger than the atomic radii because the ions have more electrons than their corresponding atoms.

(**b**) Atomic radii increase going down the group because of increasing nuclear charge.

(**c**) The ionic radii increase going down the group because of the increase in the principal quantum number of outermost electrons.

(**d**) Of these ions, Se^{2-} is the strongest base in water because it is largest.

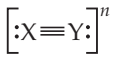
22.53 Which property of the third-row nonmetallic elements might be the one depicted here: (**a**) first ionization energy, (**b**) atomic radius, (**c**) electronegativity, (**d**) melting point, (**e**) X—X single-bond enthalpy? [Sections 22.3, 22.4, 22.6, 22.8, and 22.10]



22.54 Which of the following compounds would you expect to be the most generally reactive, and why? (Each corner in these structures represents a CH_2 group.) [Section 22.8]



22.55 (**a**) Draw the Lewis structures for at least four species that have the general formula



where X and Y may be the same or different, and n may have a value from +1 to −2. (**b**) Which of the compounds is likely to be the strongest Brønsted base? Explain. [Sections 22.1, 22.7, and 22.9]

Periodic Trends and Chemical Reactions (Section 22.1)

22.56 Identify each of the following elements as a metal, nonmetal, or metalloid: (**a**) boron, (**b**) barium, (**c**) argon, (**d**) caesium, (**e**) yttrium, (**f**) astatine.

22.57 Consider the elements N, F, Si, Rb, Te, and Ir. From this list, select the element that (**a**) is most electronegative, (**b**) exhibits a maximum oxidation state of +6, (**c**) loses an electron most readily, (**d**) forms π bonds most readily, (**e**) is a transition metal, (**f**) forms four covalent bonds to achieve octet.

22.58 Which of the following statements are true?

(**a**) Both nitrogen and phosphorus can form a pentafluoride compound.

(**b**) Although CO is a well-known compound, SiO does not exist under ordinary conditions.

(**c**) Cl_2 is easier to oxidize than I_2.

(**d**) At room temperature, the stable form of oxygen is O_2, whereas that of sulfur is S_8.

22.59 Complete and balance the following equations:

(**a**) $NaOCH_3(s) + H_2O(l) \longrightarrow$

(**b**) $CuO(s) + HNO_3(aq) \longrightarrow$

(**c**) $WO_3(s) + H_2(g) \xrightarrow{\Delta}$

(**d**) $NH_2OH(l) + O_2(g) \longrightarrow$

(**e**) $Al_4C_3(s) + H_2O(l) \longrightarrow$

Hydrogen, the Noble Gases, and the Halogens (Sections 22.2, 22.3, and 22.4)

22.60 The physical properties of D_2O differ from those of H_2O because

(**a**) D has a different electron configuration than O.

(**b**) D is radioactive.

(**c**) D forms stronger bonds with O than H does.

(**d**) D is much more massive than H.

22.61 Give a reason why hydrogen might be placed along with the Group 1 elements of the periodic table.

22.62 Complete and balance the following equations:

(**a**) $NaH(s) + H_2O(l) \longrightarrow$

(**b**) $Fe(s) + H_2SO_4(aq) \longrightarrow$

(**c**) $H_2(g) + Br_2(g) \longrightarrow$

(**d**) $Na(l) + H_2(g) \longrightarrow$

(**e**) $PbO(s) + H_2(g) \longrightarrow$

22.63 Identify the following hydrides as ionic, metallic, or molecular: (**a**) H_2S, (**b**) LiH, (**c**) $VH_{0.56}$.

22.64 Describe two characteristics of hydrogen that are favorable for its use as a general energy source in vehicles.

22.65 Why does xenon form stable compounds with fluorine, whereas argon does not?

22.66 Write the chemical formula for each of the following, and indicate the oxidation state of the halogen or noble-gas atom in each: (**a**) xenon trioxide difluoride, (**b**) chlorine dioxide, (**c**) molybdenum hexafluoride, (**d**) iodic acid, (**e**) sodium hypobromite, (**f**) magnesium iodite.

22.67 Name the following compounds and assign oxidation states to the halogens in them: (**a**) $Co(IO_3)_3$, (**b**) $Ca(IO_4)_2$, (**c**) PF_6^-, (**d**) ICl_4^-, (**e**) HBrO, (**f**) AtH.

22.68 Explain each of the following observations: (**a**) At room temperature I_2 is a solid, Br_2 is a liquid, and Cl_2 and F_2 are both gases. (**b**) F_2 cannot be prepared by electrolytic oxidation of aqueous F^- solutions. (**c**) The boiling point of HF is much higher than those of the other hydrogen halides. (**d**) The halogens decrease in oxidizing power in the order $F_2 > Cl_2 > Br_2 > I_2$.

Oxygen and the Other Group 16 Elements (Sections 22.5 and 22.6)

22.69 Write balanced equations for each of the following reactions. (**a**) When mercury(II) oxide is heated, it decomposes to form O_2 and mercury metal. (**b**) When copper(II) nitrate is heated strongly, it decomposes to form copper(II) oxide, nitrogen dioxide, and oxygen. (**c**) Lead(II) sulfide, PbS(*s*), reacts with ozone to form $PbSO_4(s)$ and $O_2(g)$. (**d**) When heated in air, ZnS(*s*) is converted to ZnO. (**e**) Potassium peroxide reacts with $CO_2(g)$ to give potassium carbonate and O_2. (**f**) Oxygen is converted to ozone in the upper atmosphere.

22.70 Predict whether each of the following oxides is acidic, basic, amphoteric, or neutral: (**a**) SO_3, (**b**) Li_2O, (**c**) SnO, (**d**) ZnO.

22.71 Write the chemical formula for each of the following compounds, and indicate the oxidation state of the Group 16 elements in each: (**a**) potassium peroxide, (**b**) potassium thiosulfate, (**c**) selenium oxychloride, (**d**) sodium telluride, (**e**) magnesium sulfite, (**f**) selenium hexafluoride.

22.72 In aqueous solution, hydrogen sulfide reduces (**a**) Fe^{3+} to Fe^{2+}, (**b**) Br_2 to Br^-, (**c**) MnO_4^- to Mn^{2+}, (**d**) HNO_3 to NO_2. In all cases, under appropriate conditions, the product is elemental sulfur. Write a balanced net ionic equation for each reaction.

22.73 Write the Lewis structure for each of the following species, and indicate the structure of each: (**a**) $SeOCl_2$; (**b**) CS_2; (**c**) Telluric acid, H_2TeO_4 (hydrogen is bonded to oxygen).

22.74 Write a balanced equation for each of the following reactions: (**a**) Sulfur dioxide reacts with water. (**b**) Solid zinc sulfide reacts with hydrochloric acid. (**c**) Elemental sulfur reacts with sulfite ion to form thiosulfate. (**d**) Sulfur trioxide is dissolved in sulfuric acid.

Nitrogen and the Other Group 15 Elements (Sections 22.7 and 22.8)

22.75 Write the chemical formula for each of the following compounds, and indicate the oxidation state of nitrogen in each: (**a**) sodium azide, (**b**) ammonium ion, (**c**) nitrous acid, (**d**) magnesium nitride, (**e**) diazene, (**f**) sodium nitrate, (**g**) nitrogen trifluoride, (**h**) nitric acid.

22.76 Write the Lewis structure for each of the following species, describe its geometry, and indicate the oxidation state of the nitrogen: (**a**) HNO_2, (**b**) N_3^-, (**c**) $N_2H_5^+$, (**d**) NO_3^-.

22.77 Complete and balance the following equations:

(**a**) $Mg_3N_2(s) + H_2O(l) \longrightarrow$

(**b**) $NO(g) + O_2(g) \longrightarrow$

(**c**) $N_2O_5(g) + H_2O(l) \longrightarrow$

(**d**) $NH_3(aq) + H^+(aq) \longrightarrow$

(**e**) $N_2H_4(l) + O_2(g) \longrightarrow$

Which ones of these are redox reactions?

22.78 Write complete balanced half-reactions for (**a**) oxidation of nitrous acid to nitrate ion in acidic solution, (**b**) oxidation of N_2 to N_2O in acidic solution.

22.79 Write a molecular formula for each compound, and indicate the oxidation state of the Group 15 element in each formula: (**a**) hexafluoroantimonate(V) ion, (**b**) calcium phosphate, (**c**) potassium dihydrogen phosphate, (**d**) arsenic trioxide, (**e**) tetraphosphorus hexaoxide, (**f**) arsenic trifluoride.

22.80 Account for the following observations: (**a**) Phosphorus forms a pentachloride, but nitrogen does not. (**b**) H_3PO_2 is a monoprotic acid. (**c**) Phosphonium salts, such as PH_4Cl, can be formed under anhydrous conditions, but they cannot be made in aqueous solution. (**d**) White phosphorus is more reactive than red phosphorus.

22.81 Write a balanced equation for each of the following reactions: (**a**) preparation of white phosphorus from calcium phosphate, (**b**) hydrolysis of PBr_3, (**c**) reduction of PBr_3 to P_4 in the gas phase, using H_2.

Carbon, the Other Group 14 Elements, and Boron (Sections 22.9, 22.10, and 22.11)

22.82 Give the chemical formula for (**a**) copper(II) carbonate, (**b**) carbon monoxide, (**c**) magnesium hydrogen carbonate, (**d**) lithium acetylide, (**e**) carbon tetrafluoride.

22.83 Complete and balance the following equations:

(**a**) $ZnCO_3(s) \xrightarrow{\Delta}$

(**b**) $BaC_2(s) + H_2O(l) \longrightarrow$

(**c**) $C_2H_2(g) + O_2(g) \longrightarrow$

(**d**) $CS_2(g) + O_2(g) \longrightarrow$

(**e**) $Ca(CN)_2(s) + HBr(aq) \longrightarrow$

22.84 Write a balanced equation for each of the following reactions: (**a**) Hydrogen cyanide is formed commercially by passing a mixture of methane, ammonia, and air over a catalyst at 800 °C. Water is a by-product of the reaction. (**b**) Baking soda reacts with acids to produce carbon dioxide gas. (**c**) When barium carbonate reacts in air with sulfur dioxide, barium sulfate and carbon dioxide form.

22.85 Select the member of Group 14 that best fits each description: (**a**) has the highest electronegativity, (**b**) a metalloid which is commonly used in computer chips, (**c**) is used for shielding for radiation.

22.86 (**a**) What is the characteristic geometry about silicon in all silicate minerals? (**b**) Metasilicic acid has the empirical formula H_2SiO_3. Which of the structures shown in Figure 22.32 would you expect metasilicic acid to have?

22.87 (**a**) Determine the number of calcium ions in the chemical formula of the mineral hardystonite, $Ca_xZn(Si_2O_7)$.

(**b**) Determine the number of hydroxide ions in the chemical formula of the mineral pyrophyllite, $Al_2(Si_2O_5)_2(OH)_x$.

22.88 Write the formulas for the following compounds, and indicate the oxidation state of the Group 14 element or of boron in each: (**a**) silane, (**b**) germanium dichloride, (**c**) tin(II) sulfide, (**d**) sodium borohydride, (**e**) lead(IV) nitrate, (**f**) tin dioxide.

22.89 (**a**) How does the structure of diborane (B_2H_6) differ from that of ethane (C_2H_6)? (**b**) Explain why diborane adopts the geometry that it does. (**c**) What is the significance of the statement that the hydrogen atoms in diborane are described as "hydridic"?

Additional Exercises

22.90 Indicate whether each of the following statements is true or false (**a**) $H_2(g)$ and $D_2(g)$ are allotropic forms of hydrogen. (**b**) ClF_3 is an interhalogen compound. (**c**) $MgO(s)$ is an acidic anhydride. (**d**) $SO_2(g)$ is an acidic anhydride. (**e**) $2\,H_3PO_4(l) \rightarrow H_4P_2O_7(l) + H_2O(g)$ is an example of a condensation reaction. (**f**) Tritium is an isotope of the element hydrogen. (**g**) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ is an example of a disproportionation reaction.

22.91 Although the ClO_4^- and IO_4^- ions have been known for a long time, BrO_4^- was not synthesized until 1965. The ion was synthesized by oxidizing the bromate ion with xenon difluoride, producing xenon, hydrofluoric acid, and the perbromate ion. (**a**) Write the balanced equation for this reaction. (**b**) What are the oxidation states of Br in the Br-containing species in this reaction?

22.92 Write a balanced equation for the reaction of each of the following compounds with water: (**a**) $PCl_5(s)$, (**b**) $CO_2(g)$, (**c**) $K_2O_2(s)$, (**d**) $Mg_3P_2(s)$, (**e**) $LiAlH_4(s)$, (**f**) $Cl_2O(g)$, (**g**) $NO_2(g)$.

22.93 What is the anhydride for each of the following acids: (**a**) H_2SO_4, (**b**) $HClO_3$, (**c**) HNO_2, (**d**) H_2CO_3, (**e**) H_3PO_4?

22.94 Hydrogen peroxide is capable of oxidizing (**a**) hydrazine to N_2 and H_2O, (**b**) SO_2 to SO_4^{2-}, (**c**) NO_2^- to NO_3^-, (**d**) $H_2S(g)$ to $S(s)$, (**e**) Fe^{2+} to Fe^{3+}. Write a balanced net ionic equation for each of these redox reactions.

22.95 A sulfuric acid plant produces a considerable amount of heat. This heat is used to generate electricity, which helps reduce operating costs. The synthesis of H_2SO_4 consists of three main chemical processes: (**a**) oxidation of S to SO_2, (**b**) oxidation of SO_2 to SO_3, (**c**) the dissolving of SO_3 in H_2SO_4 and the subsequent reaction with water to form H_2SO_4. If the third process produces 130 kJ/mol, how much heat is produced in preparing a mole of H_2SO_4 from a mole of S? How much heat is produced in preparing 2000 kg of H_2SO_4?

22.96 (**a**) What is the oxidation state of P in PF_6^- and of N in NF_3? (**b**) Why doesn't N form NF_6^- ion analogous to P?

22.97 (**a**) The P_4, P_4O_6 and P_4O_{10} molecules have a common structural feature of four P atoms arranged in a tetrahedron (Figures 22.27 and 22.28). Does this mean that the bonding between the P atoms is the same in all these cases? Explain. (**b**) Sodium trimetaphosphate ($Na_3P_3O_9$) and sodium tetrametaphosphate ($Na_4P_4O_{12}$) are used as water-softening agents. They contain cyclic $P_3O_9^{3-}$ and $P_4O_{12}^{4-}$ ions, respectively. Propose reasonable structures for these ions.

22.98 Write a balanced chemical reaction for the condensation reaction between H_3PO_4 molecules to form $H_6P_4O_{13}$.

22.99 Ultrapure germanium, like silicon, is used in semiconductors. Germanium of "ordinary" purity is prepared by the high-temperature reduction of GeO_2 with carbon. The Ge is converted to $GeCl_4$ by treatment with Cl_2 and then purified by distillation; $GeCl_4$ is then hydrolyzed in water to GeO_2 and reduced to the elemental form with H_2. The element is then zone refined. Write a balanced chemical equation for each of the chemical transformations in the course of forming ultrapure Ge from GeO_2.

22.100 When aluminum replaces up to half of the silicon atoms in SiO_2, a mineral class called feldspars result. The feldspars are the most abundant rock-forming minerals, comprising about 50% of the minerals in Earth's crust. Orthoclase is a feldspar in which Al replaces one-fourth of the Si atoms of SiO_2, and charge balance is completed by K^+ ions. Determine the chemical formula for orthoclase.

22.101 (**a**) Determine the charge of the silicate ion whose composition is Si_4O_{11}. (**b**) Using Figure 22.32, propose a reasonable description of the structure of this silicate.

Integrative Exercises

22.102 (**a**) How many grams of H_2 can be stored in 100.0 kg of the alloy FeTi if the hydride $FeTiH_2$ is formed? (**b**) What volume does this quantity of H_2 occupy at STP? (**c**) If this quantity of hydrogen was combusted in air to produce liquid water, how much energy could be produced?

22.103 Using the thermochemical data in Table 22.1 and Appendix C, calculate the average Xe—F bond enthalpies in XeF_2, XeF_4, and XeF_6, respectively. What is the significance of the trend in these quantities?

22.104 Hydrogen gas has a higher fuel value than natural gas on a mass basis but not on a volume basis. Thus, hydrogen is not competitive with natural gas as a fuel transported long distances through pipelines. Calculate the heats of combustion of H_2 and CH_4 (the principal component of natural gas) (**a**) per mole of each, (**b**) per gram of each, (**c**) per cubic meter of each at STP. Assume $H_2O(l)$ as a product.

22.105 Using ΔG_f° for NO and NO_2, from Appendix C, calculate the equilibrium constant for the oxidation of NO to NO_2 at 298.0 K as described in equation 22.38.

22.106 The solubility of Cl_2 in 100 g of water at STP is 310 cm^3. Assume that this quantity of Cl_2 is dissolved and equilibrated as follows:

$$Cl_2(aq) + H_2O \rightleftharpoons Cl^-(aq) + HClO(aq) + H^+(aq)$$

(**a**) If the equilibrium constant for this reaction is 4.7×10^{-4}, calculate the equilibrium concentration of HClO formed. (**b**) What is the pH of the final solution?

22.107 When ammonium perchlorate decomposes thermally, the products of the reaction are $N_2(g)$, $O_2(g)$, $H_2O(g)$, and $HCl(g)$. (**a**) Write a balanced equation for the reaction. (*Hint:* You might find it easier to use fractional coefficients for the products.) (**b**) Calculate the enthalpy change in the reac-

tion per mole of NH_4ClO_4. The standard enthalpy of formation of $NH_4ClO_4(s)$ is −295.8 kJ. (**c**) When $NH_4ClO_4(s)$ is employed in solid-fuel booster rockets, it is packed with powdered aluminum. Given the high temperature needed for $NH_4ClO_4(s)$ decomposition and what the products of the reaction are, what role does the aluminum play? (**d**) Calculate the volume of all the gases that would be produced at STP, assuming complete reaction of one pound of ammonium perchlorate.

22.108 The dissolved oxygen present in any highly pressurized, high-temperature steam boiler can be extremely corrosive to its metal parts. Hydrazine, which is completely miscible with water, can be added to remove oxygen by reacting with it to form nitrogen and water. (**a**) Write the balanced equation for the reaction between gaseous hydrazine and oxygen. (**b**) Calculate the enthalpy change accompanying this reaction. (**c**) Oxygen in air dissolves in water to the extent of 9.1 ppm at 20 °C at sea level. How many grams of hydrazine are required to react with all the oxygen in 3.0×10^4 L (the volume of a small swimming pool) under these conditions?

22.109 One method proposed for removing SO_2 from the flue gases of power plants involves scrubbing with an alkali solid such as calcium carbonate to form calcium sulfite and carbon dioxide gas. (**a**) Write a balanced chemical equation for the reaction. (**b**) What mass of $CaCO_3$ would be required to remove the SO_2 formed by burning 1000 kg of coal containing 8.0% S by mass? (**c**) What volume of CO_2 is formed under standard temperature and pressure? Assume that all reactions are 100% efficient.

22.110 The maximum allowable concentration of $H_2S(g)$ in air is 20 mg per kilogram of air (20 ppm by mass). How many grams of FeS would be required to react with hydrochloric acid to produce this concentration at 101.3 kPa and 25 °C in an average room measuring 3.5 m × 6.0 m × 2.5 m? (Under these conditions, the average molar mass of air is 29.0 g/mol.)

22.111 The standard heats of formation of $H_2O(g)$, $H_2S(g)$, $H_2Se(g)$, and $H_2Te(g)$ are −241.8, −20.17, +29.7, and +99.6 kJ/mol, respectively. The enthalpies necessary to convert the elements in their standard states to one mole of gaseous atoms are 248, 277, 227, and 197 kJ/mol of atoms for O, S, Se, and Te, respectively. The enthalpy for dissociation of H_2 is 436 kJ/mol. Calculate the average H—O, H—S, H—Se, and H—Te bond enthalpies, and comment on their trend.

22.112 Manganese silicide has the empirical formula MnSi and melts at 1280 °C. It is insoluble in water but does dissolve in aqueous HF. (**a**) What type of compound do you expect MnSi to be: metallic, molecular, covalent-network, or ionic? (**b**) Write a likely balanced chemical equation for the reaction of MnSi with concentrated aqueous HF.

22.113 Nitric acid is a powerful oxidizing agent. Using standard reduction potentials, predict whether the following metals can be oxidized to +2 ions by nitric acid: (**a**) iron, (**b**) copper, (**c**) rhodium, (**d**) zinc, (**e**) lead, (**f**) tin.

22.114 Both dimethylhydrazine, $(CH_3)_2NNH_2$, and methylhydrazine, CH_3NHNH_2, have been used as rocket fuels. When dinitrogen tetroxide (N_2O_4) is used as the oxidizer, the products are H_2O, CO_2, and N_2. If the thrust of the rocket depends on the volume of the products produced, which of the substituted hydrazines produces a greater thrust per gram total mass of oxidizer plus fuel? (Assume that both fuels generate the same temperature and that $H_2O(g)$ is formed.)

22.115 Borazine, $(BH)_3(NH)_3$, is an analog of C_6H_6, benzene. It can be prepared from the reaction of diborane with ammonia, with hydrogen as another product; or from lithium borohydride and ammonium chloride, with lithium chloride and hydrogen as the other products. (**a**) Write balanced chemical equations for the production of borazine using both synthetic methods. (**b**) Draw the Lewis dot structure of borazine. (**c**) How many grams of borazine can be prepared from 2.00 L of ammonia at STP, assuming diborane is in excess?

Designing an Experiment

You are given samples of five substances. At room temperature, three are colorless gases, one is a colorless liquid, and one is a white solid. You are told that the substances are NF_3, PF_3, PCl_3, PF_5, and PCl_5. Let's design experiments to determine which substance is which, using concepts from this and earlier chapters.

(**a**) Assuming that you don't have access to either the Internet or to a handbook of chemistry (as is the case during your exams!), design experiments that would allow you to identify the substances. (**b**) How might you proceed differently if you had access to data from the Internet? (**c**) Which of the substances could undergo reaction to add more atoms around the central atom? What types of reactions might you choose to test this hypothesis? (**d**) Based on what you know about intermolecular forces, which of the substances is likely the solid?

WHAT'S AHEAD

23.1 ▶ The Transition Metals

23.2 ▶ Transition-Metal Complexes

23.3 ▶ Common Ligands in Coordination Chemistry

23.4 ▶ Nomenclature and Isomerism in Coordination Chemistry

23.5 ▶ Color and Magnetism in Coordination Chemistry

23.6 ▶ Crystal-Field Theory

23

TRANSITION METALS AND COORDINATION CHEMISTRY

23.1 | The Transition Metals



Humans, like all vertebrates, have red blood. The red color is due to an iron-containing protein called hemoglobin found in red blood cells. Hemoglobin is responsible for binding oxygen in the lungs and transporting it to cells throughout the body.

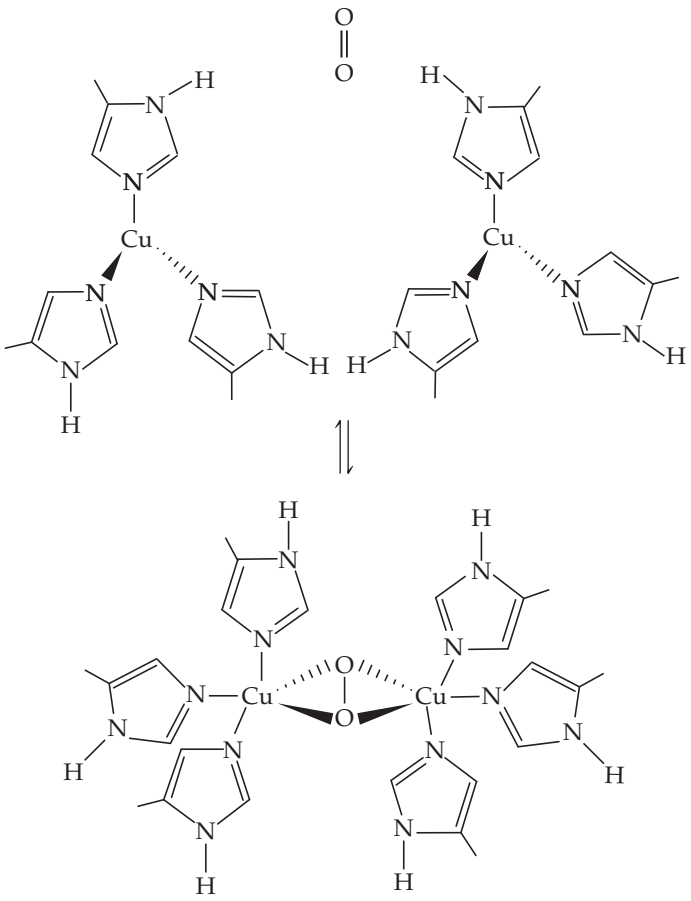
However, not all animals have red blood. Some marine animals, including octopuses, squids, and lobsters, have blue blood because they rely on a copper-containing protein called hemocyanine for transporting oxygen. In the deoxygenated state, hemocyanine contains two Cu^+ ions separated from each other by over 400 pm, a distance too long to form a bond. When an oxygen molecule encounters this site in the protein, an electron transfer reaction takes place in which the O_2 molecule is reduced to the peroxide ion, O_2^{2-}, while both copper ions are oxidized to Cu^{2+}, as shown in **Figure 23.1**. The presence of Cu^{2+} ions in oxygenated hemocyanine is responsible for the blue color of the blood.

Among the blue bloods of the animal kingdom, the blood of the horseshoe crab (as shown in the image at the beginning of this section) is the most valuable. That's because the primitive immune system of the horseshoe crab contains a substance called limulus amoebocyte lysate (LAL), which protects the crabs from infection by binding to potentially harmful viruses and bacterial endotoxins. It was discovered in the early 1960s that LAL could be used to detect trace amounts of toxic substances in drugs and medical devices.

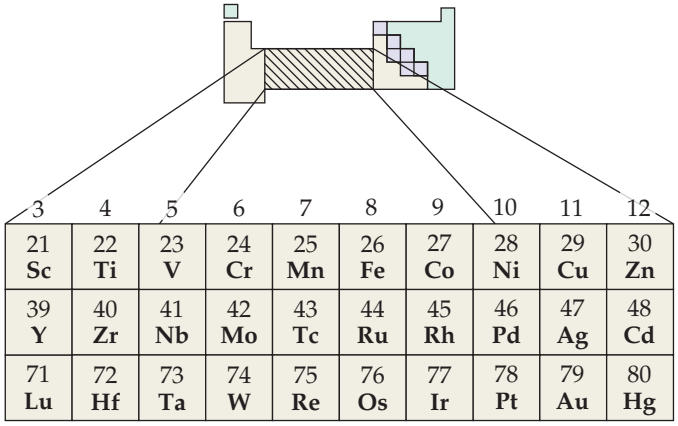
The importance of transition metals such as iron and copper is not limited to biology and medicine. Transition metals and their alloys are used as structural materials as well as in numerous other applications such as coins and jewelry and as electronic conductors in wires and electronic devices. The presence of partially filled *d*-orbitals allows transition-metal compounds to act as catalysts, magnets, and pigments.

In earlier chapters, we saw that metal ions can function as Lewis acids, forming covalent bonds with molecules and ions that act as Lewis bases. (Section 16.8) We have encountered many ions and compounds that result from such interactions, such as $[Ag(NH_3)_2]^+$ in Section 17.5 and hemoglobin in Section 13.6. In this chapter, we focus on the rich and important chemistry associated with such complex assemblies of metal ions surrounded by molecules and ions. Metal compounds of this kind are called *coordination compounds*, and the branch of chemistry that focuses on them is called *coordination chemistry*. We start by reviewing the general physical properties of the transition metals. By the end of this section, you should be able to

- Understand the physical properties of transition metals including metallic radius and magnetic properties.



▲ **Figure 23.1 Hemocyanine binds oxygen.** The Cu^+ ions are each bound by three nitrogen atoms from the hemocyanine protein in the deoxygenated state (left). As the O_2 molecule binds between the Cu^+ ions, it is reduced to O_2^{2-} while the Cu^+ ions are oxidized to Cu^{2+} ions.



▲ **Figure 23.2 The position of the transition metals in the periodic table.** They are Groups 3–12 in Periods 4, 5, and 6. The short-lived, radioactive transition metals from Period 7 are not shown.

The part of the periodic table in which the *d* orbitals are being filled as we move left to right across a row is the home of the transition metals (**Figure 23.2**).

With some exceptions (e.g., platinum, gold), metallic elements are found in nature as solid inorganic compounds called **minerals**. Notice from **Table 23.1** that minerals are identified by common names rather than chemical names.

Most transition metals in minerals have oxidation states ranging from +1 to +4. To obtain a pure metal from its mineral, various chemical processes must be performed to reduce the metal to its elemental form. **Metallurgy** is the science and technology of extracting metals from their natural sources and preparing them for practical use. It usually involves several steps: (1) mining, that is, removing the relevant *ore* (a mixture of minerals)

TABLE 23.1 Principal Mineral Sources of Some Transition Metals

Metal	Mineral	Mineral Composition
Chromium	Chromite	$FeCr_2O_4$
Cobalt	Cobaltite	CoAsS
Copper	Chalcocite	Cu_2S
	Chalcopyrite	$CuFeS_2$
	Malachite	$Cu_2CO_3(OH)_2$
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Molybdenum	Molybdenite	MoS_2
Titanium	Rutile	TiO_2
	Ilmenite	$FeTiO_3$
Zinc	Sphalerite	ZnS

from the ground, (2) concentrating the ore or otherwise preparing it for further treatment, (3) reducing the ore to obtain the free metal, (4) purifying the metal, and (5) mixing it with other elements to modify its properties. This last process produces an *alloy*, a metallic material composed of two or more elements.

Physical Properties

Some physical properties of the Period 4 (also known as "first-row") transition metals are listed in Table 23.2. The properties of the heavier transition metals vary similarly across Periods 5 and 6.

Figure 23.3 shows the atomic radius observed in close-packed metallic structures as a function of group number.* The trends seen in the graph are a result of two competing forces. On the one hand, increasing effective nuclear charge favors a decrease in radius as we move left to right across each period. On the other hand, the metallic bonding strength increases until we reach the middle of each period and then decreases as we fill antibonding orbitals. As a general rule, a bond shortens as it becomes stronger. For Groups 3 through 6, these two effects work cooperatively and the result is a marked decrease in radius. In elements to the right of Group 6, the two effects counteract each other, reducing the decrease and eventually leading to an increase in radius.

TABLE 23.2 Properties of the Period 4 Transition Metals

Group	3	4	5	6	7	8	9	10	11	12
Element:	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ground-state electron configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
First ionization energy (kJ/mol)	631	658	650	653	717	759	758	737	745	906
Metallic radius (pm)	164	147	135	129	137	126	125	125	128	137
Density (g/cm^3)	3.0	4.5	6.1	7.9	7.2	7.9	8.7	8.9	8.9	7.1
Melting point (°C)	1541	1660	1917	1857	1244	1537	1494	1455	1084	420
Crystal structure*	hcp	hcp	bcc	bcc	**	bcc	hcp	fcc	fcc	hcp

*Abbreviations for crystal structures are hcp = hexagonal close packed, fcc = face-centered cubic, bcc = body-centered cubic.

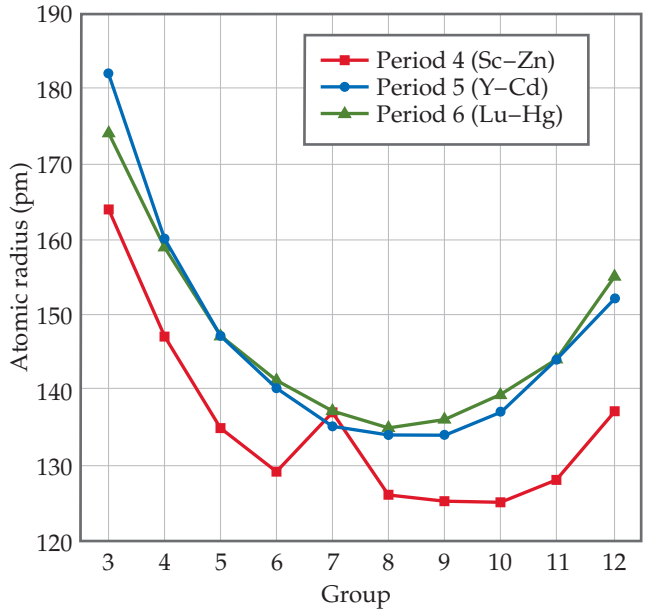
**Manganese has a more complex crystal structure.

*Note that the radii defined in this way, often referred to as metallic radii, differ somewhat from the bonding atomic radii defined in Section 7.3.

In general, atomic radii increase as we move down in a given group in the periodic table because of the increasing principal quantum number of the outer-shell electrons. However, Figure 23.2 shows that once we move beyond the Group 3 elements, the Period 5 and Period 6 transition elements in a given group have virtually the same radii. In Group 5, for example, tantalum in Period 6 has virtually the same radius as niobium in Period 5. This interesting and important effect has its origin in the lanthanide series, elements 57 through 70. The filling of 4*f* orbitals through the lanthanide elements causes a steady increase in the effective nuclear charge, producing a size decrease, called the **lanthanide contraction**, that just offsets the increase we expect as we go from Period 5 transition metals to Period 6. Thus, the Period 5 and Period 6 transition metals in each group have very similar radii and chemical properties. For example, the Group 4 metals zirconium (Period 5) and hafnium (Period 6) always occur together in nature and are very difficult to separate.

Go Figure

Does the variation in radius of the transition metals follow the same trend as the effective nuclear charge on moving from left to right across the periodic table?



▲ **Figure 23.3** Radii of transition metals as a function of group number.

Electron Configurations and Oxidation States

Transition metals owe their location in the periodic table to the filling of the *d* subshells, as you saw in Figure 6.28. Many of the chemical and physical properties of transition metals result from the unique characteristics of the *d* orbitals. For a given transition-metal atom, the valence $(n - 1)d$ orbitals are smaller than the corresponding valence *ns* and *np* orbitals. In quantum mechanical terms, the $(n - 1)d$ orbital wave functions drop off more rapidly as we move away from the nucleus than do the *ns* and *np* orbital wave functions. This characteristic feature of the *d* orbitals limits their interaction with orbitals on neighboring atoms, but not so much that they are insensitive to surrounding atoms. As a result, electrons in these orbitals behave sometimes like valence electrons and sometimes like core electrons. The details depend on location in the periodic table and the atom's environment.

When transition metals are oxidized, *they lose their outer* s *electrons before they lose electrons from the* d *subshell*. The electron configuration of Fe is $[Ar]3d^64s^2$, for example, whereas that of Fe^{2+} is $[Ar]3d^6$. Formation of Fe^{3+} requires loss of one 3*d* electron, giving $[Ar]3d^5$. Most transition-metal ions contain partially occupied *d* subshells, which are responsible in large part for three characteristics:

1. Transition metals often have more than one stable oxidation state.
2. Many transition-metal compounds are colored, as shown in **Figure 23.4**.
3. Transition metals and their compounds often exhibit magnetic properties.

Figure 23.5 shows the common nonzero oxidation states for the Period 4 transition metals. The +2 oxidation state, which is common for most transition metals, is due to the loss of the two outer 4*s* electrons. This oxidation state is found for all these elements except Sc, where the 3+ ion with an [Ar] configuration is particularly stable.

Oxidation states above +2 are due to successive losses of 3*d* electrons. From Sc through Mn the maximum oxidation state increases from +3 to +7, equaling in each case the total number of 4*s* plus 3*d* electrons in the atom. Thus, manganese has a maximum oxidation state of $2 + 5 = +7$. As we move to the right beyond Mn in Figure 23.5, the maximum oxidation state decreases. This decrease is due to the attraction of *d* orbital electrons to the nucleus, which increases faster than the attraction of the *s* orbital electrons to the nucleus as we move left to right across the periodic table. In other words, in each period the *d* electrons become more corelike as the atomic number increases. By the time we get to zinc, it is not possible to remove electrons from the 3*d* orbitals through chemical oxidation.

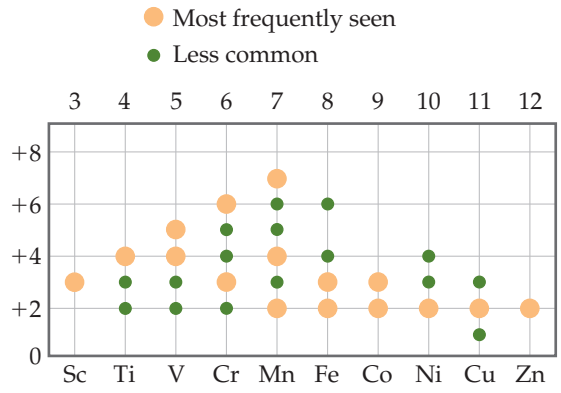
Go Figure In which transition-metal ion of this group are the 3*d* orbitals completely filled?



▲ **Figure 23.4 Aqueous solutions of transition metal ions.** Left to right: Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The counterion is nitrate in all cases.

Go Figure

Are there any ions in this figure for which the 4*s* orbitals are not empty? For which ions are the 3*d* orbitals empty?



▲ **Figure 23.5 Nonzero oxidation states of the Period 4 transition metals.**

In the transition metals of Periods 5 and 6, the increased size of the 4*d* and 5*d* orbitals makes it possible to attain maximum oxidation states as high as +8, which is achieved in RuO_4 and OsO_4. In general, the maximum oxidation states are found only when the metals are combined with the most electronegative elements, especially O, F, and in some cases Cl.

Magnetism

The spin that an electron possesses gives the electron a *magnetic moment*, a property that causes the electron to behave like a tiny magnet. In a *diamagnetic* solid, defined as one in which all the electrons in the solid are paired, the spin-up and spin-down electrons cancel one another. Diamagnetic substances are generally described as being nonmagnetic, but when a diamagnetic substance is placed in a magnetic field, the motions of the electrons cause the substance to be very weakly repelled by the magnet. In other words, these supposedly nonmagnetic substances do show some very faint magnetic character in the presence of a magnetic field.

A substance in which the atoms or ions have one or more unpaired electrons is *paramagnetic*. In a paramagnetic solid, the electrons on one atom or ion do not influence the unpaired electrons on neighboring atoms or ions. As a result, the magnetic moments on the atoms or ions are randomly oriented and constantly changing direction, as shown in **Figure 23.6(a)**. When a paramagnetic substance is placed in a magnetic field, however, the magnetic moments tend to align parallel to one another, producing a net attractive interaction with the magnet. Thus, unlike a diamagnetic substance, which is weakly repulsed by a magnetic field, a paramagnetic substance is attracted to a magnetic field.

When you think of a magnet, you probably picture a simple iron magnet. Iron exhibits **ferromagnetism**, a form of magnetism much stronger than paramagnetism. Ferromagnetism arises when the unpaired electrons of the atoms or ions in a solid are influenced by the orientations of the electrons in neighboring atoms or ions. The most stable (lowest-energy) arrangement is when the spins of electrons on adjacent atoms or ions are aligned in the same direction, as in Figure 23.6(b). When a ferromagnetic solid is placed in a magnetic field, the electrons tend to align strongly in a direction parallel to the magnetic field. The attraction to the magnetic field that results may be as much as a million times stronger than that for a paramagnetic substance.

When a ferromagnet is removed from an external magnetic field, the interactions between the electrons cause the ferromagnetic substance to maintain a magnetic moment. We then refer to it as a *permanent magnet* (Figure 23.7).

The only ferromagnetic transition metals are Fe, Co, and Ni, but many alloys also exhibit ferromagnetism, which is in some cases stronger than the ferromagnetism of the pure metals. Particularly powerful ferromagnetism is found in compounds containing both transition metals and lanthanide metals. Two of the most important examples are $SmCo_5$ and $Nd_2Fe_{14}B$.

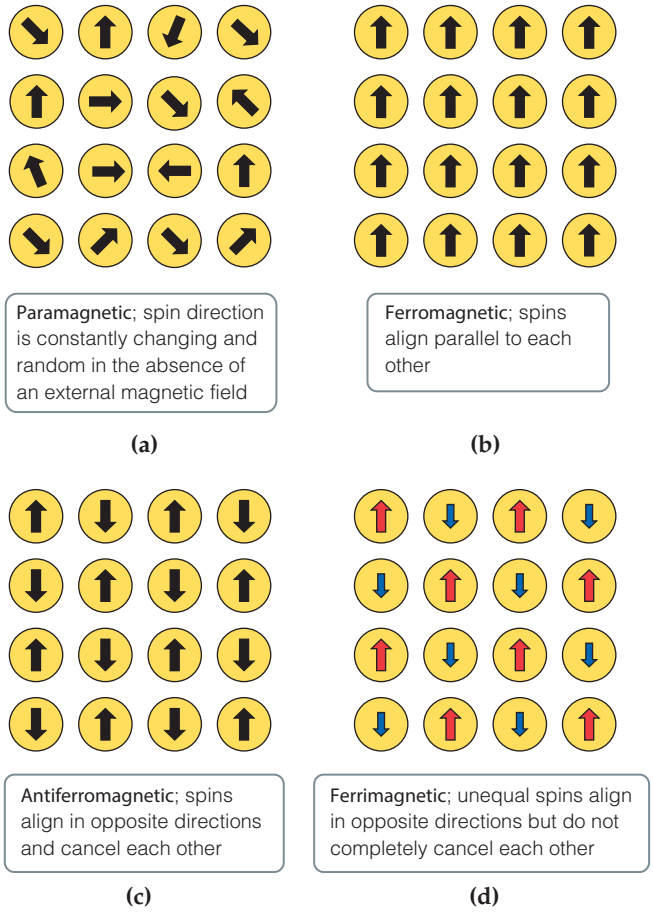
Two additional types of magnetism involving ordered arrangements of unpaired electrons are depicted in Figure 23.6. In materials that exhibit **antiferromagnetism** [Figure 23.6(c)], the unpaired electrons on a given atom or ion align so that their spins are oriented in the direction opposite the spin direction on neighboring atoms. This means that the spin-up and spin-down electrons cancel each other. Examples of antiferromagnetic substances are chromium metal, FeMn alloys, and such transition-metal oxides as Fe_2O_3, $LaFeO_3$, and MnO.

A substance that exhibits **ferrimagnetism** [Figure 23.6(d)] has both ferromagnetic and antiferromagnetic characteristics. Like an antiferromagnet, the unpaired electrons align so that the spins in adjacent atoms or ions point in opposite directions. However, unlike an antiferromagnet, the net magnetic moments of the spin-up electrons are not fully canceled by the spin-down electrons. This can happen because the magnetic centers have different numbers of unpaired electrons ($NiMnO_3$), because the number of magnetic sites aligned in one direction is larger than the number aligned in the other direction ($Y_3Fe_5O_{12}$), or because both of these conditions apply (Fe_3O_4). Because the magnetic moments do not cancel, the properties of ferrimagnetic materials are similar to the properties of ferromagnetic materials.

Ferromagnets, ferrimagnets, and antiferromagnets all become paramagnetic when heated above a critical temperature. This happens when the thermal energy is sufficient to overcome the forces determining the spin directions of the electrons. This temperature is called the *Curie temperature*, T_C, for ferromagnets and ferrimagnets and the *Néel temperature*, T_N, for antiferromagnets.

Go Figure

Describe how the representation shown for the paramagnetic material would change if the material were placed in a magnetic field.



▲ **Figure 23.6** **The relative orientation of electron spins in various types of magnetic substances.**



▲ **Figure 23.7** **A permanent magnet.** Permanent magnets are made from ferromagnetic and ferrimagnetic materials.

Self-Assessment Exercise

23.1 Do you expect $TiCl_4$ to exhibit any of the magnetic properties shown in figure 23.6?

(a) Yes
(b) No

Exercises

23.2 Which periodic trend is partially responsible for the observation that the maximum oxidation state of the transition-metal elements peaks near Groups 7 and 8? (**a**) The number of valence electrons reaches a maximum at Group 8. (**b**) The effective nuclear charge increases on moving left across each period. (**c**) The radii of the transition-metal elements reach a minimum for Group 8, and as the size of the atoms decreases it becomes easier to remove electrons.

23.3 For each of the following compounds, determine the electron configuration of the transition-metal ion. (**a**) CuO, (**b**) Cu_2O, (**c**) V_2O_5, (**d**) MnO.

23.4 How many electrons are in the valence *d* orbitals in these transition-metal ions? (**a**) Ru^{3+}, (**b**) Pd^{2+}, (**c**) Ti^{2+}, (**d**) W^{6+}.

23.5 Which type of magnetic material cannot be used to make permanent magnets, a ferromagnetic substance, an antiferromagnetic substance, or a ferrimagnetic substance?

Answers to Self-Assessment Exercise

23.1 (b)

23.2 | Transition-Metal Complexes



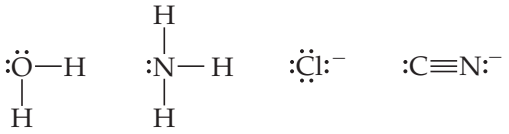
Gold has been highly valued for thousands of years. It is one of the few metals to occur naturally as an element. Its distribution is widespread but almost always in extremely low concentrations. In the few places where it has been concentrated into alluvial deposits, nuggets may be extracted by panning or using a separation table. The high density of gold means that it drops to the bottom of the pan and the slurry of unwanted material above it can be decanted. Panning for gold is still performed by artisan prospectors but requires nuggets to be visible to the eye. Commercial gold mines use an extraction process to recover fine grained gold. Here, the gold-bearing rock is crushed and leeched with a sodium cyanide solution in the presence of air. This forms the soluble gold ion, $[Au(CN)_2]^-$, which is concentrated in by absorption onto fine carbon particles and recovered electrolytically. The hazards associated with using large quantities of cyanide have stimulated research into an alternate leeching material but the inertness of gold—one of the properties that makes it so desirable—means the choices are limited.

In this section, we start our discussion of coordination chemistry, and by the end, you should be able to

- Understand the component parts of a coordination compound
- Determine the charge on the metal in a complex ion

The transition metals occur in many interesting and important molecular forms. Species that are assemblies of a central transition-metal ion bonded to a group of surrounding molecules or ions, such as $[Ag(NH_3)_2]^+$ and $[Fe(H_2O)_6]^{3+}$, are called **metal complexes**, or merely *complexes*.* If the complex carries a net charge, it is generally called a *complex ion*. Compounds that contain complexes are known as **coordination compounds**.

The molecules or ions that bond to the metal ion in a complex are known as **ligands** (from the Latin word *ligare*, "to bind"). There are two NH_3 ligands bonded to Ag^+ in the complex ion $[Ag(NH_3)_2]^+$, for instance, and six H_2O ligands bonded to Fe^{3+} in $[Fe(H_2O)_6]^{3+}$. Each ligand functions as a Lewis base and so donates a pair of electrons to form the ligand–metal bond. Thus, every ligand has at least one unshared pair of valence electrons. Four of the most frequently encountered ligands,



illustrate that most ligands are either polar molecules or anions. In forming a complex, the ligands are said to *coordinate* to the metal.

The Development of Coordination Chemistry: Werner's Theory

Because compounds of the transition metals are beautifully colored, the chemistry of these elements fascinated chemists even before the periodic table was introduced. During the late 1700s through the 1800s, the many coordination compounds that were isolated and studied had properties that were puzzling in light of the bonding theories prevailing at the time. **Table 23.3**, for example, lists a series of $CoCl_3$–NH_3 compounds that have strikingly different colors. Note that the third and fourth species have different colors, even though the originally assigned formula was the same for both, $CoCl_3 \cdot 4\,NH_3$.

The modern formulations of the compounds in Table 23.3 are based on various lines of experimental evidence. For example, all four compounds are strong electrolytes but yield different numbers of ions when dissolved in water. Dissolving $CoCl_3 \cdot 6\,NH_3$ in water yields four ions per formula unit ($[Co(NH_3)_6]^{3+}$ plus three Cl^- ions), whereas $CoCl_3 \cdot 5\,NH_3$ yields only three ions per formula unit ($[Co(NH_3)_5Cl]^{2+}$ and two Cl^- ions). Furthermore, the reaction of the compounds with excess aqueous silver nitrate leads to the precipitation of different amounts of AgCl(*s*). When $CoCl_3 \cdot 6\,NH_3$ is treated with excess $AgNO_3(aq)$, 3 mol of AgCl(*s*) precipitate per mole of complex, which means all three Cl^- ions in the complex can react to form AgCl(*s*). By contrast, when $CoCl_3 \cdot 5\,NH_3$ is treated with excess $AgNO_3(aq)$, only 2 mol of AgCl(*s*) precipitate per mole of complex,

TABLE 23.3 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

*Most of the coordination compounds we examine in this chapter contain transition-metal ions, although ions of other metals can also form complexes.

telling us that one of the Cl^- ions in the complex does not react. These results are summarized in Table 23.3.

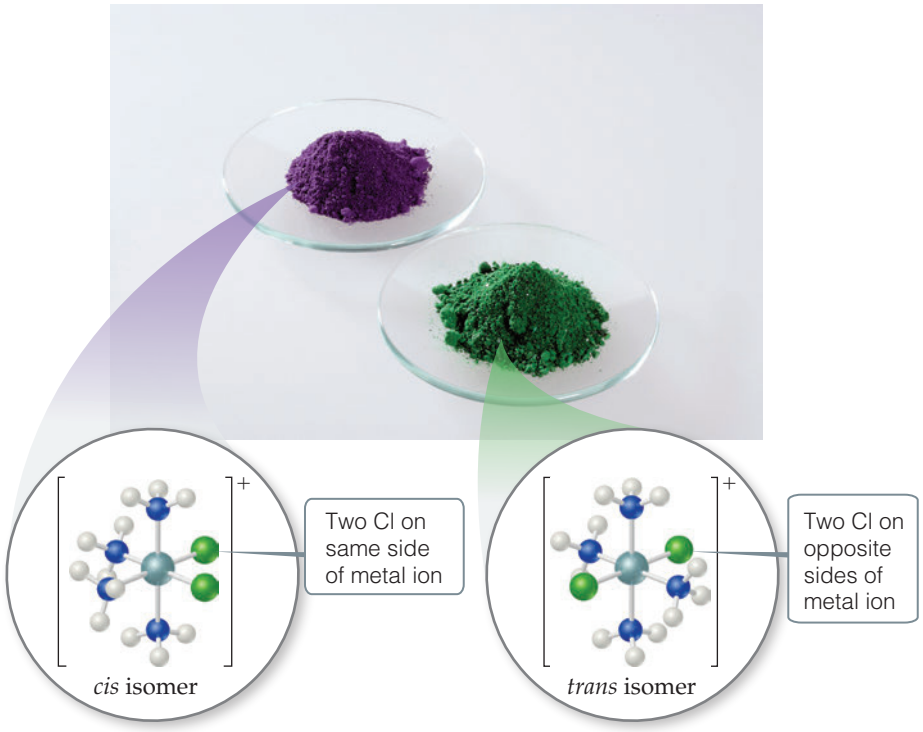
In 1893, the Swiss chemist Alfred Werner (1866–1919) proposed a theory that successfully explained the observations in Table 23.3. In a theory that became the basis for understanding coordination chemistry, Werner proposed that any metal ion exhibits both a primary valence and a secondary valence. The *primary valence* is the oxidation state of the metal, which is +3 for the complexes in Table 23.3. The *secondary valence* is the number of atoms bonded to the metal ion, which is also called the **coordination number**. For these cobalt complexes, Werner deduced a coordination number of 6 with the ligands in an octahedral arrangement around the Co^{3+} ion.

Werner's theory provided a beautiful explanation for the results in Table 23.3. The NH_3 molecules are ligands bonded to the Co^{3+} ion (through the nitrogen atom as we will see later); if there are fewer than six NH_3 molecules, the remaining ligands are Cl^- ions. The central metal and the ligands bound to it constitute the **coordination sphere** of the complex.

In writing the chemical formula for a coordination compound, Werner suggested using square brackets to signify the makeup of the coordination sphere in any given compound. He therefore proposed that $CoCl_3 \cdot 6\,NH_3$ and $CoCl_3 \cdot 5\,NH_3$ are better written as $[Co(NH_3)_6]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2$, respectively. He further proposed that the chloride ions that are part of the coordination sphere are bound so tightly that they do not dissociate when the complex is dissolved in water. Thus, dissolving $[Co(NH_3)_5Cl]Cl_2$ in water produces a $[Co(NH_3)_5Cl]^{2+}$ ion and two Cl^- ions.

Werner's ideas also explained why there are two forms of $CoCl_3 \cdot 4\,NH_3$. Using Werner's postulates, we write the formula as $[Co(NH_3)_4Cl_2]Cl$. As shown in **Figure 23.8**, there are two ways to arrange the ligands in the $[Co(NH_3)_4Cl_2]^+$ complex, called the *cis* and *trans* forms. In the *cis* form, the two chloride ligands occupy adjacent vertices of the octahedral arrangement. In *trans*-$[Co(NH_3)_4Cl_2]^+$ the two chlorides are opposite each other. It is this difference in positions of the Cl ligands that leads to two compounds, one violet and one green.

Go Figure Is there another way to arrange the chloride ions in the $[Co(NH_3)_4Cl_2]^+$ ion besides the two shown in this figure?



▲ **Figure 23.8 Isomers of $[Co(NH_3)_4Cl_2]^+$.** The *cis* isomer is violet, and the *trans* isomer is green.

The insight Werner provided into the bonding in coordination compounds is even more remarkable when we realize that his theory predated Lewis's ideas of covalent bonding by more than 20 years! Because of his tremendous contributions to coordination chemistry, Werner was awarded the 1913 Nobel Prize in Chemistry.

Sample Exercise 23.1

Identifying the Coordination Sphere of a Complex

Palladium(II) tends to form complexes with coordination number 4. A compound has the composition $PdCl_2 \cdot 3\ NH_3$. (**a**) Write the formula for this compound that best shows the coordination structure. (**b**) When an aqueous solution of the compound is treated with excess $AgNO_3(aq)$, how many moles of $AgCl(s)$ are formed per mole of $PdCl_2 \cdot 3\ NH_3$?

SOLUTION

Analyze We are given the coordination number of Pd(II) and a chemical formula indicating that the complex contains NH_3 and Cl^-. We are asked to determine (**a**) which ligands are attached to Pd(II) in the compound and (**b**) how the compound behaves toward $AgNO_3$ in aqueous solution.

Plan (**a**) Because of their charge, the Cl^- ions can be either in the coordination sphere, where they are bonded directly to the metal, or outside the coordination sphere, where they are bonded ionically to the complex. The electrically neutral NH_3 ligands must be in the coordination sphere, and we will assume that four ligands are bonded to the Pd(II) ion. (**b**) Any chlorides in the coordination sphere do not precipitate as AgCl.

Solve

(**a**) By analogy to the ammonia complexes of cobalt(III) shown in Figure 23.7, we predict that the three NH_3 are ligands attached to the Pd(II) ion. The fourth ligand around Pd(II) is one chloride ion. The second chloride ion is not a ligand; it serves only as a *counterion* (a noncoordinating ion that balances charge) in the compound. We conclude that the formula showing the structure best is $[Pd(NH_3)_3Cl]Cl$.

(**b**) Because only the non-ligand Cl^- can react, we expect to produce 1 mol of $AgCl(s)$ per mole of complex. The balanced equation is

$$[Pd(NH_3)_3Cl]Cl(aq) + AgNO_3(aq) \longrightarrow [Pd(NH_3)_3Cl]NO_3(aq) + AgCl(s)$$

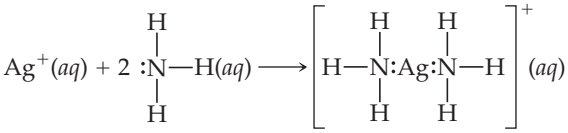
This is a metathesis reaction in which one of the cations is the $[Pd(NH_3)_3Cl]^+$ complex ion.

Practice Exercise

When the compound $RhCl_3 \cdot 4\ NH_3$ is dissolved in water and treated with excess $AgNO_3(aq)$ one mole of $AgCl(s)$ is formed for every mole of $RhCl_3 \cdot 4\ NH_3$. What is the correct way to write the formula of this compound?
(**a**) $[Rh(NH_3)_4Cl_3]$ (**b**) $[Rh(NH_3)_4Cl_2]Cl$ (**c**) $[Rh(NH_3)_4Cl]Cl_2$ (**d**) $[Rh(NH_3)_4]Cl_3$ (**e**) $[RhCl_3](NH_3)_4$

The Metal–Ligand Bond

The bond between a ligand and a metal ion forms as a result of a Lewis acid–base interaction. Because the ligands have available pairs of electrons, they can function as Lewis bases (electron-pair donors). Metal ions (particularly transition-metal ions) have empty valence orbitals, so they can act as Lewis acids (electron-pair acceptors). We can picture the bond between the metal ion and ligand as the result of their sharing a pair of electrons initially on the ligand:



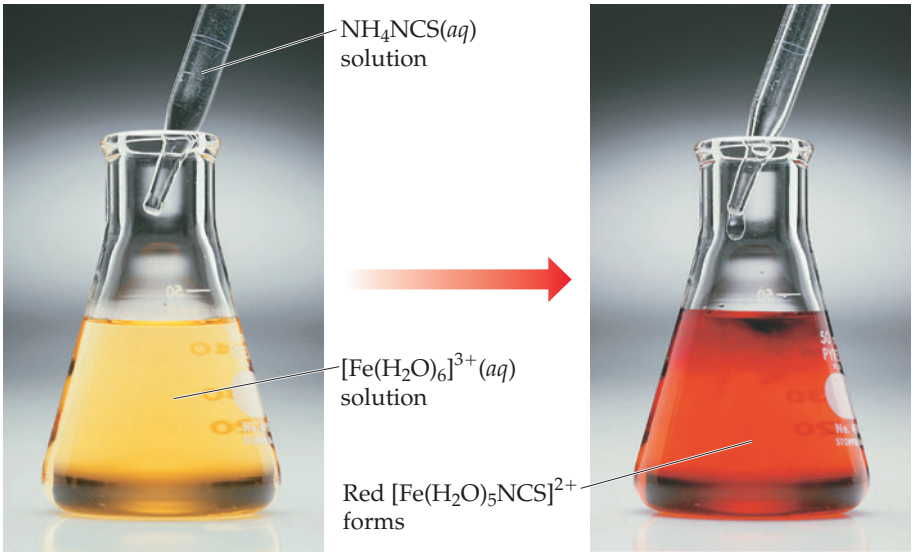
$$Ag^+(aq) + 2\ H_3N{:}(aq) \longrightarrow [H_3N{:}Ag{:}NH_3]^+(aq) \qquad [23.1]$$

The formation of metal–ligand bonds can markedly alter the properties we observe for the metal ion. A metal complex is a distinct chemical species that has physical and chemical properties different from those of the metal ion and ligands from which it is formed. As one example, **Figure 23.9** shows the color change that occurs when aqueous solutions of NCS^- (colorless) and Fe^{3+} (yellow) are mixed, forming $[Fe(H_2O)_5NCS]^{2+}$.

Complex formation can also significantly change other properties of metal ions, such as their ease of oxidation or reduction. Silver ion, for example, is readily reduced in water,

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E^\circ = +0.799\ V \qquad [23.2]$$

Go Figure Does the coordination number of iron change during this reaction? Does the oxidation number of iron change?



▲ **Figure 23.9** **The reaction between $[Fe(H_2O)_6]^{3+}(aq)$ and $NCS^-(aq)$.**

but the $[Ag(CN)_2]^-$ ion is not so easily reduced because complexation by CN^- ions stabilizes silver in the +1 oxidation state:

$$[Ag(CN)_2]^-(aq) + e^- \longrightarrow Ag(s) + 2\,CN^-(aq) \quad E^\circ = -0.31\,V \qquad [23.3]$$

Hydrated metal ions are complexes in which the ligand is water. Thus, $Fe^{3+}(aq)$ consists largely of $[Fe(H_2O)_6]^{3+}$. It is important to realize that ligands can undergo reaction. For example, we saw in Figure 16.18 that a water molecule in $[Fe(H_2O)_6]^{3+}(aq)$ can be deprotonated to yield $[Fe(H_2O)_5OH]^{2+}(aq)$ and $H^+(aq)$. The iron ion retains its oxidation state; the coordinated hydroxide ligand, with a 1− charge, reduces the complex charge to 2+. Ligands can also be displaced from the coordination sphere by other ligands, if the incoming ligands bind more strongly to the metal ion than the original ones. For example, ligands such as NH_3, NCS^-, and CN^- can replace H_2O in the coordination sphere of metal ions.

Charges, Coordination Numbers, and Geometries

The charge of a complex is the sum of the charges on the metal and on the ligands. In $[Cu(NH_3)_4]SO_4$ we can deduce the charge on the complex ion because we know that the charge of the sulfate ion is 2−. Because the compound is electrically neutral, the complex ion must have a 2+ charge, $[Cu(NH_3)_4]^{2+}$. We can then use the charge of the complex ion to deduce the oxidation number of copper. Because the NH_3 ligands are uncharged molecules, the oxidation number of copper must be +2:

$$\underset{\downarrow}{+2} + \underset{\downarrow}{4(0)} = \underset{\downarrow}{2+}$$
$$[Cu(NH_3)_4]^{2+}$$

Recall that the number of atoms directly bonded to the metal atom in a complex is the *coordination number* of the complex. Thus, the silver ion in $[Ag(NH_3)_2]^+$ has a

Sample Exercise 23.2

Determining the Oxidation Number of a Metal in a Complex

What is the oxidation number of the metal in $[Rh(NH_3)_5Cl](NO_3)_2$?

SOLUTION

Analyze We are given the chemical formula of a coordination compound and asked to determine the oxidation number of its metal atom.

Plan To determine the oxidation number of Rh, we need to figure out what charges are contributed by the other groups. The overall charge is zero, so the oxidation number of the metal must balance the charge due to the rest of the compound.

Solve The NO_3 group is the nitrate anion, which has a 1− charge. The NH_3 ligands carry zero charge, and the Cl is a coordinated chloride ion, which has a 1− charge. The sum of all the charges must be zero:

$$x + 5(0) + (-1) + 2(-1) = 0$$

$$[Rh(NH_3)_5Cl](NO_3)_2$$

The oxidation number of rhodium, x, must therefore be +3.

Practice Exercise

In which of the following compounds does the transition-metal have the highest oxidation number?
(**a**) $[Co(NH_3)_4Cl_2]$ (**b**) $K_2[PtCl_6]$ (**c**) $Rb_3[MoO_3F_3]$
(**d**) $Na[Ag(CN)_2]$ (**e**) $K_4[Mn(CN)_6]$

coordination number of 2, and the cobalt ion has a coordination number of 6 in all four complexes in Table 23.3.

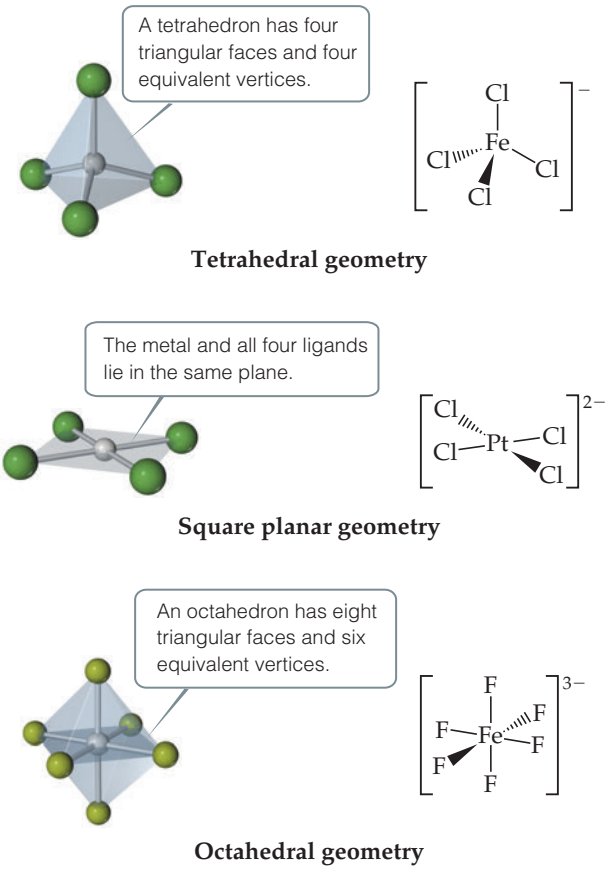
Some metal ions have only one observed coordination number. The coordination number of chromium(III) and cobalt(III) is invariably 6, for example, and that of platinum(II) is always 4. For most metals, however, the coordination number is different for different ligands. In these complexes, the most common coordination numbers are 4 and 6.

The coordination number of a metal ion is often influenced by the relative sizes of the metal ion and the ligands. As the ligand gets larger, fewer of them can coordinate to the metal ion. Thus, iron(III) is able to coordinate to six fluorides in $[FeF_6]^{3-}$ but to only four chlorides in $[FeCl_4]^-$. Ligands that transfer substantial negative charge to the metal also produce reduced coordination numbers. For example, six ammonia molecules can coordinate to nickel(II), forming $[Ni(NH_3)_6]^{2+}$, but only four cyanide ions can coordinate to this ion, forming $[Ni(CN)_4]^{2-}$.

The most common coordination geometries for coordination complexes are shown in **Figure 23.10**. Complexes in which the coordination number is 4 have two geometries—tetrahedral and square planar. The tetrahedral geometry is the more common of the two and is especially prevalent among nontransition metals. The square planar geometry is characteristic of transition-metal ions with eight *d* electrons in the valence shell, such as platinum(II) and gold(III). Complexes with a coordination number of 6 almost always have an octahedral geometry. Even though the octahedron can be drawn as a square with one ligand above and another below the plane, all six vertices are equivalent.

Go Figure

In the drawings on the right-hand side, what does the solid wedge connecting atoms represent? What does the dashed wedge connecting atoms represent?



▲ **Figure 23.10 Common geometries of coordination complexes.** In complexes having coordination number 4, the geometry is typically either tetrahedral or square planar. In complexes having coordination number 6, the geometry is nearly always octahedral.

Self-Assessment Exercise

23.6 What is the coordination number, charge on the metal, and geometry of the complex: $[Au(CN)_2]^-$?

(a) Au^+, Coordination number = 2, Linear geometry
(b) Au^{3+}, Coordination number = 3, Linear geometry
(c) Au^-, Coordination number = 6, Octahedral geometry

Exercises

23.7 Which species are more likely to act as ligands? (**a**) Positively charged ions or negatively charged ions? (**b**) Neutral molecules that are polar or those that are nonpolar?

23.8 Crystals of hydrated chromium(III) chloride are green, have an empirical formula of $CrCl_3 \cdot 6\,H_2O$, and are highly soluble, (**a**) Write the complex ion that exists in this compound. (**b**) If the complex is treated with excess $AgNO_3(aq)$, how many moles of AgCl will precipitate per mole of $CrCl_3 \cdot 6\,H_2O$ dissolved in solution? (**c**) Crystals of anhydrous chromium(III) chloride are violet and insoluble in aqueous solution. The coordination geometry of chromium in these crystals is octahedral, as is almost always the case for Cr^{3+}. How can this be the case if the ratio of Cr to Cl is not 1:6?

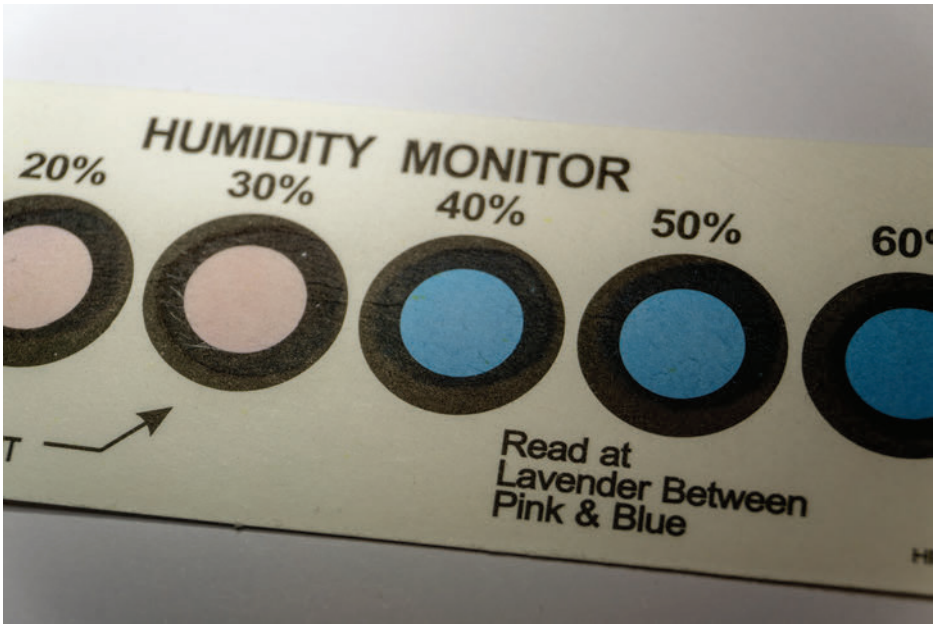
23.9 Indicate the coordination number and the oxidation number of the metal for each of the following complexes:

(**a**) K_2PtCl_4
(**b**) $[Ni(CO)_4]Br_2$
(**c**) OsO_4
(**d**) $[Mn(en)_3](NO_3)_2$
(**e**) $[Cr(en)(NH_3)_4]Cl_3$
(**f**) $[Zn(bipy)_2](ClO_4)_2$

Answers to Self-Assessment Exercise

23.6 (a)

23.3 Common Ligands in Coordination Chemistry



We have already seen that the color of a complex can vary greatly even when the same metal ion is involved. Cobalt provides another good example of this, having a blue $[CoCl_4]^{2-}$ complex and pink $[Co(OH_2)_6]^{2+}$ complex. The two complexes, when dissolved in water, are in equilibrium:

$$[CoCl_4]^{2-}(aq) + 6H_2O(l) \rightleftharpoons [Co(OH_2)_6]^{2+}(aq) + 4Cl^-(aq)$$

Blue Pink

When the complexes are immobilized in a gel, the equilibrium can still operate and provides a visual guide to the degree of hydration of the gel. This is frequently used in combination with silica gel desiccants to indicate when the drying agents need regenerating.

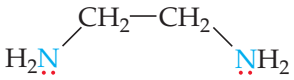
By the end of this section, you should be able to

- Identify common ligands and distinguish between chelating and nonchelating ligands.

The ligand atom that binds to the central metal ion in a coordination complex is called the **donor atom** of the ligand. Ligands having only one donor atom are called **monodentate ligands** (from the Latin, meaning "one-toothed"). These ligands are able to occupy only one site in a coordination sphere. Ligands having two donor atoms are **bidentate ligands** ("two-toothed"), and those having three or more donor atoms are **polydentate ligands** ("many-toothed"). In both bidentate and polydentate species, the multiple donor atoms can simultaneously bond to the metal ion, thereby occupying two or more sites in a coordination sphere. **Table 23.4** gives examples of all three types of ligands.

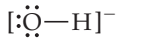
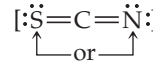
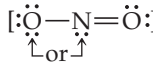
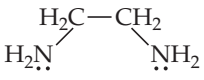
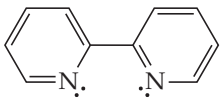
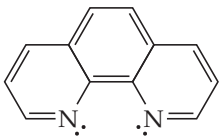
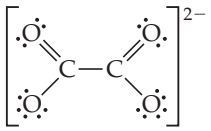
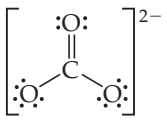
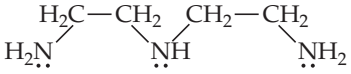
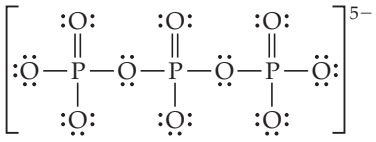
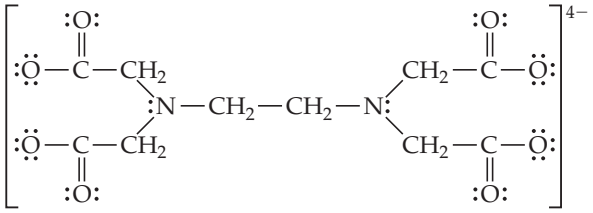
Because they appear to grasp the metal between two or more donor atoms, bidentate and polydentate ligands are also known as **chelating agents** (pronounced "KEE-lay-ting"; from the Greek *chele*, "claw").

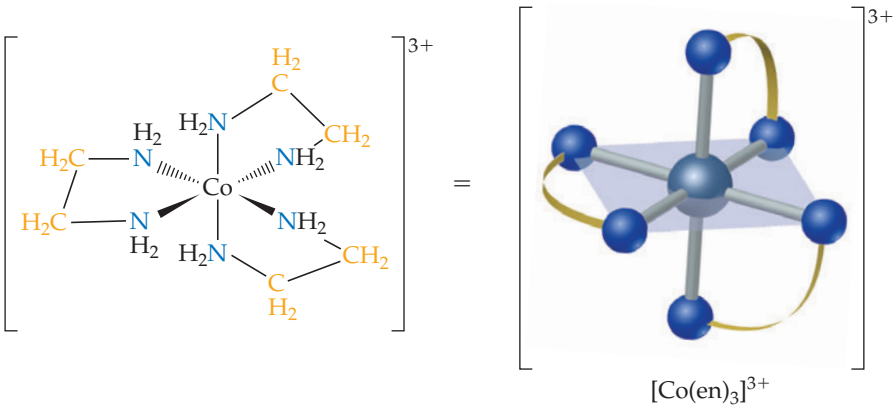
One common chelating agent is the bidentate ligand *ethylenediamine*, denoted en:



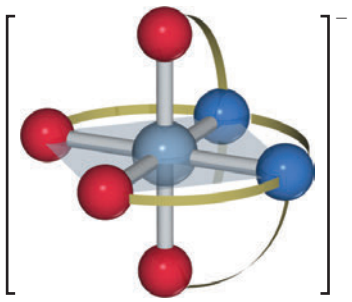
in which each donor nitrogen atom has one nonbonding electron pair. These donor atoms are sufficiently far apart to allow both of them to bond to the metal ion in

TABLE 23.4 Some Common Ligands

Ligand Type	Examples								
Monodentate		Water		Fluoride ion		Cyanide ion		Hydroxide ion	
		Ammonia		Chloride ion		Thiocyanate ion		Nitrite ion	
Bidentate		Ethylenediamine (en)		Bipyridine (bipy or bpy)		*Ortho*-phenanthroline (*o*-phen)		Oxalate ion	 Carbonate ion
Polydentate		Diethylenetriamine		Triphosphate ion					
		Ethylenediaminetetraacetate ion ($EDTA^{4-}$)							



▶ **Figure 23.11 The $[Co(en)_3]^{3+}$ ion.** The ligand is ethylenediamine.



▲ **Figure 23.12 The complex ion $[Co(EDTA)]^-$.** The ligand is the polydentate ethylenediaminetetraacetate ion, whose full representation is given in Table 23.4. This representation shows how the two N and four O donor atoms coordinate to cobalt.

adjacent positions. The $[Co(en)_3]^{3+}$ complex ion, which contains three ethylenediamine ligands in the octahedral coordination sphere of cobalt(III), is shown in **Figure 23.11**. Notice that in the image on the right the en is written in a shorthand notation as two nitrogen atoms connected by an arc.

The ethylenediaminetetraacetate ion, $[EDTA]^{4-}$, is an important polydentate ligand that has six donor atoms. It can wrap around a metal ion using all six donor atoms, as shown in **Figure 23.12**, although it sometimes binds to a metal using only five of its donor atoms.

In general, the complexes formed by chelating ligands (that is, bidentate and polydentate ligands) are more stable than the complexes formed by related monodentate ligands. The equilibrium formation constants for $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ illustrate this observation:

$$[Ni(H_2O)_6]^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6\,H_2O(l)$$
$$K_f = 1.2 \times 10^9 \qquad [23.4]$$

$$[Ni(H_2O)_6]^{2+}(aq) + 3\,en(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6\,H_2O(l)$$
$$K_f = 6.8 \times 10^{17} \qquad [23.5]$$

Although the donor atom is nitrogen in both instances, $[Ni(en)_3]^{2+}$ has a formation constant that is more than 10^8 times larger than that of $[Ni(NH_3)_6]^{2+}$. This trend of generally larger formation constants for bidentate and polydentate ligands, known as the **chelate effect**, is examined in the "A Closer Look" essay on page 1118.

Chelating agents are often used to prevent one or more of the customary reactions of a metal ion without removing the ion from solution. For example, a metal ion that interferes with a chemical analysis can often be complexed and its interference thereby removed. In a sense, the chelating agent hides the metal ion. For this reason, scientists sometimes refer to these ligands as *sequestering agents*.

Phosphate ligands, such as sodium triphosphate, $Na_5[OPO_2OPO_2OPO_3]$, are used to sequester Ca^{2+} and Mg^{2+} ions in hard water so that these ions cannot interfere with the action of soap or detergents.

Chelating agents are used in many prepared foods, such as salad dressings and frozen desserts, to complex trace metal ions that catalyze decomposition reactions. Chelating agents are used in medicine to remove toxic heavy metal ions that have been ingested, such as Hg^{2+}, Pb^{2+}, and Cd^{2+}. One method of treating lead poisoning, for example, is to administer $Na_2Ca(EDTA)$. The EDTA chelates the lead, allowing it to be removed from the body via urine.

Metals and Chelates in Living Systems

Nine of the 29 elements known to be necessary for human life are transition metals. These 10 elements—V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Mo form complexes with a variety of groups present in biological systems.

Although our bodies require only small quantities of metals, deficiencies can lead to serious illness. A deficiency of manganese, for example, can lead to convulsive disorders. Some epilepsy patients have been helped by the addition of manganese to their diets.

Among the most important chelating agents in nature are those derived from the *porphine* molecule (**Figure 23.13**). This molecule can coordinate to a metal via its four nitrogen donor atoms. Once porphine bonds to a metal ion, the two H atoms on the nitrogens are displaced to form complexes called **porphyrins**. Two important porphyrins are *heme*, in which the metal ion is Fe(II), and *chlorophyll*, with a Mg(II) central ion.

Figure 23.14 shows a schematic structure of myoglobin, a protein that contains one heme group. Myoglobin is a *globular protein*, one that folds into a compact, roughly spherical shape. Myoglobin is found in the cells of skeletal muscle, particularly in seals, whales, and porpoises. It stores oxygen in cells, one molecule of O_2 per myoglobin, until it is needed for metabolic activities. Hemoglobin, the protein that transports oxygen in human blood, is made up of four heme-containing subunits, each of which is very similar to myoglobin. One hemoglobin can bind up to four O_2 molecules.

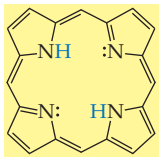
In both myoglobin and hemoglobin, the iron is coordinated to the four nitrogen atoms of a porphyrin and to a nitrogen atom from the protein chain (**Figure 23.15**). In hemoglobin, the sixth position around the iron is occupied either by O_2 (in oxyhemoglobin, the bright red form) or by water (in deoxyhemoglobin, the purplish red form). The oxy form is the one shown in Figure 23.15.

Carbon monoxide is poisonous because the equilibrium binding constant of human hemoglobin for CO is about 210 times greater than that for O_2. As a result, a relatively small quantity of CO can inactivate a substantial fraction of the hemoglobin in the blood by displacing the O_2 molecule from the heme-containing subunit. For example, a person breathing air that contains only 0.1% CO takes in enough CO after a few hours to convert up to 60% of the hemoglobin (Hb) into COHb, thereby reducing the blood's normal oxygen-carrying capacity by 60%.

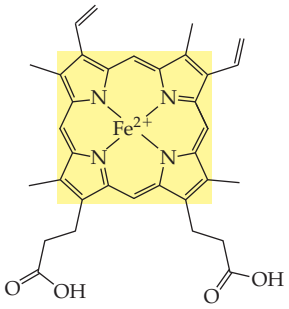
Under normal conditions, a nonsmoker breathing unpolluted air has about 0.3 to 0.5% COHb in her or his blood. This amount

Go Figure

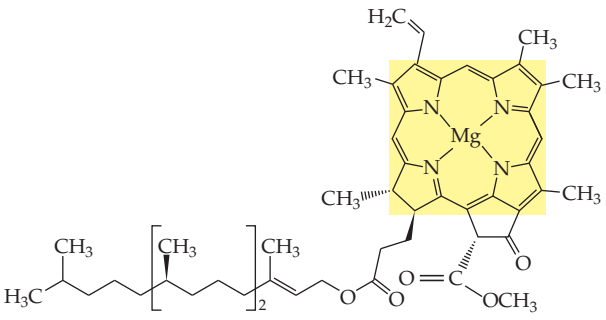
How many carbon atoms are there in porphine? How many have sp^3 hybridization? How many have sp^2 hybridization?



Porphine

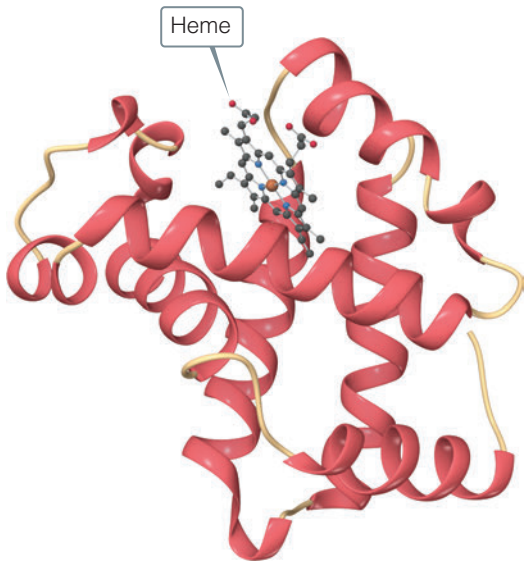


Heme b



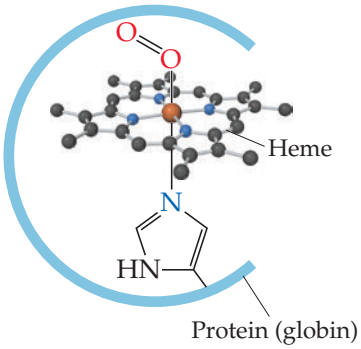
Chlorophyll a

▲ **Figure 23.13 Porphine and two porphyrins, heme b and chlorophyll a.** Fe(II) and Mg(II) ions replace the two blue H atoms in porphine and bond with all four nitrogens in heme b and chlorophyll a, respectively.



◀ **Figure 23.14 Myoglobin.** This ribbon diagram does not show most of the atoms.

Go Figure What is the coordination number of iron in the heme unit shown here? What is the identity of the blue donor atoms in the heme?



▲ **Figure 23.15** **Coordination sphere of the hemes in oxymyoglobin and oxyhemoglobin.**

arises mainly from the production of small quantities of CO in the course of normal body chemistry and from the small amount of CO present in clean air. Exposure to higher concentrations of CO causes the COHb level to increase, which in turn leaves fewer Hb sites to which O_2 can bind. If the level of COHb becomes too high, oxygen transport is effectively shut down and death occurs. Because CO is colorless and odorless, CO poisoning occurs with very little warning. Improperly ventilated combustion devices, such as kerosene lanterns and stoves, thus pose a potential health hazard.

A CLOSER LOOK Entropy and the Chelate Effect

We learned in Section 19.5 that chemical processes are favored by positive entropy changes and by negative enthalpy changes. The special stability associated with the formation of chelates, called the *chelate effect*, can be explained by comparing the entropy changes that occur with monodentate ligands with the entropy changes that occur with polydentate ligands.

We begin with the reaction in which two H_2O ligands of the square-planar Cu(II) complex $[Cu(H_2O)_4]^{2+}$ are replaced by monodentate NH_3 ligands at 27 °C:

$$[Cu(H_2O)_4]^{2+}(aq) + 2\,NH_3(aq) \rightleftharpoons [Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + 2\,H_2O(l)$$

$$\Delta H^\circ = -46\text{ kJ};\quad \Delta S^\circ = -8.4\text{ J/K};\quad \Delta G^\circ = -43\text{ kJ}$$

The thermodynamic data tell us about the relative abilities of H_2O and NH_3 to serve as ligands in this reaction. In general, NH_3 binds more tightly to metal ions than does H_2O, so this substitution reaction is exothermic ($\Delta H < 0$). The stronger bonding of the NH_3 ligands also causes the $[Cu(H_2O)_2(NH_3)_2]^{2+}$ ion to be more rigid, which is probably the reason ΔS° is slightly negative.

We can use Equation 19.20, $\Delta G^\circ = -RT \ln K$, to calculate the equilibrium constant of the reaction at 27 °C. The result, $K = 3.1 \times 10^7$, tells us that the equilibrium lies far to the right, favoring replacement of H_2O by NH_3. For this equilibrium, therefore, the enthalpy change, $\Delta H^\circ = -46$ kJ, is large enough and negative enough to overcome the entropy change, $\Delta S^\circ = -8.4$ J/K.

Now let's use a single bidentate ethylenediamine (en) ligand in our substitution reaction:

$$[Cu(H_2O)_4]^{2+}(aq) + \text{en}(aq) \rightleftharpoons [Cu(H_2O)_2(\text{en})]^{2+}(aq) + 2\,H_2O(l)$$

$$\Delta H^\circ = -54\text{ kJ};\quad \Delta S^\circ = +23\text{ J/K};\quad \Delta G^\circ = -61\text{ kJ}$$

The en ligand binds slightly more strongly to the Cu^{2+} ion than two NH_3 ligands, so the enthalpy change here (−54 kJ) is slightly more negative than for $[Cu(H_2O)_2(NH_3)_2]^{2+}$(−46 kJ). There is a big difference in the entropy change, however: ΔS° is −8.4 J/K for the NH_3 reaction but +23 J/K for the en reaction. We can explain the positive ΔS° value using concepts discussed in Section 19.3. Because a single en ligand occupies two coordination sites, two molecules of H_2O are released when one en ligand bonds. Thus, there are three product molecules in the reaction but only two reactant molecules. The greater number of product molecules leads to the positive entropy change for the equilibrium.

The slightly more negative value of ΔH° for the en reaction (−54 kJ versus −46 kJ) coupled with the positive entropy change leads to a much more negative value of ΔG° (–61 kJ for en, −43 kJ for NH_3) and thus a larger equilibrium constant: $K = 4.2 \times 10^{10}$.

We can combine our two equations using Hess's law to calculate the enthalpy, entropy, and free-energy changes that occur for en to replace ammonia as ligands on Cu(II):

$$[Cu(H_2O)_2(NH_3)_2]^{2+}(aq) + \text{en}(aq) \rightleftharpoons [Cu(H_2O)_2(\text{en})]^{2+}(aq) + 2\,NH_3(aq)$$

$$\Delta H^\circ = (-54\text{ kJ}) - (-46\text{ kJ}) = -8\text{ kJ}$$

$$\Delta S^\circ = (+23\text{ J/K}) - (-8.4\text{ J/K}) = +31\text{ J/K}$$

$$\Delta G^\circ = (-61\text{ kJ}) - (-43\text{ kJ}) = -18\text{ kJ}$$

Notice that at 27 °C, the entropic contribution ($-T\Delta S^\circ$) to the free-energy change, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Equation 19.12), is negative and greater in magnitude than the enthalpic contribution (ΔH°). The equilibrium constant for the NH_3–en reaction, 1.4×10^3, shows that the replacement of NH_3 by en is thermodynamically favorable.

The chelate effect is important in biochemistry and molecular biology. The additional thermodynamic stabilization provided by entropy effects helps stabilize biological metal–chelate complexes, such as porphyrins, and can allow changes in the oxidation state of the metal ion while retaining the structural integrity of the complex.

Related Exercises: 23.3, 23.104

The **chlorophylls**, which are porphyrins that contain Mg(II) (Figure 23.13), are the key components in the conversion of solar energy into forms that can be used by living organisms. This process, called **photosynthesis**, occurs in the leaves of green plants:

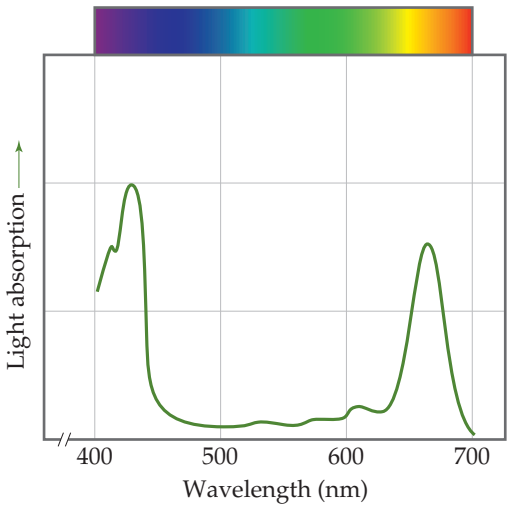
$$6\,CO_2(g) + 6\,H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6\,O_2(g) \qquad [23.6]$$

The formation of 1 mol of glucose, $C_6H_{12}O_6$, requires the absorption of 48 mol of photons from sunlight or other sources of light. Chlorophyll-containing pigments in the leaves of plants absorb the photons. Figure 23.13 shows that the chlorophyll molecule has a series of alternating, or *conjugated*, double bonds in the ring surrounding the metal ion. This system of conjugated double bonds makes it possible for chlorophyll to absorb light strongly in the visible region of the spectrum. As Figure 23.16 shows, chlorophyll is green because it absorbs red light (maximum absorption at 655 nm) and blue light (maximum absorption at 430 nm) and transmits green light.

Photosynthesis is nature's solar energy-conversion machine, and thus all living systems on Earth depend on photosynthesis for continued existence.

Go Figure

Which peak in this curve corresponds to the lowest-energy transition by an electron in a chlorophyll molecule?

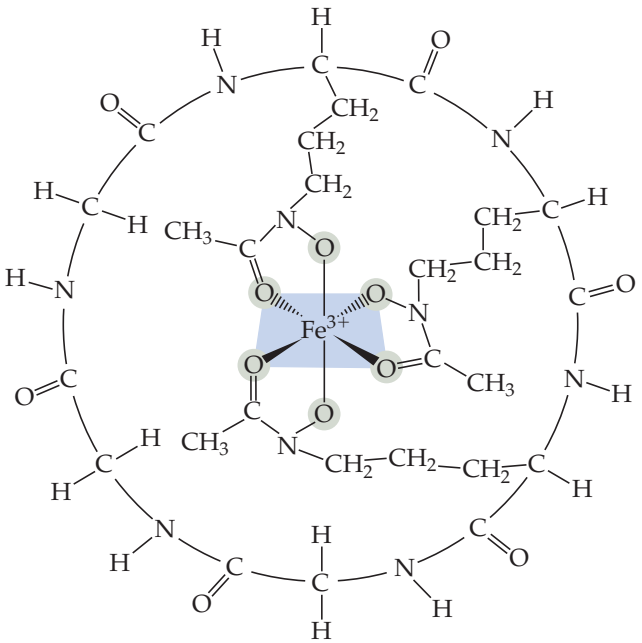


▲ **Figure 23.16** The absorption of sunlight by chlorophyll.

CHEMISTRY AND LIFE The Battle for Iron in Living Systems

Because living systems have difficulty assimilating enough iron to satisfy their nutritional needs, iron-deficiency anemia is a common problem in humans. Chlorosis, an iron deficiency in plants that makes leaves turn yellow, is also commonplace.

Living systems have difficulty assimilating iron because most iron compounds found in nature are not very soluble in water. Microorganisms have adapted to this problem by secreting an iron-binding compound, called a *siderophore*, that forms an extremely stable water-soluble complex with iron(III). One such complex is *ferrichrome* (Figure 23.17). The iron-binding strength of a siderophore is so great that it can extract iron from iron oxides.

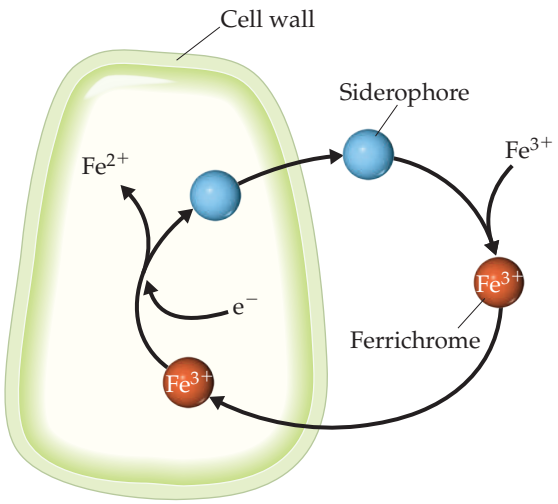


▲ **Figure 23.17** Ferrichrome.

When ferrichrome enters a living cell, the iron it carries is removed through an enzyme-catalyzed reaction that reduces the strongly bonding iron(III) to iron(II), which is only weakly complexed by the siderophore (Figure 23.18). Microorganisms thus acquire iron by excreting a siderophore into their immediate environment and then taking the resulting iron complex into the cell.

In humans, iron is assimilated from food in the intestine. A protein called *transferrin* binds iron and transports it across the intestinal wall to distribute it to other tissues in the body. The normal adult body contains about 4 g of iron. At any one time, about 3 g of this iron is in the blood, mostly in the form of hemoglobin. Most of the remainder is carried by transferrin.

A bacterium that infects the blood requires a source of iron if it is to grow and reproduce. The bacterium excretes a siderophore into the blood to compete with transferrin for iron. The equilibrium constants



▲ **Figure 23.18** The iron-transport system of a bacterial cell.

Continued

for forming the iron complex are about the same for transferrin and siderophores. The more iron available to the bacterium, the more rapidly it can reproduce and thus the more harm it can do.

Several years ago, New Zealand clinics regularly gave iron supplements to infants soon after birth. However, the incidence of certain bacterial infections was eight times higher in treated than in untreated infants. Presumably, the presence of more iron in the blood than absolutely necessary makes it easier for bacteria to obtain the iron needed for growth and reproduction.

In the United States, it is common medical practice to supplement infant formula with iron sometime during the first year of life. However, iron supplements are not necessary for infants who breast-feed because breast milk contains two specialized proteins, lactoferrin and transferrin, which provide sufficient iron while denying its availability to bacteria. Even for infants fed with infant formulas, supplementing with iron during the first several months of life may be ill-advised.

For bacteria to continue to multiply in the blood, they must synthesize new supplies of siderophores. Synthesis of siderophores in bacteria slows, however, as the temperature is increased above the normal body temperature of 37 °C and stops completely at 40 °C. This suggests that fever in the presence of an invading microbe is a mechanism used by the body to deprive bacteria of iron.

Related Exercise: 23.88

Self-Assessment Exercise

23.10 Cobalt(III) has a coordination number of 6 in all its complexes. Is the carbonate ion a monodentate or bidentate ligand in the $[Co(NH_3)_4(CO_3)]^+$ ion?

(a) Monodentate

(b) Bidentate

Exercises

23.11 For each of the following polydentate ligands, determine (i) the maximum number of coordination sites that the ligand can occupy on a single metal ion and (ii) the number and type of donor atoms in the ligand: (**a**) acetylacetonate ion (acac), (**b**) phenanthroline (phen), (**c**) diethylenetriamine, (**d**) carbonate ion, (**e**) triphosphate ion.

23.12 Indicate the likely coordination number of the metal in each of the following complexes:

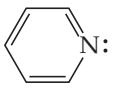
(**a**) $[Ru(bipy)_3](NO_3)_2$

(**b**) $Re(o\text{-}phen)_2(C_2O_4)_2$

(**c**) $Pd(PPh3)_3Cl$

(**d**) $(NH_4)_2Mn(EDTA)$

23.13 Pyridine (C_5H_5N), abbreviated py, is the molecule

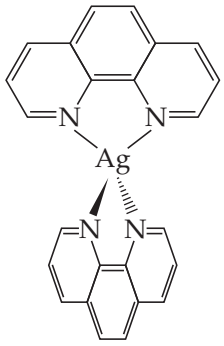


(**a**) Would you expect pyridine to act as a monodentate or bidentate ligand? (**b**) For the equilibrium reaction

$$[Ru(py)_4(bipy)]^{2+} + 2\,py \rightleftharpoons [Ru(py)_6]^{2+} + bipy$$

would you predict the equilibrium constant to be larger or smaller than one?

23.14 When silver nitrate is reacted with the molecular base *ortho*-phenanthroline, colorless crystals form that contain the transition-metal complex shown here. (**a**) What is the coordination geometry of silver in this complex? (**b**) Assuming no oxidation or reduction occurs during the reaction, what is charge of the complex shown here? (**c**) Do you expect any nitrate ions will be present in the crystal? (**d**) Write a formula for the compound that forms in this reaction.



Answers to Self-Assessment Exercise

23.10 (b)

23.4 Nomenclature and Isomerism in Coordination Chemistry

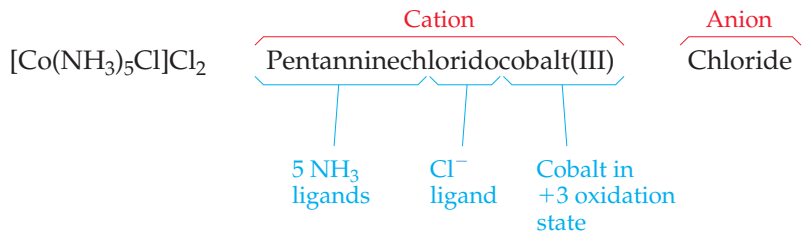


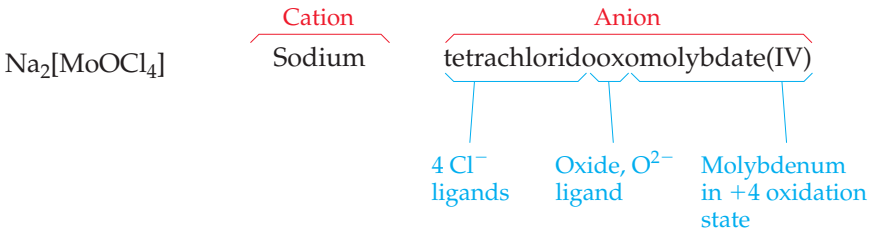
$[Pt(NH_3)_2Cl_2]$ is a simple looking coordination compound but it has a far reaching influence. It was the first of a series of platinum complexes that have been successful in the treatment of a wide range of cancers. Perhaps not surprisingly, it is on the World Health Organization's list of essential medicines. The therapeutic compound is introduced intravenously (using a medical set up similar to the one shown here) where the complex migrates to the inside of the tumour cell. Here the chloride concentration is low and one of the chloride ligands dissociates from the complex and is replaced by a water molecule. In turn, the water ligand is displaced and a nitrogen that is part of the DNA base guanine coordinates to the metal. The process is repeated with the remaining chloride ligand and the DNA-bound complex disrupts the replication of the DNA and the cell dies. There are two isomers of this complex only one of which, cisplatin, has therapeutic value. We touch on the reason for this in this shortly.

By the end of this section, you should be able to

- Systematically name simple coordination compounds and write a formula of a complex ion from its name.

When complexes were first discovered, they were named after the chemist who originally prepared them. A few of these names persist, as, for example, with the dark red substance $NH_4[Cr(NH_3)_2(NCS)_4]$, which is still known as Reinecke's salt. Once the structures of complexes were more fully understood, it became possible to name them in a more systematic manner. Let's use two substances to illustrate how coordination compounds are named:





How to Name Coordination Compounds

1. **In naming complexes that are salts, the name of the cation is given before the name of the anion**. Thus, in $[Co(NH_3)_5Cl]Cl_2$ we name the $[Co(NH_3)_5Cl]^{2+}$ cation and then the Cl^-.
2. **In naming complex ions or molecules, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of their charges. Prefixes that give the number of ligands are not considered part of the ligand name in determining alphabetical order**. Thus, the $[Co(NH_3)_5Cl]^{2+}$ ion is pentaamminechloridocobalt(III). (Be careful to note, however, that the metal is written first in the chemical formula.)
3. **The names of anionic ligands end in the letter *ido*, but electrically neutral ligands ordinarily bear the name of the molecules** (Table 23.5). Special names are used for H_2O (aqua), NH_3 (ammine), and CO (carbonyl). For example, $[Fe(CN)_2(NH_3)_2(H_2O)_2]^+$ is the diamminediaquadicyanidoiron(III) ion.
4. **Greek prefixes (*di-, tri-, tetra-, penta-, hexa-*) are used to indicate the number of each kind of monodentate ligand when more than one is present. If the ligand or is polydentate, the alternate prefixes *bis-, tris-, tetrakis-,* are used and the ligand name is placed in parentheses**. For example, the name for $[Co(en)_3]Br_3$ is tris(ethylenediamine)cobalt(III) bromide.
5. **If the complex is an anion, its name ends in *-ate***. The compound $K_4[Fe(CN)_6]$ is potassium hexacyanidoferrate(II), for example, and the ion $[CoCl_4]^{2-}$ is tetrachloridocobaltate(II) ion.
6. **The oxidation number of the metal is given in parentheses in Roman numerals following the name of the metal**.

Three examples for applying these rules are

$[Ni(NH_3)_6]Br_2$	Hexaamminenickel(II) bromide
$[Co(en)_2(H_2O)(CN)]Cl_2$	Aquacyanidobis(ethylenediamine)cobalt(III) chloride
$Na_2[MoOCl_4]$	Sodium tetrachloridooxomolybdate(IV)

TABLE 23.5 Some Common Ligands and Their Names

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxido	Pyridine, C_5H_5N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

When writing the formula of complexes, it is preferable to write the donor atom of the ligand closest to the metal. So $[Cu(OH_2)_6]^{2+}$ is preferred to $[Cu(H_2O)_6]^{2+}$.

Sample Exercise 23.3

Naming Coordination Compounds

Name the compounds (**a**) $[Cr(OH_2)_4Cl_2]Cl$, (**b**) $K_4[Ni(CN)_4]$.

SOLUTION

Analyze We are given the chemical formulas for two coordination compounds and assigned the task of naming them.

Plan To name the complexes, we need to determine the ligands in the complexes, the names of the ligands, and the oxidation state of the metal ion. We then put the information together following the rules listed in the text.

Solve

(**a**) The ligands are four water molecules—tetraaqua—and two chloride ions—dichlorido. By assigning all the oxidation numbers we know for this molecule, we see that the oxidation number of Cr is +3:

$$+3 + 4(0) + 2(-1) + (-1) = 0$$
$$[Cr(OH_2)_4Cl_2]Cl$$

Thus, we have chromium(III). Finally, the anion is chloride. The name of the compound is tetraaquadichloridochromium(III) chloride.

(**b**) The complex has four cyanide ion ligands, CN^-, which means tetracyanido, and the oxidation state of the nickel is zero:

$$4(+1) + 0 + 4(-1) = 0$$
$$K_4[Ni(CN)_4]$$

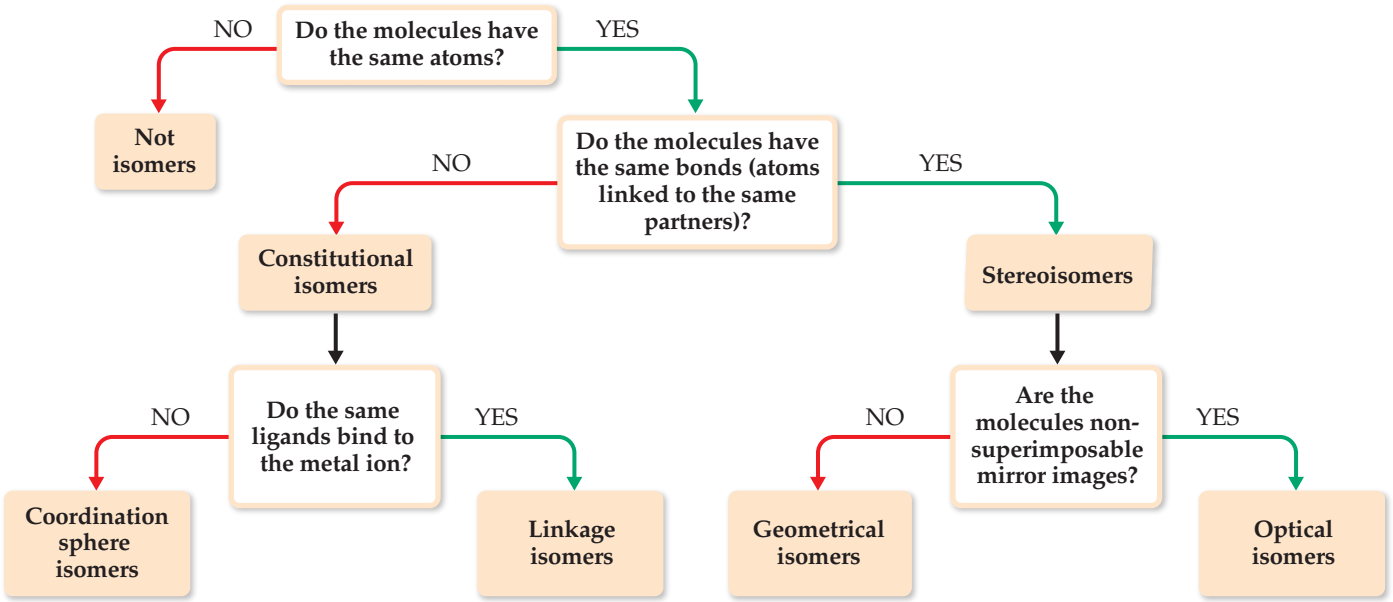
Because the complex is an anion, the metal is indicated as nickelate(0). Putting these parts together and naming the cation first, we have potassium tetracyanidonickelate(0).

Practice Exercise

What is the name of the compound $[Rh(NH_3)_4Cl_2]Cl$?
(**a**) Rhodium(III) tetraamminedichlorido chloride
(**b**) Tetraammoniadichloridorhodium(III) chloride
(**c**) Tetraamminedichloridorhodium(III) chloride
(**d**) Tetraamminetrichlorido-rhodium(III)
(**e**) Tetraamminedichloridorhodium(II) chloride

Isomerism

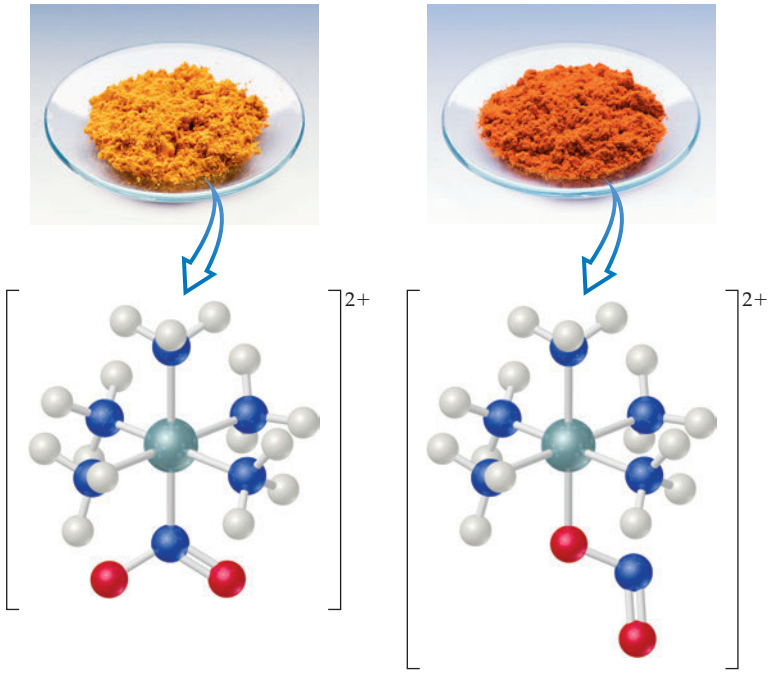
When two or more compounds have the same composition but a different arrangement of atoms, we call them **isomers**. Here we consider two main kinds of isomers in coordination compounds: **constitutional isomers** (which have different bonds) and **stereoisomers** (which have the same bonds but different ways in which the ligands occupy the space around the metal center). Each of these classes also has subclasses, as shown in Figure 23.19.



▲ Figure 23.19 Forms of isomerism in coordination compounds.

Go Figure

What are the chemical formula and name for each of the complex ions in this figure?



Nitro isomer
Bonding via ligand N atom

Nitrito isomer
Bonding via ligand O atom

▲ **Figure 23.20** **Linkage isomerism.**

Constitutional Isomerism

Many types of constitutional isomerism are known in coordination chemistry, including the two named in Figure 23.19: linkage isomerism and coordination-sphere isomerism. **Linkage isomerism** is a relatively rare but interesting type that arises when a particular ligand is capable of coordinating to a metal in two ways. The nitrite ion, NO_2^-, for example, can coordinate to a metal ion through either its nitrogen or one of its oxygens (**Figure 23.20**). When it coordinates through the nitrogen atom, the NO_2^- ligand is called *nitro*; when it coordinates through the oxygen atom, it is called *nitrito* and is generally written ONO^-. The isomers shown in Figure 23.20 have different properties. The nitro isomer is yellow, for example, whereas the nitrito isomer is red.

Another ligand capable of coordinating through either of two donor atoms is thiocyanate, SCN^-, whose potential donor atoms are N and S.

Coordination-sphere isomers are isomers that differ in which species in the complex act as ligands, and which are outside the coordination sphere. For example, three isomers have the formula $CrCl_3(OH_2)_6$. When the ligands are six H_2O and the chloride ions are in the crystal lattice (as counterions), we have the violet compound $[Cr(OH_2)_6]Cl_3$. When the ligands are five H_2O and one Cl^-, with the sixth H_2O and the two Cl^- out in the lattice, we have the green compound $[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$. The third isomer, $[Cr(OH_2)_4Cl_2]Cl \cdot 2\,H_2O$, is also a green compound. In the two green compounds, either one or two water molecules have been displaced from the coordination sphere by chloride ions. The displaced H_2O molecules occupy a site in the crystal lattice.

Stereoisomerism

Stereoisomers have the same chemical bonds but different spatial arrangements. In the square-planar complex $[Pt(NH_3)_2Cl_2]$, for example, the chlorido ligands can be either adjacent to or opposite each other (**Figure 23.21**). (We saw an earlier example of this type of isomerism in the cobalt complex of Figure 23.8, and we will return to that complex in a moment.) This form of stereoisomerism, in which the arrangement of the atoms is different but the same bonds are present, is called **geometric isomerism**. The isomer with like ligands in adjacent positions is the *cis* isomer, and the isomer with like ligands across from one another is the *trans* isomer.

Geometric isomers generally have different physical properties and may also have markedly different chemical reactivities. For example, *cis*-$[Pt(NH_3)_2Cl_2]$, also called *cisplatin*, is effective in the treatment of testicular, ovarian, and certain other cancers, whereas the *trans* isomer is ineffective. This is because cisplatin forms a chelate with two nitrogens of DNA, displacing the chloride ligands. The chloride ligands of the *trans* isomer are too far apart to form the N-Pt-N chelate with the nitrogen donors in DNA.

Geometric isomerism is also possible in octahedral complexes when two or more different ligands are present, as in the *cis* and *trans* tetraamminedichloridocobalt(III) ion in Figure 23.8. Because all four corners of a tetrahedron are adjacent to one another, *cis–trans* isomerism is not observed in tetrahedral complexes.

The second type of stereoisomerism listed in Figure 23.19 is **optical isomerism**. Optical isomers, called **enantiomers**, are mirror images that cannot be superimposed on each other. They bear the same resemblance to each other that your left hand bears to

your right hand. If you look at your left hand in a mirror, the image is identical to your right hand (Figure 23.22). No matter how hard you try, however, you cannot superimpose your two hands on each other. An example of a complex that exhibits this type of isomerism is the $[Co(en)_3]^{3+}$ ion. Figure 23.22 shows the two enantiomers of this complex and their mirror-image relationship. Just as there is no way that we can twist or turn our right hand to make it look identical to our left, so also there is no way to rotate one of these enantiomers to make it identical to the other. Molecules or ions that are not superimposable on their mirror image are said to be **chiral** (pronounced KY-rul).

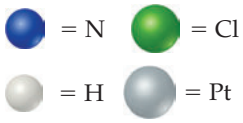
The properties of two optical isomers differ only if the isomers are in a chiral environment—that is, an environment in which there is a sense of right- and left-handedness. A chiral enzyme, for example, might catalyze the reaction of one optical isomer but not the other. Consequently, one optical isomer may produce a specific physiological effect in the body, with its mirror image producing either a different effect or none at all. Chiral reactions are also extremely important in the synthesis of pharmaceuticals and other industrially important chemicals.

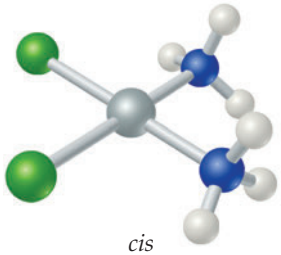
Optical isomers are usually distinguished from each other by their interaction with plane-polarized light. If light is polarized—for example, by being passed through a sheet of polarizing film—the electric-field vector of the light is confined to a single plane (Figure 23.23). If the polarized light is then passed through a solution containing one optical isomer, the plane of polarization is rotated either to the right or to the left. The isomer that rotates the plane of polarization to the right is **dextrorotatory**; it is the dextro, or *d*, isomer (Latin *dexter*, "right"). Its mirror image rotates the plane of polarization to the left; it is **levorotatory** and is the levo, or *l*, isomer (Latin *laevus*, "left"). The $[Co(en)_3]^{3+}$ isomer on the right in Figure 23.22 is found experimentally to be the *l* isomer of this ion. Its mirror image is the *d* isomer. Because of their effect on plane-polarized light, chiral molecules are said to be **optically active**.

When a substance with optical isomers is prepared in the laboratory, the chemical environment during the synthesis is not usually chiral. Consequently, equal amounts of the two isomers are obtained, and the mixture is said to be **racemic**. A racemic mixture does not rotate polarized light because the rotatory effects of the two isomers cancel each other.

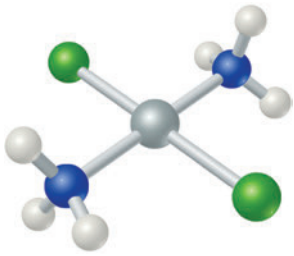
Go Figure

Which of these isomers has a nonzero dipole moment?



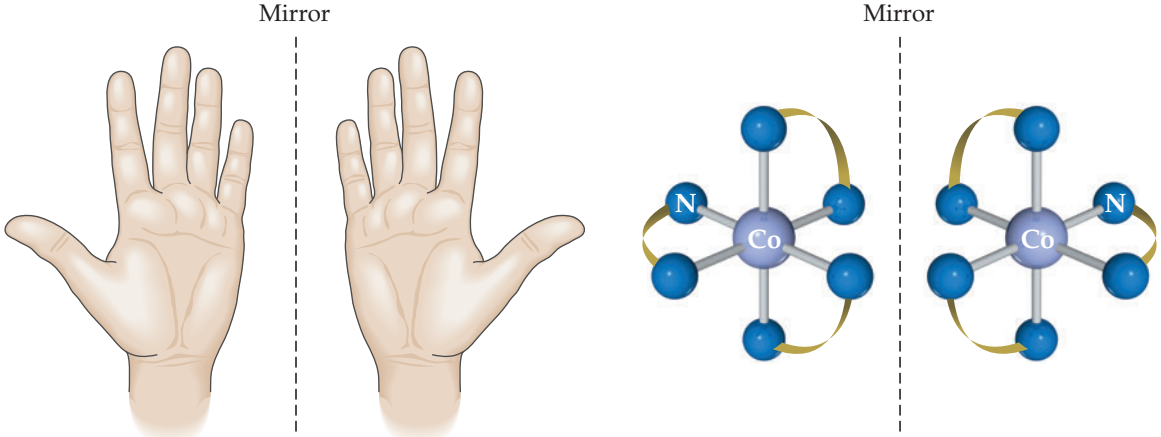


cis
Cl ligands adjacent to each other
NH_3 ligands adjacent to each other



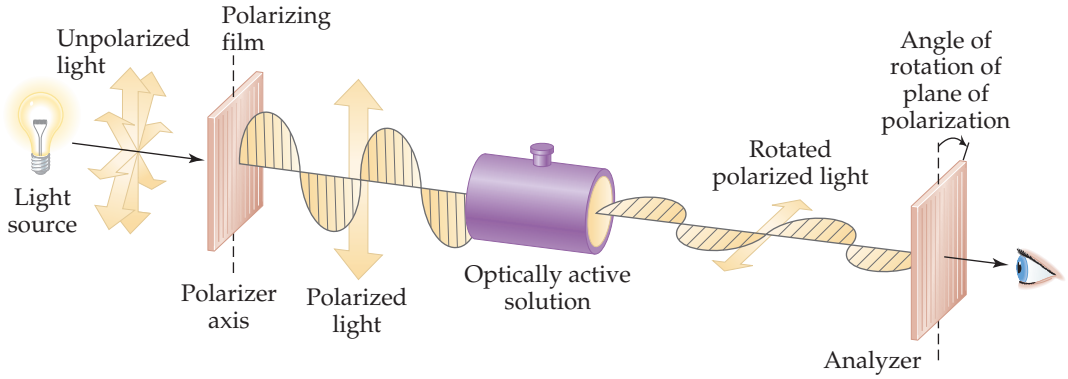
trans
Cl ligands on opposite sides of central atom
NH_3 ligands on opposite sides of central atom

▲ Figure 23.21 Geometric isomerism.



Left hand
Mirror image of left hand is identical to right hand
Enantiomers of $[Co(en)_3]^{3+}$

▲ Figure 23.22 Optical isomerism.



▲ **Figure 23.23** **Using polarized light to detect optical activity.**

Sample Exercise 23.4

Determining the Number of Geometric Isomers

The Lewis structure :C≡O: indicates that the CO molecule has two lone pairs of electrons. When CO binds to a transition-metal atom, it nearly always does so by using the C lone pair. How many geometric isomers are there for tetracarbonyldichloridoiron(II)?

SOLUTION

Analyze We are given the name of a complex containing only monodentate ligands, and we must determine the number of isomers the complex can form.

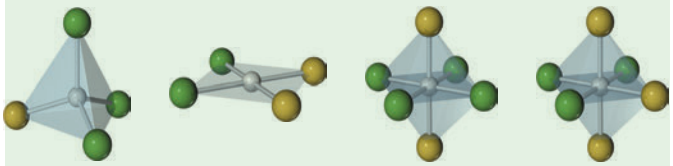
Plan We can count the number of ligands to determine the coordination number of the Fe and then use the coordination number to predict the geometry. We can then either make a series of drawings with ligands in different positions to determine the number of isomers or deduce the number of isomers by analogy to cases we have discussed.

Solve The name indicates that the complex has four carbonyl (CO) ligands and two chlorido (Cl^-) ligands, so its formula is $Fe(CO)_4Cl_2$. The complex therefore has a coordination number of 6, and we can assume an octahedral geometry. Like $[Co(NH_3)_4Cl_2]^+$ (Figure 23.8), it has four ligands of one type and two of another. Consequently, there are two isomers possible: one with the Cl^- ligands across the metal from each other, *trans*-$[Fe(CO)_4Cl_2]$, and one with the Cl^- ligands adjacent to each other, *cis*-$[Fe(CO)_4Cl_2]$.

Comment It is easy to overestimate the number of geometric isomers. Sometimes different orientations of a single isomer are incorrectly thought to be different isomers. If two structures can be rotated so that they are equivalent, they are not isomers of each other. The problem of identifying isomers is compounded by the difficulty we often have in visualizing three-dimensional molecules from their two-dimensional representations. It is sometimes easier to determine the number of isomers if we use three-dimensional models.

Practice Exercise

Which of the following molecules does not have a geometric isomer?



$[MX_3Y]$ (a) $[MX_2Y_2]$ (b) $[MX_4Y_2]$ (c) $[MX_3Y_3]$ (d)

Sample Exercise 23.5

Predicting Whether a Complex Has Optical Isomers

Does either *cis*-$[Co(en)_2Cl_2]^+$ or *trans*-$[Co(en)_2Cl_2]^-$ have optical isomers?

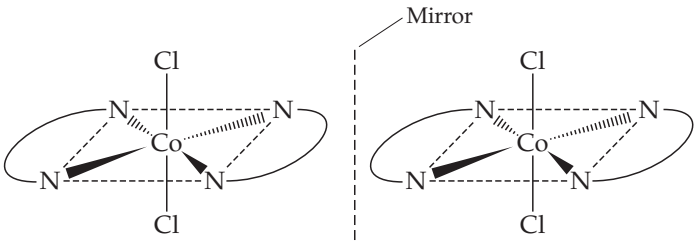
SOLUTION

Analyze We are given the chemical formula for two geometric isomers and asked to determine whether either one has optical isomers. Because en is a bidentate ligand, we know that both complexes are octahedral and both have coordination number 6.

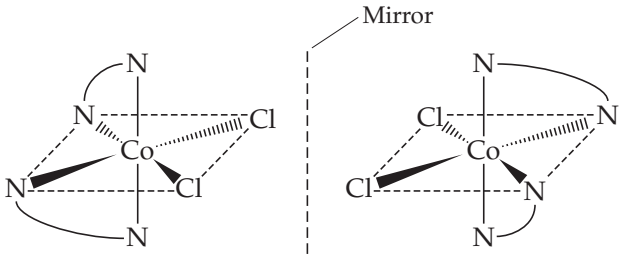
Plan We need to sketch the structures of the *cis* and *trans* isomers and their mirror images. We can draw the en ligand as two N atoms connected by an arc. If the mirror image cannot be superimposed on the original structure, the complex and its mirror image are optical isomers.

Solve

The *trans* isomer of $[Co(en)_2Cl_2]^+$ and its mirror image are shown here. Notice that the mirror image of the isomer is identical to the original. Consequently *trans*-$[Co(en)_2Cl_2]^+$ does not exhibit optical isomerism.



The *cis* isomer of $[Co(en)_2Cl_2]^+$ and its mirror image are shown here. In this case the two cannot be superimposed on each other. Thus, the two *cis* structures are optical isomers (enantiomers). We say that *cis*-$[Co(en)_2Cl_2]^+$ is a chiral complex.



Practice Exercise

Which of the following complexes has an optical isomer?

(**a**) Tetrahedral $[CdBr_2Cl_2]^{2-}$ (**b**) Octahedral $[CoCl_4(en)]^{2-}$ (**c**) Octahedral $[Co(NH_3)_4Cl_2]^{2+}$ (**d**) Tetrahedral $[Co(NH_3)BrClI]^-$

Self-Assessment Exercise

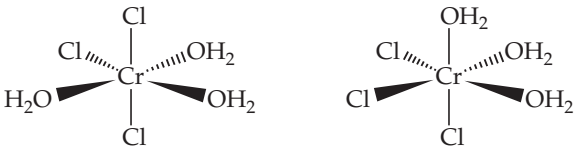
23.15 How many isomers are possible for the complex: $[Cr(OH_2)_3Cl_3]^+$?

(a) 1

(b) 2

(c) 3

(d) 4



Exercises

23.16 Write the formula for each of the following compounds, being sure to use brackets to indicate the coordination sphere:

(**a**) hexaammineiron(II) nitrate

(**b**) tetraaquadibromidochromium(III) perchlorate

(**c**) ammonium hexachloridopalladate(IV)

(**d**) diammineoxolatonickel(II)

(**e**) Hexaamminemolybdenum(III) tetrachloridocuprate(II)

23.17 Write names for the following coordination compounds:

(**a**) $Na_3[Fe(CN)_5NO]$

(**b**) $[CoO(NH_3)_5]Br$

(**c**) $Na_2[NiBr_4]$

(**d**) $[Rh(OH_2)_6][Ag(CN)_2]_3$

23.18 Consider the following three complexes:

(Complex 1) $[Co(NH_3)_5SCN]^{2+}$

(Complex 2) $[Co(NH_3)_3Cl_3]^{2+}$

(Complex 3) $CoClBr \cdot 5NH_3$

Which of the three complexes can have (**a**) geometric isomers, (**b**) linkage isomers, (**c**) optical isomers, (**d**) coordination-sphere isomers?

23.19 Consider an octahedral complex, MA_2B_4. How many geometric isomers are expected for this compound? Will any of the isomers be optically active? If so, which ones?

23.20 Determine if each of the following complexes exhibits geometric isomerism. If geometric isomers exist, determine how many there are. (**a**) $[Rh(bipy)(o\text{-}phen)_2]^{3+}$, (**b**) $[Co(NH_3)_3(bipy)Br]^{2+}$, (**c**) square-planar $[Pd(en)(CN)_2]$.

23.21 Determine if each of the following metal complexes is chiral and therefore has an optical isomer: (**a**) square planar $[Pd(en)(CN)_2]$, (**b**) octahedral $[Ni(en)(NH_3)_4]^{2+}$, (**c**) octahedral *cis*-$[V(en)_2ClBr]$.

Answers to Self-Assessment Exercise

23.15 (b)

23.5 Color and Magnetism in Coordination Chemistry



Studies of the colors and magnetic properties of transition-metal complexes have played an important role in the development of modern models for metal–ligand bonding. We discussed the various types of magnetic behavior of the transition metals in Section 23.1, and we discussed the interaction of radiant energy with matter in Section 6.3. Let's briefly examine the significance of these two properties for transition-metal complexes before we develop a model for metal–ligand bonding.

By the end of this section, you should be able to

- Appreciate the relationship between absorbed light and perceived color.

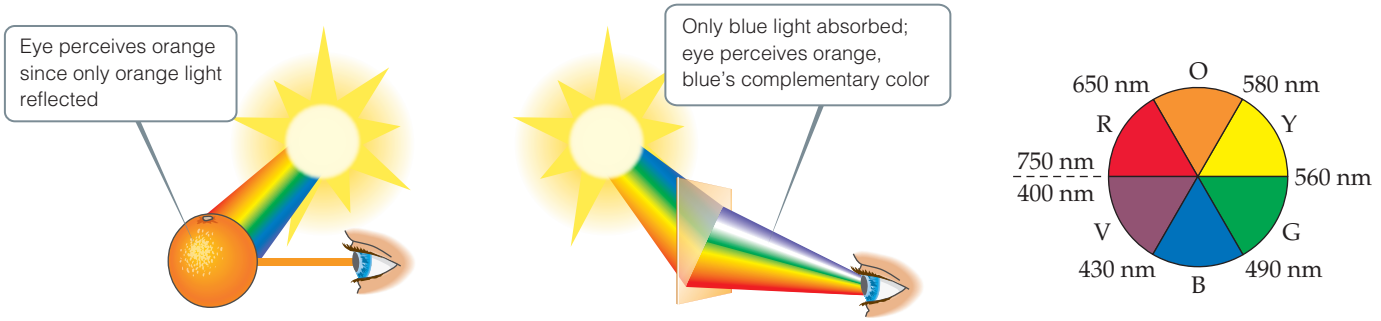
Color

In Figure 23.4, we saw the diverse range of colors seen in salts of transition-metal ions and their aqueous solutions. In general, the color of a complex depends on the identity of the metal ion, on its oxidation state, and on the ligands bound to it. **Figure 23.24**, for

Go Figure Is the equilibrium binding constant of ammonia for Cu(II) likely to be larger or smaller than that of water for Cu(II)?



▲ **Figure 23.24** **The color of a coordination complex changes when the ligand changes.**



▲ **Figure 23.25 Two ways of perceiving the color orange.** An object appears orange either when it reflects orange light to the eye (left) or when it transmits to the eye all colors except blue, the complement of orange (middle). Complementary colors lie opposite to each other on an artist's color wheel (right).

instance, shows how the pale blue color characteristic of $[Cu(OH_2)_4]^{2+}$ changes to deep blue-violet as NH_3 ligands replace the H_2O ligands to form $[Cu(NH_3)_4]^{2+}$.

For a substance to have color we can see, it must absorb some portion of the spectrum of visible light. Absorption happens, however, only if the energy needed to move an electron in the substance from its ground state to an excited state corresponds to the energy of some portion of the visible spectrum. Thus, the particular energies of radiation a substance absorbs dictate the color we see for the substance.

When an object absorbs some portion of the visible spectrum, the color we perceive is the sum of the unabsorbed portions, which are either reflected or transmitted by the object and strike our eyes. (Opaque objects *reflect* light, and transparent ones *transmit* it.) If an object absorbs all wavelengths of visible light, none reaches our eyes and the object appears black. If it absorbs no visible light, it is white if opaque or colorless if transparent. If it absorbs all but orange light, the orange light is what reaches our eye and therefore is the color we see.

An interesting phenomenon of vision is that we also perceive an orange color when an object absorbs only the blue portion of the visible spectrum and all the other colors strike our eyes. This is because orange and blue are **complementary colors**, which means that the removal of blue from white light makes the light look orange (and the removal of orange makes the light look blue).

Complementary colors can be determined with an artist's color wheel, which shows complementary colors on opposite sides (**Figure 23.25**).

The amount of light absorbed by a sample as a function of wavelength is known as the sample's **absorption spectrum**. The visible absorption spectrum of a transparent sample can be determined using a spectrometer, as described in the "A Closer Look" box on page 667. The absorption spectrum of the ion $[Ti(H_2O)_6]^{3+}$ is shown in **Figure 23.26**. The absorption maximum is at 500 nm, but the graph shows that much of the yellow, green, and blue light is absorbed. Because the sample absorbs all of these colors, what we see is the unabsorbed red and violet light, which we perceive as purple (the color purple is classified as a tertiary color located between red and violet on an artist's color wheel).

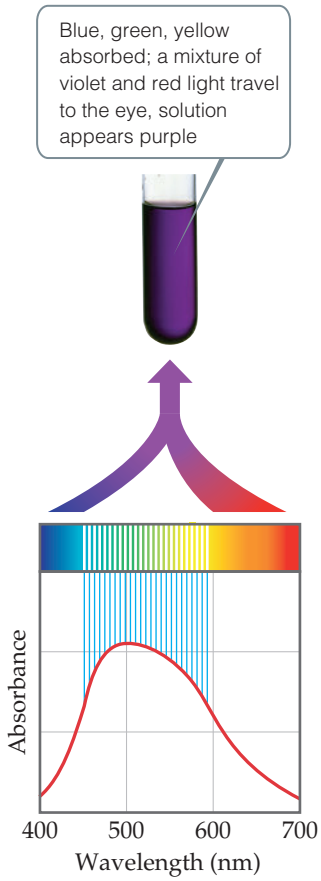
Magnetism of Coordination Compounds

Many transition-metal complexes exhibit paramagnetism, as described in Sections 9.8 and 23.1. In such compounds, the metal ions possess some number of unpaired electrons. It is possible to experimentally determine the number of unpaired electrons per metal ion from the measured degree of paramagnetism, and experiments reveal some interesting comparisons.

Compounds of the complex ion $[Co(CN)_6]^{3-}$ have no unpaired electrons, for example, but compounds of the $[CoF_6]^{3-}$ ion have four unpaired electrons per metal ion. Both complexes contain Co(III) with a $3d^6$ electron configuration. Clearly, there is a major difference in the ways in which the electrons are arranged in these two cases. Any successful bonding theory must explain this difference, and we present such a theory in the next section.

Go Figure

How would this absorbance spectrum change if you decreased the concentration of the $[Ti(H_2O)_6]^{3+}$ in solution?



▲ **Figure 23.26 The color of $[Ti(H_2O)_6]^{3+}$** A solution containing the $[Ti(H_2O)_6]^{3+}$ ion appears purple because, as its visible absorption spectrum shows, the solution does not absorb light from the violet and red ends of the spectrum. That unabsorbed light is what reaches our eyes.

Sample Exercise 23.6

Relating Color Absorbed to Color Observed

The complex ion *trans*-$[Co(NH_3)_4Cl_2]^+$ absorbs light primarily in the red region of the visible spectrum (the most intense absorption is at 680 nm). What is the color of the complex ion?

SOLUTION

Analyze We need to relate the color absorbed by a complex (red) to the color observed for the complex.

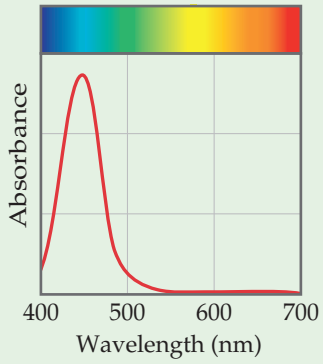
Plan For an object that absorbs only one color from the visible spectrum, the color we see is complementary to the color absorbed. We can use the color wheel of Figure 23.25 to determine the complementary color.

Solve From Figure 23.25, we see that green is complementary to red, so the complex appears green.

Comment As noted in Section 23.2, this green complex was one of those that helped Werner establish his theory of coordination (Table 23.3). The other geometric isomer of this complex, *cis*-$[Co(NH_3)_4Cl_2]^+$, absorbs yellow light and therefore appears violet.

Practice Exercise

A solution containing a certain transition-metal complex ion has the absorption spectrum shown here.



What color would you expect a solution containing this ion to be? (**a**) violet (**b**) blue (**c**) green (**d**) orange (**e**) red

Self-Assessment Exercise

23.22 What is the electron configuration and number of unpaired electrons in a Co atom and Co^{3+} ion?

(a) Co: [Ar] $4s^2\ 3d^7$; 3 unpaired electrons. Co^{3+}: [Ar] $3d^6$; 0 unpaired electrons.

(b) Co: [Ar] $4s^2\ 3d^7$; 3 unpaired electrons. Co^{3+}: [Ar] $3d^6$; 4 unpaired electrons.

(c) Co: [Ar] $4s^2\ 4d^7$; 3 unpaired electrons. Co^{3+}: [Ar] $4d^6$; 4 unpaired electrons.

(d) Co: [Ar] $4s^2\ 3d^7$; 3 unpaired electrons. Co^{3+}: [Ar] $4s^2\ 3d^4$; 4 unpaired electrons.

Exercises

23.23 (**a**) A complex absorbs photons with an energy of 4.51×10^{-19} J. What is the wavelength of these photons? (**b**) If this is the only place in the visible spectrum where the complex absorbs light, what color would you expect the complex to be?

23.24 Identify each of the following coordination complexes as either diamagnetic or paramagnetic:

(**a**) $[ZnBr_4)]^{2-}$

(**b**) $[Mn(H_2O)_6]^{3+}$

(**c**) OsO_4

(**d**) $[PtCl_4]^{2-}$

Answers to Self-Assessment Exercise

23.22 (b)

23.6 | Crystal-Field Theory



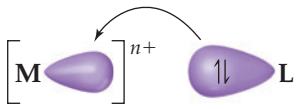
Ruby and emerald are allochromatic minerals. This means that their color arises from a trace impurity rather than from the bulk of the material. In these two cases it is the substitution of ~1% of the Al^{3+} in the crystal lattice by Cr^{3+} that gives the red color of a ruby and the green of an emerald. Why such different colors if they both arise from the same transition metal ion? The answer lies, in part, with the nature of the crystal lattice around the chromium ion. Ruby is composed of Al_2O_3, which is colorless when pure. The lattice is compact and the distance between O and a Cr^{3+} ion is relatively short, resulting in a strong interaction and absorption of green light (giving the red appearance). In emerald, which is composed of $Be_3Al_2Si_6O_{18}$, the lattice is expanded and there is a longer O—Cr^{3+} distance. This means less interaction with the Cr^{3+} ion and lower-energy red light is absorbed giving a green appearance to the mineral.

In this section, we discuss a model that explains the wide variety of colors observed in transition metal compounds. By the end of this section, you should be able to

- Predict the number of unpaired electrons in a transition metal complex.
- Use the spectrochemical series to qualitatively predict the crystal-field splitting in a complex.

Scientists have long recognized that many of the magnetic properties and colors of transition-metal complexes are related to the presence of *d* electrons in the metal cation. In this section, we consider a model for bonding in transition-metal complexes, **crystal-field theory**, that accounts for many of the observed properties of these substances.* Because many predictions of crystal-field theory are qualitatively the same as those obtained with more advanced molecular-orbital theories, crystal-field theory is an excellent place to start in considering the electronic structure of coordination compounds.

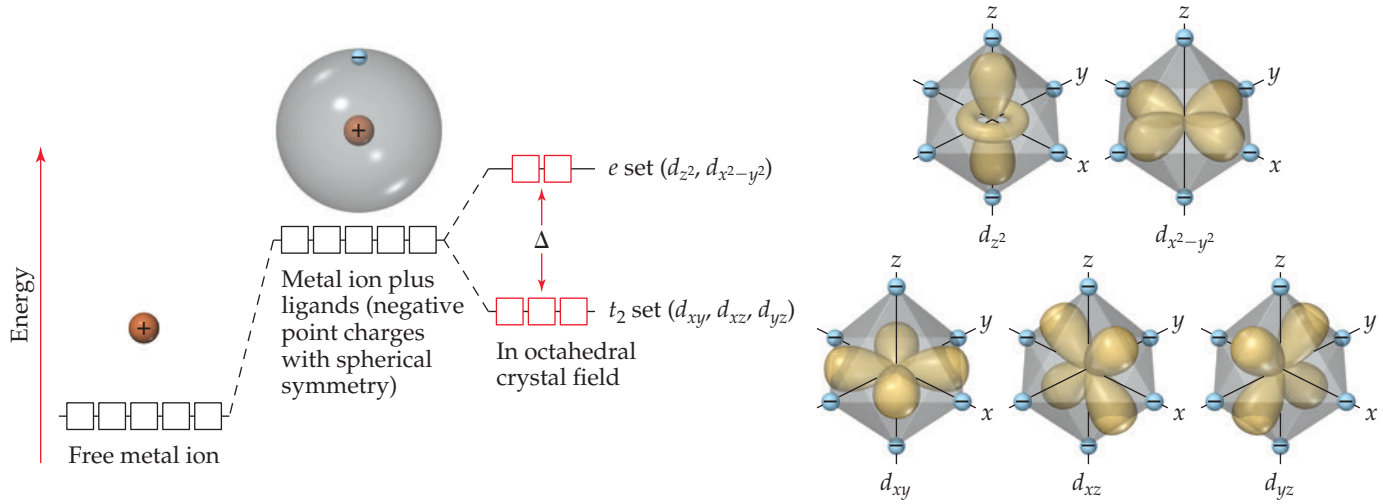
The attraction of a ligand to a metal ion is essentially a Lewis acid–base interaction in which the base—that is, the ligand—donates a pair of electrons to an empty orbital on the metal ion (Figure 23.27). Much of the attractive interaction between the metal ion and the ligands is due, however, to the electrostatic forces between the positive charge on the metal ion and negative charges on the ligands. An ionic ligand, such as Cl^- or SCN^-, experiences the usual cation–anion attraction. When the ligand is a neutral molecule, as in the case of H_2O or NH_3, the negative ends of these polar molecules, which contain an unshared electron pair, are directed toward the metal ion. In this case, the attractive interaction is of



▲ **Figure 23.27 Metal–ligand bond formation.** The ligand acts as a Lewis base by donating its nonbonding electron pair to an empty orbital on the metal ion. The bond that results is strongly polar with some covalent character.

*The name *crystal-field* arose because the theory was first developed to explain the properties of solid crystalline materials. The theory applies equally well to complexes in solution, however.

Go Figure Which *d* orbitals have lobes that point directly toward the ligands in an octahedral crystal-field?



▲ **Figure 23.28** **Energies of *d* orbitals in a free metal ion, a spherically symmetric crystal-field, and an octahedral crystal-field.**

the ion–dipole type. In either case, the ligands are attracted strongly toward the metal ion. Because of the metal–ligand electrostatic attraction, the energy of the complex is lower than the combined energy of the separated metal ion and ligands.

Although the metal ion is attracted to the ligand electrons, the metal ion's *d* electrons are repulsed by the ligands. Let's examine this effect more closely, specifically the case in which the ligands form an octahedral array around a metal ion that has coordination number 6.

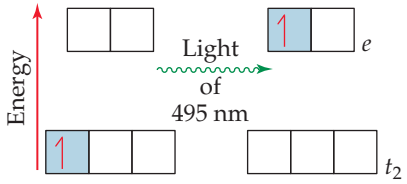
In crystal-field theory, we consider the ligands to be negative points of charge that repel the negatively charged electrons in the *d* orbitals of the metal ion. The energy diagram in **Figure 23.28** shows how these ligand point charges affect the energies of the *d* orbitals. First, we imagine the complex as having all the ligand point charges uniformly distributed on the surface of a sphere centered on the metal ion. The *average* energy of the metal ion's *d* orbitals is raised by the presence of this uniformly charged sphere. Hence, the energies of all five *d* orbitals are raised by the same amount.

This energy picture is only a first approximation, however, because the ligands are not distributed uniformly on a spherical surface and, therefore, do not approach the metal ion equally from every direction. Instead, we envision the six ligands approaching along *x*-, *y*-, and *z*-axes, as shown on the right in Figure 23.28. This arrangement of ligands is called an *octahedral crystal-field*. Because the metal ion's *d* orbitals have different orientations and shapes, they do not all experience the same repulsion from the ligands and, therefore, do not all have the same energy under the influence of the octahedral crystal-field. To see why, we must consider the shapes of the *d* orbitals and how their lobes are oriented relative to the ligands.

Figure 23.28 shows that the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals are directed *along* the *x*-, *y*-, and *z*-axes and so point directly toward the ligand point charges. The lobes of the d_{xy}, d_{xz}, and d_{yz} orbitals, however, are directed *between* the axes and so do not point directly toward the charges. The result of this difference in orientation—$d_{x^2-y^2}$ and d_{z^2} lobes point directly toward the ligand charges; d_{xy}, d_{xz}, and d_{yz} lobes do not—is that an electron residing in either the $d_{x^2-y^2}$ or d_{z^2} orbitals feels more repulsion from the negatively charged ligands. Hence the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals is higher than the energy of the d_{xy}, d_{xz}, and d_{yz} orbitals. This difference in energy is represented by the red boxes in the energy diagram of Figure 23.28.

Go Figure

How would you calculate the energy gap between the t_2 and e orbitals from this diagram?



◀ **Figure 23.29** The *d-d* transition in $[Ti(H_2O)_6]^{3+}$ is produced by the absorption of 495-nm light.

The three lower-energy *d* orbitals are called the t_2 set of orbitals, and the two higher-energy ones are called the *e* set.* The energy gap Δ between the two sets is called the *crystal-field splitting energy*.

It might seem like the energy of the $d_{x^2-y^2}$ orbital should be different from that of the d_{z^2} orbital because the $d_{x^2-y^2}$ has four lobes pointing at ligands and the d_{z^2} has only two lobes pointing at ligands. However, the d_{z^2} orbital does have electron density in the *xy* plane, represented by the ring encircling the point where the two lobes meet. More advanced calculations show that two orbitals do indeed have the same energy in the presence of the octahedral crystal-field.

Crystal-field theory helps us account for the colors observed in transition-metal complexes. The energy gap Δ between the *e* and t_2 sets of *d* orbitals is of the same order of magnitude as the energy of a photon of visible light. It is therefore possible for a transition-metal complex to absorb visible light that excites an electron from a lower-energy (t_2) *d* orbital into a higher-energy (*e*) *d* orbital. In $[Ti(OH_2)_6]^{3+}$, for example, the Ti(III) ion has an $[Ar]3d^1$ electron configuration. (Recall from Section 7.4 that when determining the electron configurations of transition-metal ions, we remove the *s* electrons first.) Ti(III) is thus called a d^1 *ion*. In the ground state of $[Ti(OH_2)_6]^{3+}$, the single 3*d* electron resides in an orbital in the t_2 set (**Figure 23.29**). Absorption of 495 nm light excites this electron up to an orbital in the *e* set, generating the absorption spectrum shown in Figure 23.26. Because this transition involves exciting an electron from one set of *d* orbitals to the other, we call it a ***d-d* transition**. As noted earlier, the absorption of visible radiation that produces this *d-d* transition causes the $[Ti(H_2O)_6]^{3+}$ ion to appear purple.

The magnitude of the crystal-field splitting energy and, consequently, the color of a complex depend on both the metal and the ligands. For example, we saw in Figure 23.4 that the color of $[M(OH_2)_6]^{2+}$ complexes changes from reddish-pink when the metal ion is Co^{2+}, to green for Ni^{2+}, to pale blue for Cu^{2+}. If we change the ligands in the $[Ni(OH_2)_6]^{2+}$ ion, the color also changes. $[Ni(NH_3)_6]^{2+}$ has a blue-violet color, while $[Ni(en)_3]^{2+}$ is purple (**Figure 23.30**). In a ranking called the **spectrochemical series**, ligands are arranged in order of their abilities to increase the crystal-field splitting energy, as in this abbreviated list:

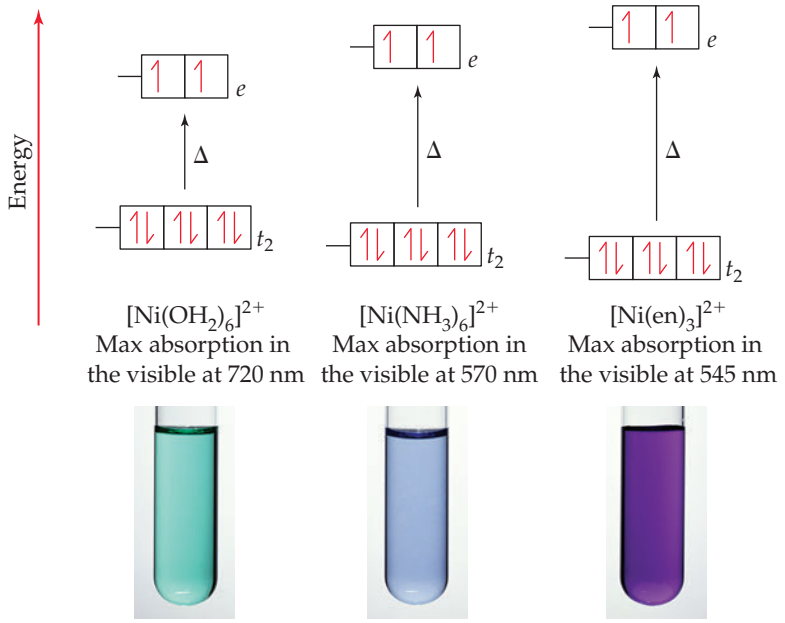
$$\text{——Increasing } \Delta \longrightarrow$$
$$Cl^- < F^- < H_2O < NH_3 < en < NO_2^-(\text{N-bonded}) < CN^-$$

The magnitude of Δ increases by roughly a factor of 2 from the far left to the far right of the spectrochemical series. Ligands at the low-Δ end of the spectrochemical series are termed *weak-field ligands*; those at the high-Δ end are termed *strong-field ligands*.

Let's take a closer look at the colors and crystal-field splitting as we vary the ligands for the series of Ni^{2+} complexes discussed earlier. Because the Ni atom has an $[Ar]3d^84s^2$ electron configuration, Ni^{2+} has the configuration $[Ar]3d^8$ and therefore is a d^8 ion. The t_2 set of orbitals holds six electrons, two in each orbital, while the last two electrons go into the *e* set of orbitals. Consistent with Hund's rule, each *e* orbital holds one electron and both electrons have the same spin.

*The labels t_2 for the d_{xy}, d_{xz}, and d_{yz} orbitals and *e* for the d_{z^2} and $d_{x^2y^2}$ orbitals come from the application of a branch of mathematics called *group theory* to crystal-field theory. Group theory can be used to analyze the effects of symmetry on molecular properties.

Go Figure If you were to use a ligand L that was a stronger field ligand than ethylenediamine, what color would you expect the $[NiL_6]^{2+}$ complex ion to have?



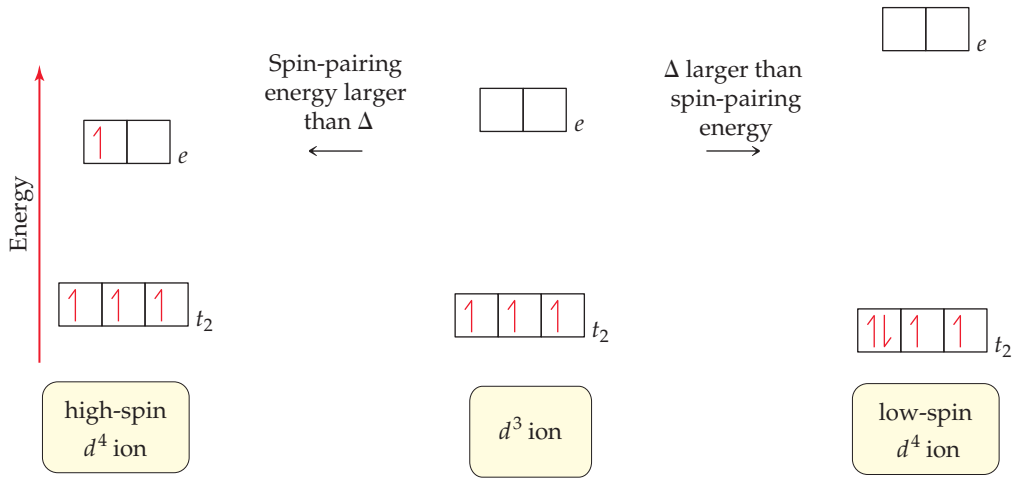
▲ **Figure 23.30 Effect of ligand on crystal-field splitting.** The greater the crystal-field strength of the ligand, the greater the energy gap Δ it causes between the t_2 and e sets of the metal ion's orbitals. This shifts the wavelength of the absorption maximum to shorter values.

As the ligand changes from H_2O to NH_3 to ethylenediamine, the spectrochemical series tells us that the crystal-field, Δ, exerted by the six ligands should increase. When there is more than one electron in the d orbitals, interactions between the electrons make the absorption spectra more complicated than the spectrum shown for $[Ti(H_2O)_6]^{3+}$ in Figure 23.26, which complicates the task of relating changes in Δ with color. With d^8 ions like Ni^{2+} three peaks are observed in the absorption spectra. Fortunately, for Ni^{2+} complexes we can simplify the analysis because only one of these three peaks falls in the visible region of the spectrum.* Because the energy separation Δ is increasing, the wavelength of the absorption peak should shift to a shorter wavelength. In the case of $[Ni(OH_2)_6]^{2+}$ the absorption peak in the visible part of the spectrum reaches a maximum near 720 nm, in the red region of the spectrum. So the complex ion takes the complementary color—green. For $[Ni(NH_3)_6]^{2+}$ the absorption peak reaches its maximum at 570 nm near the boundary between orange and yellow. The resulting color of the complex ion is a mixture of the complementary colors—blue and violet. Finally, for $[Ni(en)_3]^{2+}$ the peak shifts to an even shorter wavelength, 540 nm, which lies near the boundary between green and yellow. The resulting color purple is a mixture of the complementary colors red and violet.

Electron Configurations in Octahedral Complexes

Crystal-field theory helps us understand the magnetic properties and some important chemical properties of transition-metal ions. From Hund's rule, we expect electrons to always occupy the lowest-energy vacant orbitals first and to occupy a set of degenerate (same-energy) orbitals one at a time with their spins parallel. Thus, if we have a d^1, d^2, or d^3 octahedral complex, the electrons go into the lower-energy t_2 orbitals, with their spins parallel. When a fourth electron must be added, we have the two choices shown in **Figure 23.31**: The electron can either go into an e orbital, where it will be the sole electron in the orbital or become the second electron in a t_2 orbital. Because the

*The other two peaks fall in the infrared (IR) and ultraviolet (UV) regions of the spectrum. For $[Ni(H_2O)_6]^{2+}$ the IR peak is found at 1176 nm and the UV peak at 388 nm.



▲ **Figure 23.31 Two possibilities for adding a fourth electron to a d^6 octahedral complex.** Whether the fourth electron goes into a t_2 orbital or into an e orbital depends on the relative energies of the crystal-field splitting energy and the spin-pairing energy.

energy difference between the t_2 and e sets is the splitting energy Δ, the energy cost of going into an e orbital rather than a t_2 orbital is also Δ. Thus, the goal of filling lowest-energy available orbitals first is met by putting the electron in a t_2 orbital.

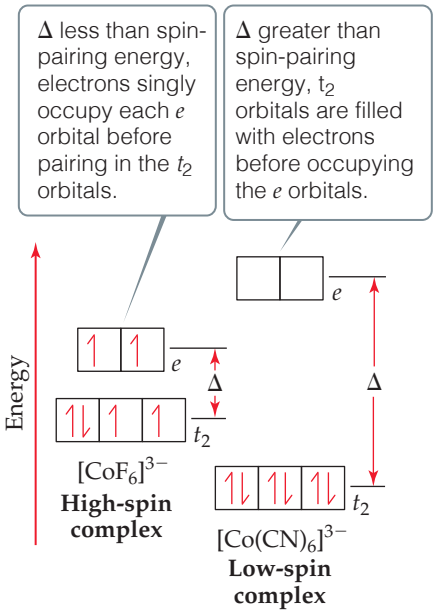
There is a penalty for doing this, however, because the electron must now be paired with the electron already occupying the orbital. The difference between the energy required to pair an electron in an occupied orbital and the energy required to place that electron in an empty orbital is called the **spin-pairing energy**. The spin-pairing energy arises from the fact that the electrostatic repulsion between two electrons that share an orbital (and so must have opposite spins) is greater than the repulsion between two electrons that are in different orbitals and have parallel spins.

In coordination complexes, the nature of the ligands and the charge on the metal ion often play major roles in determining which of the two electron arrangements shown in Figure 23.31 is used. In $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$, both ligands have a 1− charge. The F^- ion, however, is on the low end of the spectrochemical series, so it is a weak-field ligand. The CN^- ion is on the high end and so is a strong-field ligand, which means it produces a larger energy gap Δ than the F^- ion. The splittings of the d-orbital energies in these two complexes are compared in **Figure 23.32**.

Cobalt(III) has an $[Ar]3d^6$ electron configuration, so both complexes in Figure 23.32 are d^6 complexes. Let's imagine that we add these six electrons one at a time to the d orbitals of the $[CoF_6]^{3-}$ ion. The first three go into the t_2 orbitals with their spins parallel. The fourth electron could pair up in one of the t_2 orbitals. The F^- ion is a weak-field ligand, however, and so the energy gap Δ between the t_2 set and the e set is small. In this case, the more stable arrangement is the fourth electron in one of the e orbitals. By the same energy argument, the fifth electron goes into the other e orbital. With all five d orbitals containing one electron, the sixth must pair up, and the energy needed to place the sixth electron in a t_2 orbital is less than that needed to place it in an e orbital. We end up with four t_2 electrons and two e electrons.

Figure 23.32 shows that the crystal-field splitting energy Δ is much larger in the $[Co(CN)_6]^{3-}$ complex. In this case, the spin-pairing energy is smaller than Δ, so the lowest-energy arrangement is to place all six electrons in the t_2 orbitals.

The $[CoF_6]^{3-}$ complex is a **high-spin complex**; that is, the electrons are arranged so that they remain unpaired as much as possible. The $[Co(CN)_6]^{3-}$ ion is a **low-spin complex**; that is, the electrons are arranged so that they remain paired as much as possible while still following Hund's rule. These two electronic arrangements can be readily distinguished by measuring the magnetic properties of the complex. Experiments show that $[CoF_6]^{3-}$ has four unpaired electrons and is paramagnetic, while $[Co(CN)_6]^{3-}$ has no unpaired electrons and is diamagnetic. The absorption spectrum also shows peaks corresponding to the different values of Δ in these two complexes.



▲ **Figure 23.32 High-spin and low-spin complexes.** The high-spin $[CoF_6]^{3-}$ ion has a weak-field ligand and so a small Δ value. The low-spin $[Co(CN)_6]^{3-}$ ion has a strong-field ligand and so a large Δ value. Because $[CoF_6]^{3-}$ has unpaired electrons it is paramagnetic, while $[Co(CN)_6]^{3-}$ is diamagnetic.

In the transition metal ions of Periods 5 and 6 (which have 4*d* and 5*d* valence electrons), the *d* orbitals are larger than in the Period 4 ions (which have only 3*d* electrons). Thus, ions from Periods 5 and 6 interact more strongly with ligands, resulting in a larger crystal-field splitting. *Consequently, metal ions in Periods 5 and 6 are invariably low spin in an octahedral crystal-field.*

Sample Exercise 23.7

The Spectrochemical Series, Crystal-Field Splitting, Color, and Magnetism

The compound hexaamminecobalt(III) chloride is diamagnetic and orange in color with a single absorption peak in its visible absorption spectrum. (**a**) What is the electron configuration of the cobalt(III) ion? (**b**) Is $[Co(NH_3)_6]^{3+}$ a high-spin complex or a low-spin complex? (**c**) Estimate the wavelength where you expect the absorption of light to reach a maximum? (**d**) What color and magnetic behavior would you predict for the complex ion $[Co(en)_3]^{3+}$?

SOLUTION

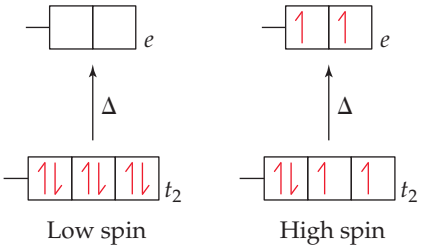
Analyze We are given the color and magnetic behavior of an octahedral complex containing Co with a +3 oxidation number. We need to use this information to determine its electron configuration, its spin state (low-spin or high-spin), and the color of light it absorbs. In part (d), we must use the spectrochemical series to predict how its properties will change if NH_3 is replaced by ethylenediamine (en).

Plan (**a**) From the oxidation number and the periodic table we can determine the number of valence electrons for Co(III), and from that we can determine the electron configuration. (**b**) The magnetic behavior can be used to determine whether this compound is a low-spin or high-spin complex. (**c**) Since there is a single peak in the visible absorption spectrum, the color of the compound should be complementary to the color of light that is absorbed most strongly. (**d**) Ethylenediamine is a stronger field ligand than NH_3, so we expect a larger Δ for $[Co(en)_3]^{3+}$ than for $[Co(NH_3)_6]^{3+}$.

Solve

(**a**) Co has an electron configuration of $[Ar]4s^23d^7$, and Co^{3+} has three fewer electrons than Co. Because transition-metal ions always lose their valence shell *s* electrons, the electron configuration of Co^{3+} is $[Ar]3d^6$.

(**b**) There are six valence electrons in the *d* orbitals. The filling of the t_2 and *e* orbitals for both high-spin and low-spin complexes is shown here. Because the compound is diamagnetic, we know all of the electrons must be paired up, which allows us to determine that $[Co(NH_3)_6]^{3+}$ is a low-spin complex.



(**c**) We are told that the compound is orange and has a single absorption peak in the visible region of the spectrum. The compound must therefore absorb the complementary color of orange, which is blue. The blue region of the spectrum ranges from approximately 430 nm to 490 nm. As an estimate we assume that the complex ion absorbs somewhere in the middle of the blue region, near 460 nm.

(**d**) Ethylenediammine is higher in the spectrochemical series than ammonia. Therefore, we expect a larger Δ for $[Co(en)_3]^{3+}$. Because Δ was already greater than the spin-pairing energy for $[Co(NH_3)_6]^{3+}$, we expect $[Co(en)_3]^{3+}$ to be a low-spin complex as well, with a d^6 configuration, so it will also be diamagnetic. The wavelength at which the complex absorbs light will shift to higher energy. If we assume a shift in the absorption maximum from blue to violet, the color of the complex will become yellow.

Comment The compound $[Co(en)_3]Cl_3$, which contains the $[Co(en)_3]^{3+}$ ion, was made and studied by Alfred Werner. This compound forms diamagnetic, golden-yellow crystals.

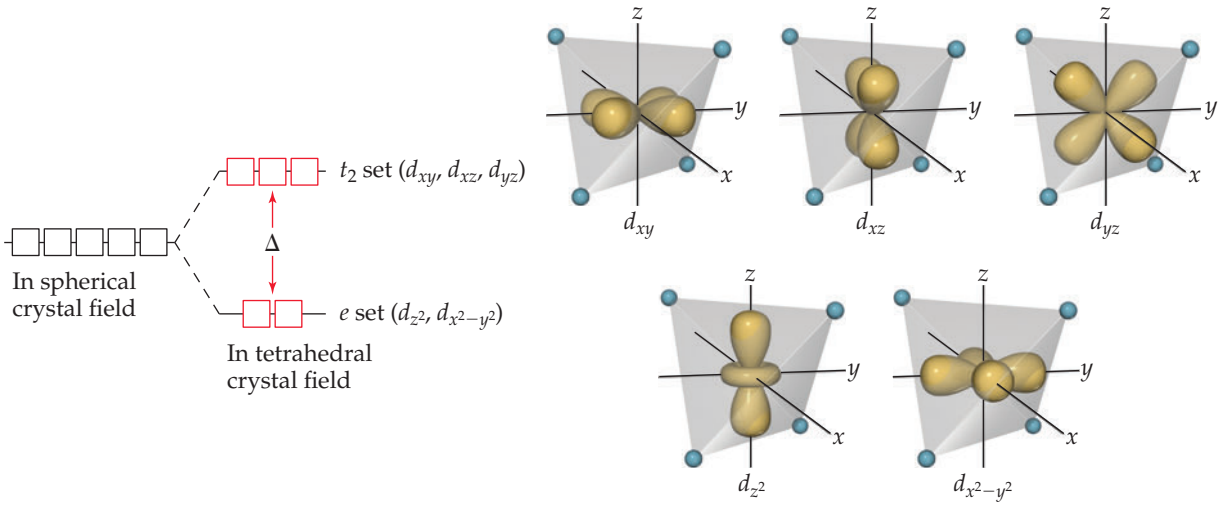
Practice Exercise

Which of the following octahedral complex ions will have the fewest number of unpaired electrons?
(**a**) $[Cr(OH_2)_6]^{3+}$ (**b**) $[V(H_2O)_6]^{3+}$ (**c**) $[FeF_6]^{3-}$ (**d**) $[RhCl_6]^{3-}$ (**e**) $[Ni(NH_3)_6]^{2+}$

Tetrahedral and Square-Planar Complexes

Thus far we have considered crystal-field theory only for complexes having an octahedral geometry. When there are only four ligands in a complex, the geometry is generally tetrahedral, except for the special case of d^8 metal ions, which we will discuss in a moment.

The crystal-field splitting of *d* orbitals in tetrahedral complexes differs from that in octahedral complexes. Four equivalent ligands can interact with a central metal ion



▲ **Figure 23.33 Energies of the *d* orbitals in a tetrahedral crystal-field.** The splitting of the *e* and t_2 sets of orbitals is inverted with respect to the splitting associated with an octahedral crystal-field. The crystal-field splitting energy Δ is smaller than it is in an octahedral crystal-field.

most effectively by approaching along the vertices of a tetrahedron. In this geometry the lobes of the two *e* orbitals point toward the edges of the tetrahedron, exactly in between the ligands (**Figure 23.33**). This orientation keeps the $d_{x^2-y^2}$ and d_{z^2} as far from the ligand point charges as possible. Consequently, these two *d* orbitals experience less repulsion from the ligands and lie at lower energy than the other three *d* orbitals. The three t_2 orbitals do not point directly at the ligand point charges, but they do come closer to the ligands than the *e* set, and as a result they experience more repulsion and are higher in energy. As we see in Figure 23.33, the splitting of *d* orbitals in a tetrahedral geometry is the opposite of what we find for the octahedral geometry, namely, the *e* orbitals are now *below* the t_2 orbitals. The crystal-field splitting energy Δ is much smaller for tetrahedral complexes than it is for comparable octahedral complexes, in part because there are fewer ligand point charges in the tetrahedral geometry, and in part because neither set of orbitals has lobes that point directly at the ligands. Calculations show that for the same metal ion and ligand set, Δ for the tetrahedral complex is only four-ninths as large as for the octahedral complex. For this reason, nearly all tetrahedral complexes are high spin; the crystal-field splitting energy is never large enough to overcome the spin-pairing energies.

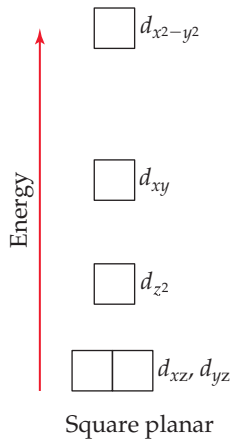
In a square-planar complex, four ligands are arranged about the metal ion such that all five species are in the *xy* plane. The resulting energy levels of the *d* orbitals are illustrated in **Figure 23.34**. Note in particular that the d_{z^2} orbital is considerably lower in energy than the $d_{x^2-y^2}$ orbital. To understand why this is so, recall from Figure 23.28 that in an octahedral field the d_{z^2} orbital of the metal ion interacts with the ligands positioned above and below the *xy* plane. There are no ligands in these two positions in a square-planar complex, which means that the d_{z^2} orbital experiences less repulsion and so remains in a lower-energy, more stable state.

Square-planar complexes are characteristic of metal ions with a d^8 electron configuration. They are nearly always low spin, with the eight *d* electrons spin-paired to form a diamagnetic complex. This pairing leaves the $d_{x^2-y^2}$ orbital empty. Such an electronic arrangement is particularly common among the d^8 ions of Periods 5 and 6, such as Pd^{2+}, Pt^{2+}, Ir^{+}, and Au^{3+}.

Crystal-field theory can be used to explain many observations in addition to those we have discussed. The theory is based on electrostatic interactions between ions and atoms, which essentially means ionic bonds. Many lines of evidence show, however, that the bonding in complexes must have some covalent character. Therefore, molecular-orbital theory can also be used to describe the bonding in complexes, but the application of molecular-orbital theory to coordination compounds is beyond the scope of our discussion. Crystal-field theory, although not entirely accurate in all details, provides an adequate and useful first description of the electronic structure of complexes.

Go Figure

For which *d* orbital(s) do the lobes point directly at the ligands in a square-planar crystal-field?



▲ **Figure 23.34 Energies of the *d* orbitals in a square-planar crystal-field.**

Sample Exercise 23.8

Populating *d* Orbitals in Tetrahedral and Square-Planar Complexes

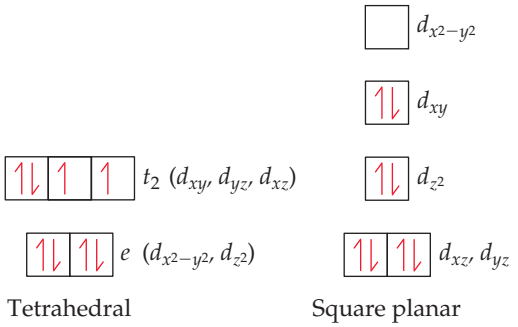
Nickel(II) complexes in which the metal coordination number is 4 can have either square-planar or tetrahedral geometry. $[NiCl_4]^{2-}$ is paramagnetic, and $[Ni(CN)_4]^{2-}$ is diamagnetic. One of these complexes is square planar, and the other is tetrahedral. Use the relevant crystal-field splitting diagrams in the text to determine which complex has which geometry.

SOLUTION

Analyze We are given two complexes containing Ni^{2+} and their magnetic properties. We are given two molecular geometry choices and asked to use crystal-field splitting diagrams from the text to determine which complex has which geometry.

Plan We need to determine the number of *d* electrons in Ni^{2+} and then use Figure 23.33 for the tetrahedral complex and Figure 23.34 for the square-planar complex.

Solve Nickel(II) has the electron configuration $[Ar]3d^8$. With very few exceptions tetrahedral complexes are high spin and square-planar complexes are low spin. Therefore, the population of the *d* orbitals in the two geometries is



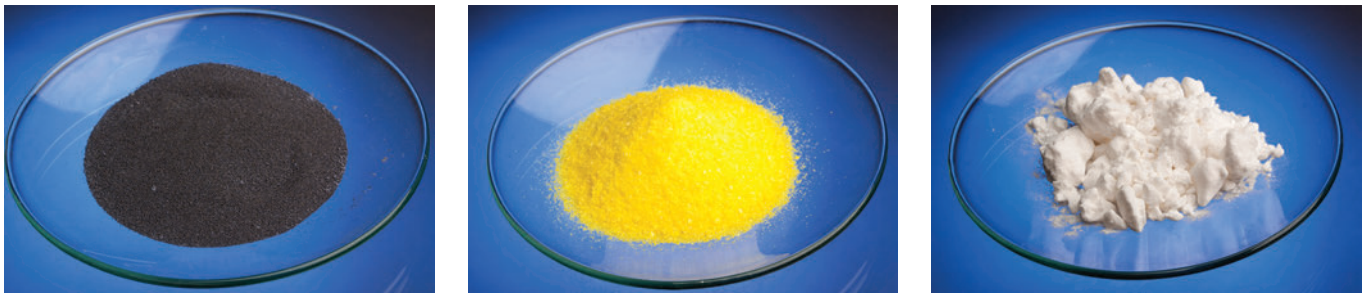
The tetrahedral complex has two unpaired electrons, and the square-planar complex has none. We know from Section 23.1 that the tetrahedral complex must be paramagnetic and the square planar must be diamagnetic. Therefore, $[NiCl_4]^{2-}$ is tetrahedral, and $[Ni(CN)_4]^{2-}$ is square planar.

Comment Nickel(II) forms octahedral complexes more frequently than square-planar ones, whereas d^8 metals from Periods 5 and 6 tend to favor square-planar coordination.

Practice Exercise

How many unpaired electrons do you predict for the tetrahedral $[MnCl_4]^{2-}$ ion?
(**a**) 1, (**b**) 2, (**c**) 3, (**d**) 4, (**e**) 5.

A CLOSER LOOK Charge-Transfer Color



$KMnO_4$ K_2CrO_4 $KClO_4$

▲ **Figure 23.35 The colors of compounds can arise from charge-transfer transitions.** $KMnO_4$ and K_2CrO_4 are colored due to ligand-to-metal charge-transfer transitions in their anions. Higher energy ultraviolet photons are needed to excite the charge-transfer transition in the perchlorate ion, therefore $KClO_4$ is white.

In the laboratory portion of your course, you have probably seen many colorful transition-metal compounds, including those shown in Figure 23.35. Many of these compounds are colored because of *d*-*d* transitions. Some colored complexes, however, including the violet permanganate ion, MnO_4^-, and the yellow chromate ion, CrO_4^{2-}, derive their color from a different type of excitation involving the *d* orbitals.

The permanganate ion strongly absorbs visible light, with a maximum absorption at 565 nm. Because violet is complementary to yellow, this strong absorption in the yellow portion of the visible spectrum is responsible for the violet color of salts and solutions of the ion. What is happening during this absorption of light? The MnO_4^- ion is a complex of Mn(VII). Because Mn(VII) has a $[Ar]3d^0$ electron configuration, the absorption cannot be due to a *d*-*d* transition because there are no *d* electrons to excite! That does not mean, however, that the *d* orbitals are not involved in the transition. The excitation in the MnO_4^- ion is due to a *charge-transfer transition*, in which an electron on one oxygen ligand is excited into a vacant *d* orbital on the Mn ion (Figure 23.36). In essence, an electron is transferred from a ligand to the metal, so this transition is called a *ligand-to-metal charge-transfer (LMCT) transition*.

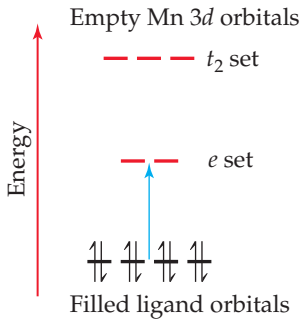
An LMCT transition is also responsible for the color of the CrO_4^{2-}, which contains the Cr(VI) ion with an $[Ar]3d^0$ electron configuration.

Also shown in Figure 23.35 is a salt of the perchlorate ion (ClO_4^-). Like MnO_4^-, ClO_4^- is tetrahedral and has its central atom in the +7 oxidation state. However, because the Cl atom does not have low-lying *d* orbitals, exciting an electron from O to Cl requires a more energetic photon than does it in MnO_4^-. The first absorption for ClO_4^- is in the ultraviolet portion of the spectrum, so no visible light is absorbed and the salt appears white.

Other complexes exhibit charge-transfer excitations in which an electron from the metal atom is excited to an empty orbital on a ligand. Such an excitation is called a *metal-to-ligand charge-transfer (MLCT) transition*.

Charge-transfer transitions are generally more intense than *d-d* transitions. Many metal-containing pigments used for oil painting, such as cadmium yellow (CdS), chrome yellow ($PbCrO_4$), and red ochre (Fe_2O_3), have intense colors because of charge-transfer transitions.

Related Exercises: 23.96, 23.97



▲ **Figure 23.36 Ligand-to-metal charge-transfer transition in MnO_4^-.** As shown by the blue arrow, an electron is excited from a nonbonding orbital on O into one of the empty *d* orbitals on Mn.

Self-Assessment Exercise

23.25 Using the spectrochemical series as a guide, predict how many unpaired *d*-electrons are in the complex: $[FeBr_6]^{3-}$.

(a) 1
(b) 3
(c) 5

Exercises

23.26 The lobes of which *d* orbitals point directly between the ligands in (**a**) octahedral geometry, (**b**) tetrahedral geometry?

23.27 As shown in Figure 23.26, the *d-d* transition of $[Ti(OH_2)_6]^{3+}$ produces an absorption maximum at a wavelength of about 500 nm. (**a**) What is the magnitude of Δ for $[Ti(OH_2)_6]^{3+}$ in kJ/mol? (**b**) How would the magnitude of Δ change if the H_2O ligands in $[Ti(OH_2)_6]^{3+}$ were replaced with NH_3 ligands?

23.28 The color and wavelength of the absorption maximum for $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, and $[Ni(en)_3]^{2+}$ are given in Figure 23.30. The absorption maximum for the $[Ni(bipy)_3]^{2+}$ ion occurs at about 520 nm. (**a**) What color would you expect for the $[Ni(bipy)_3]^{2+}$ ion? (**b**) Based on these data, where would you put bipy in the spectrochemical series?

23.29 Give the number of (valence) *d* electrons associated with the central metal ion in each of the following complexes: (**a**) $[Cr(OH_2)_6]Cl_3$, (**b**) $[Zr(OH_2)_6]SO_4$, (**c**) $Na_2[CuCl_4]$, (**d**) $(NH_4)_2[Ni(CO_3)_2(H_2O)_2]$, (**e**) $K_3[Fe(CN)_6]$

23.30 For a given metal ion and set of ligands, is the crystal-field splitting energy larger for a tetrahedral or an octahedral geometry?

23.31 For each of the following metals, write the electronic configuration of the atom and its 3+ ion: (**a**) Fe, (**b**) Mo, (**c**) Co. Draw the crystal-field energy-level diagram for the *d* orbitals of an octahedral complex, and show the placement of the *d* electrons for each 3+ ion, assuming a weak-field complex. How many unpaired electrons are there in each case?

23.32 Draw the crystal-field energy-level diagrams and show the placement of electrons for the following complexes: (**a**) $[VCl_6]^{3-}$, (**b**) $[FeF_6]^{3-}$ (a high-spin complex), (**c**) $[Ru(bipy)_3]^{3+}$ (a low-spin complex), (**d**) $[NiCl_4]^{2-}$ (tetrahedral), (**e**) $[PtBr_6]^{2-}$, (**f**) $[Ti(en)_3]^{2+}$.

23.33 The ion $[Fe(CN)_6]^{3-}$ has one unpaired electron, whereas $[Fe(NCS)_6]^{3-}$ has five unpaired electrons. From these results, what can you conclude about whether each complex is high spin or low spin? What can you say about the placement of NCS^- in the spectrochemical series?

Answers to Self-Assessment Exercise

23.25 (c)

Sample Integrative Exercise

Putting Concepts Together

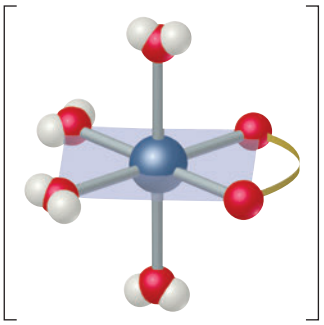
The oxalate ion has the Lewis structure shown in Table 23.4. (**a**) Show the geometry of the complex formed when this ion complexes with cobalt(II) to form $[Co(C_2O_4)(H_2O)_4]$. (**b**) Write the formula for the salt formed when three oxalate ions complex with Co(II), assuming that the charge-balancing cation is Na^+. (**c**) Sketch all the possible geometric isomers for the cobalt complex formed in part (b). Are any of these isomers chiral? Explain. (**d**) The equilibrium constant for the formation of the

Continued

cobalt(II) complex produced by coordination of three oxalate anions, as in part (b), is 5.0×10^9, and the equilibrium constant for formation of the cobalt(II) complex with three molecules of *ortho*-phenanthroline (Table 23.4) is 9×10^{19}. From these results, what conclusions can you draw regarding the relative Lewis base properties of the two ligands toward cobalt(II)? (**e**) Using the approach described in Sample Exercise 17.14, calculate the concentration of free aqueous Co(II) ion in a solution initially containing 0.040 *M* oxalate (*aq*) and 0.0010 *M* $Co^{2+}(aq)$.

SOLUTION

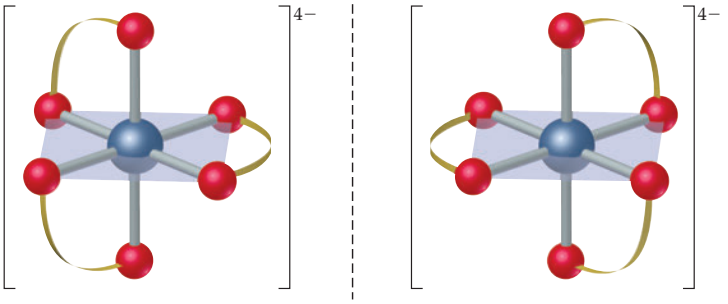
(**a**) The complex formed by coordination of one oxalate ion is octahedral:



(**b**) Because the oxalate ion has a charge of 2−, the net charge of a complex with three oxalate anions and one Co^{2+} ion is 4−. Therefore, the coordination compound has the formula:

$$Na_4[Co(C_2O_4)_3]$$

(**c**) There is only one geometric isomer. The complex is chiral, however, in the same way the $[Co(en)_3]^{3+}$ complex is chiral (Figure 23.22). The two mirror images are not superimposable, so there are two enantiomers:



(**d**) The *ortho*-phenanthroline ligand is bidentate, like the oxalate ligand, so they both exhibit the chelate effect. Thus, we conclude that *ortho*-phenanthroline is a stronger Lewis base toward Co^{2+} than oxalate. This conclusion is consistent with what we learned about bases in Section 16.6, that nitrogen bases are generally stronger than oxygen bases. (Recall, for example, that NH_3 is a stronger base than H_2O.)

(**e**) The equilibrium we must consider involves 3 mol of oxalate ion (represented as Ox^{2-}).

$$Co^{2+}(aq) + 3\,Ox^{2-}(aq) \rightleftharpoons [Co(Ox)_3]^{4-}(aq)$$

The formation-constant expression is:

$$K_f = \frac{[[Co(Ox)_3]^{4-}]}{[Co^{2+}][Ox^{2-}]^3}$$

Because K_f is so large, we can assume that essentially all the Co^{2+} is converted to the oxalato complex. Under that assumption, the final concentration of $[Co(Ox)_3]^{4-}$ is 0.0010 *M* and that of oxalate ion is $[Ox^{2-}] = (0.040) - 3(0.0010) = 0.037\,M$ (three Ox^{2-} ions react with each Co^{2+} ion). We then have:

$$[Co^{2+}] = x\,M, [Ox^{2-}] \cong 0.037\,M, [[Co(Ox)_3]^{4-}] \cong 0.0010\,M$$

Inserting these values into the equilibrium-constant expression, and solving for x, we obtain $4 \times 10^{-9}\,M$. From this, we see that the oxalate has complexed all but a tiny fraction of the Co^{2+} in solution.

$$K_f = \frac{(0.0010)}{x(0.037)^3} = 5 \times 10^9$$

$$x = 4 \times 10^{-9}\,M$$

Chapter Summary and Key Terms

THE TRANSITION METALS (SECTION 23.1) Metallic elements are obtained from **minerals**, which are solid inorganic compounds found in nature. **Metallurgy** is the science and technology of extracting metals from the earth and processing them for further use. Transition metals are characterized by incomplete filling of the *d* orbitals. The presence of *d* electrons in transition elements leads to multiple oxidation states. As we proceed through the transition metals in a given row of the periodic table, the attraction between the nucleus and the valence electrons increases more markedly for *d* electrons than for *s* electrons. As a result, the later transition elements in a period tend to have lower oxidation states.

The atomic and ionic radii of Period 5 transition metals are larger than those of Period 4 metals. The transition metals of Periods 5 and 6 have comparable atomic and ionic radii and are also similar in other properties. This similarity is due to the **lanthanide contraction**.

The presence of unpaired electrons in valence orbitals leads to magnetic behavior in transition metals and their compounds. In **ferromagnetic**, **ferrimagnetic**, and **antiferromagnetic** substances, the unpaired electron spins on atoms in a solid are affected by spins on neighboring atoms. In a ferromagnetic substance the spins all point in the same direction. In an antiferromagnetic substance the spins point in opposite directions and cancel one another. In a ferrimagnetic substance the spins point in opposite directions but do not fully cancel. Ferromagnetic and ferrimagnetic substances are used to make permanent magnets.

TRANSITION-METAL COMPLEXES (SECTION 23.2) **Coordination compounds** are substances that contain **metal complexes**. Metal complexes contain metal ions bonded to several surrounding anions or molecules known as **ligands**. The metal ion and its ligands make up the **coordination sphere** of the complex. The number of atoms attached to the metal ion is the **coordination number** of the metal ion. The most common coordination numbers are 4 and 6; the most common coordination geometries are tetrahedral, square planar, and octahedral.

COMMON LIGANDS IN COORDINATION CHEMISTRY (SECTION 23.3) Ligands that occupy only one site in a coordination sphere are called **monodentate ligands**. The atom of the ligand that bonds to the metal ion is the **donor atom**. Ligands that have two donor atoms are **bidentate ligands**. **Polydentate ligands** have three or more donor atoms. Bidentate and polydendate ligands are also called **chelating agents**. In general, chelating agents form more stable complexes than do related monodentate ligands, an observation known as the **chelate effect**. Many biologically important molecules, such as the **porphyrins**, are complexes of chelating agents. A related group of plant pigments known as **chlorophylls** are important in **photosynthesis**, the process by which plants use solar energy to convert CO_2 and H_2O into carbohydrates.

NOMENCLATURE AND ISOMERISM IN COORDINATION CHEMISTRY (SECTION 23.4) In naming coordination compounds, the number and type of ligands attached to the metal ion are specified, as is the oxidation state of the metal ion. **Isomers** are compounds with the same composition but different arrangements of atoms and therefore different properties. **Constitutional isomers** differ in the bonding arrangements of the ligands. **Linkage isomerism** occurs when a ligand can coordinate to a metal ion through different donor atoms. **Coordination-sphere isomers** contain different ligands in the coordination sphere. **Stereoisomers** are isomers with the same chemical bonding arrangements but different spatial arrangements of ligands. The most common forms of stereoisomerism are **geometric isomerism** and **optical isomerism**. Geometric isomers differ from one another in the relative locations of donor atoms in the coordination sphere; the most common being *cis* and *trans* isomers. Geometric isomers differ from one another in their chemical and physical properties. Optical isomers are nonsuperimposable mirror images of each other. Optical isomers, or **enantiomers**, are **chiral**, meaning that they have a specific "handedness" and differ only in the presence of a chiral environment. Optical isomers can be distinguished from one another by their interactions with plane-polarized light; solutions of one isomer rotate the plane of polarization to the right (**dextrorotatory**), and solutions of its mirror image rotate the plane to the left (**levorotatory**). Chiral molecules, therefore, are **optically active**. A 50–50 mixture of two optical isomers does not rotate plane-polarized light and is said to be **racemic**.

COLOR AND MAGNETISM IN COORDINATION CHEMISTRY (SECTION 23.5) A substance has a particular color because it either reflects or transmits light of that color or absorbs light of the **complementary color**. The amount of light absorbed by a sample as a function of wavelength is known as its **absorption spectrum**. The light absorbed provides the energy to excite electrons to higher-energy states.

It is possible to determine the number of unpaired electrons in a complex from its degree of paramagnetism. Compounds with no unpaired electrons are diamagnetic.

CRYSTAL-FIELD THEORY (SECTION 23.6) **Crystal-field theory** successfully accounts for many properties of coordination compounds, including their color and magnetism. In crystal-field theory, the interaction between metal ion and ligand is viewed as electrostatic. Because some *d* orbitals point directly at the ligands whereas others point between them, the ligands split the energies of the metal *d* orbitals. For an octahedral complex, the *d* orbitals are split into a lower-energy set of three degenerate orbitals (the t_2 set) and a higher-energy set of two degenerate orbitals (the *e* set). Visible light can cause a ***d-d* transition**, in which an electron is excited from a lower-energy *d* orbital to a higher-energy *d* orbital. The **spectrochemical series** lists ligands in order of their ability to increase the split in *d*-orbital energies in octahedral complexes.

Strong-field ligands create a splitting of *d*-orbital energies that is large enough to overcome the **spin-pairing energy**. The *d* electrons then preferentially pair up in the lower-energy orbitals, producing a **low-spin complex**. When the ligands exert a weak crystal-field, the splitting of the *d* orbitals is small. The electrons then occupy the higher-energy *d* orbitals in preference to pairing up in the lower-energy set, producing a **high-spin complex**. Transition metal ions from Periods 5 and 6 have large crystal-field splitting energies and adopt low spin configurations in octahedral complexes.

Crystal-field theory also applies to tetrahedral and square-planar complexes, which leads to different *d*-orbital splitting patterns. In a tetrahedral crystal-field, the splitting of the *d* orbitals results in a higher-energy t_2 set and a lower-energy *e* set, the opposite of the octahedral case. The splitting in a tetrahedral crystal-field is much smaller than that in an octahedral crystal-field, so tetrahedral complexes are nearly always high-spin complexes.

Learning Outcomes

After studying this chapter, you should be able to:

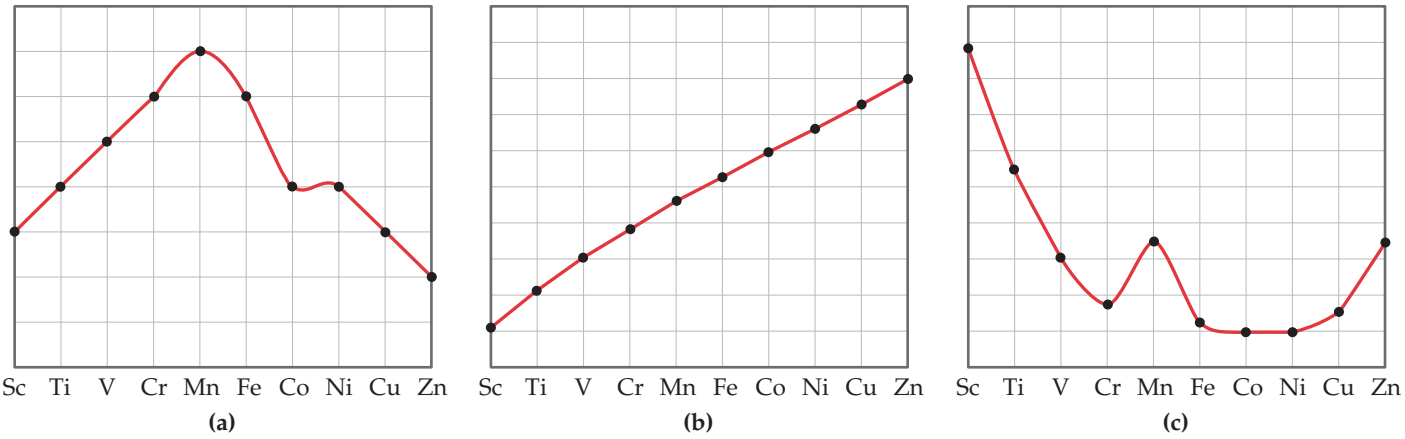
- Describe the periodic trends in radii and oxidation states of the transition-metal ions, including the origin and effect of the lanthanide contraction. (Section 23.1) *Related Exercises: 23.2, 23.34, 23.44*
- Determine the oxidation number and number of *d* electrons for metal ions in complexes. (Section 23.2) *Related Exercises: 23.3, 23.4, 23.46, 23.52*

- Identify common ligands and distinguish between chelating and nonchelating ligands. (Section 23.3) *Related Exercises: 23.12, 23.53, 23.54, 23.56*
- Name coordination compounds given their formula and write their formula given their name. (Section 23.4) *Related Exercises: 23.16, 23.17, 23.57, 23.58*
- Define isomerism and differentiate between the various types of isomers. (Section 23.4) *Related Exercises: 23.18, 23.59*
- Recognize and draw the geometric isomers of a complex. (Section 23.4) *Related Exercises: 23.19, 23.20, 23.60, 23.61*
- Recognize and draw the optical isomers of a complex. (Section 23.4) *Related Exercises: 23.21, 23.62*
- Use crystal-field theory to determine the number of unpaired electrons in a complex. (Sections 23.5 and 23.6) *Related Exercises: 23.64, 23.70, 23.71, 23.72*
- Use the spectrochemical series to predict the relative crystal-field splitting energy and colors of metal complexes. (Sections 23.5 and 23.6) *Related Exercises: 23.28, 23.67*
- Differentiate between high-spin and low-spin ions, and identify the factors that stabilize each. (Section 23.6) *Related Exercises: 23.33, 23.41, 23.69, 23.72*

Exercises

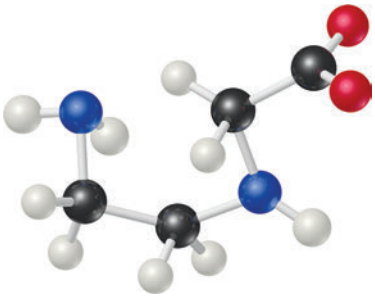
Visualizing Concepts

23.34 These three graphs show the variation in radius, effective nuclear charge, and maximum oxidation state for the transition metals of Period 4. In each part, identify which property is being plotted. [Section 23.1]



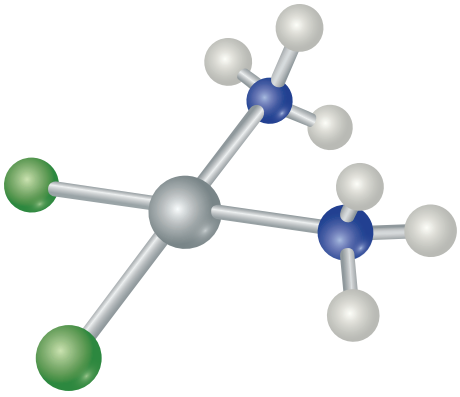
23.35 Draw the structure for $Pt(C_2O_4)(NH_3)_2$ and use it to answer the following questions: (**a**) What is the coordination number for platinum in this complex? (**b**) What is the coordination geometry? (**c**) What is the oxidation state of the platinum? (**d**) How many unpaired electrons are there? [Sections 23.2 and 23.6]

23.36 Draw the Lewis structure for the ligand shown here. (**a**) Which atoms can serve as donor atoms? Classify this ligand as monodentate, bidentate, or polydentate. (**b**) How many of these ligands are needed to fill the coordination sphere in an octahedral complex? [Section 23.2]

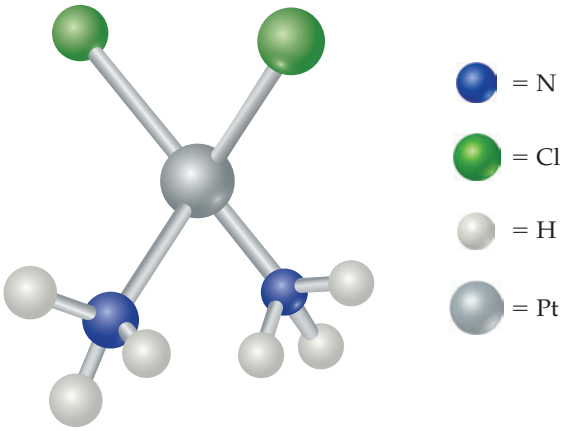


$NH_2CH_2CH_2NHCH_2CO_2^-$

23.37 Four-coordinate metals can have either a tetrahedral or a square-planar geometry; both possibilities are shown here for $[PtCl_2(NH_3)_2]$. (**a**) What is the name of this molecule? (**b**) Would the tetrahedral molecule have a geometric isomer? (**c**) Would the tetrahedral molecule be diamagnetic or paramagnetic? (**d**) Would the square-planar molecule have a geometric isomer? (**e**) Would the square-planar molecule be diamagnetic or paramagnetic? (**f**) Would determining the number of geometric isomers help you distinguish between the tetrahedral and square-planar geometries? (**g**) Would measuring the molecule's response to a magnetic field help you distinguish between the two geometries? [Sections 23.4–23.6]

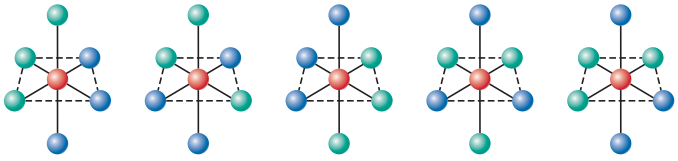


square planar



tetrahedral

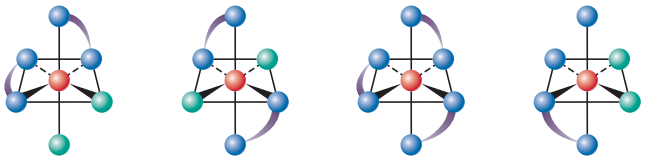
23.38 There are two geometric isomers of octahedral complexes of the type MA_3X_3, where M is a metal and A and X are monodentate ligands. Of the complexes shown here, which are identical to (1) and which are the geometric isomers of (1)? [Section 23.4]



(1) (2) (3) (4) (5)

23.39 Which of the complexes shown here are chiral? [Section 23.4]

= Cr = $NH_2CH_2CH_2NH_2$ = Cl = NH_3

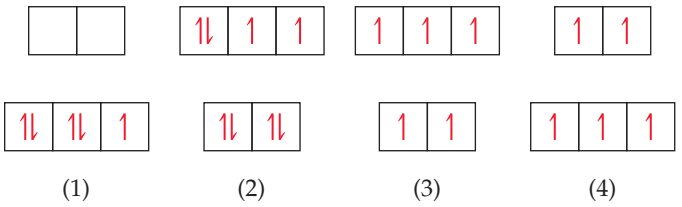


(1) (2) (3) (4)

23.40 The solutions shown here each have an absorption spectrum with a single absorption peak like that shown in Figure 23.26. What color does each solution absorb most strongly? [Section 23.5]

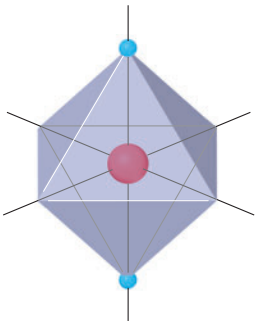


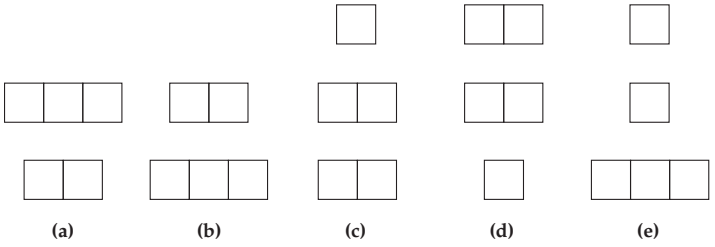
23.41 Which of these crystal-field splitting diagrams represents: (**a**) a weak-field octahedral complex of Fe^{3+}, (**b**) a strong-field octahedral complex of Fe^{3+}, (**c**) a tetrahedral complex of Fe^{3+}, (**d**) a tetrahedral complex of Ni^{2+}? (The diagrams do not indicate the relative magnitudes of Δ.) [Section 23.6]



(1) (2) (3) (4)

23.42 In the linear crystal-field shown here, the negative charges are on the *z*-axis. Using Figure 23.28 as a guide, predict which of the following choices most accurately describes the splitting of the *d* orbitals in a linear crystal-field? [Section 23.6]





(a) (b) (c) (d) (e)

23.43 Two Co(III) complexes are both low spin but have different ligands. A solution of one is orange and a solution of the other is yellow. Which solution is likely to contain the complex that has the stronger-field ligand? [Section 23.6]

The Transition Metals (Section 23.1)

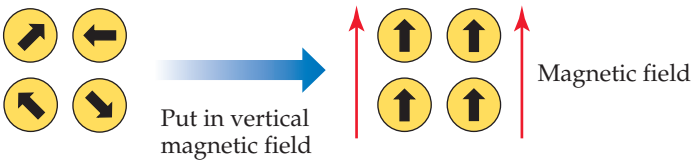
23.44 The lanthanide contraction explains which of the following periodic trends? (**a**) The atomic radii of the transition metals first decrease and then increase when moving horizontally across each period. (**b**) When forming ions the Period 4 transition metals lose their 4*s* electrons before their 3*d* electrons. (**c**) The radii of the Period 5 transition metals (Y–Cd) are very similar to the radii of the Period 6 transition metals (Lu–Hg).

23.45 Among the Period 4 transition metals (Sc–Zn), which elements do not form ions where there are partially filled 3*d* orbitals?

23.46 Write out the ground-state electron configurations of (**a**) Sc^{2+}, (**b**) Mo^{2+}, (**c**) Rh^{3+}, (**d**) Fe^{3+}.

23.47 Which type of substance is attracted by a magnetic field, a diamagnetic substance or a paramagnetic substance?

23.48 What kind of magnetism is exhibited by this diagram?



23.49 The most important oxides of iron are magnetite, Fe_3O_4, and hematite, Fe_2O_3. (**a**) What are the oxidation states of iron in these compounds? (**b**) One of these iron oxides is ferrimagnetic, and the other is antiferromagnetic. Which iron oxide is more likely to be ferrimagnetic? Explain.

Transition-Metal Complexes (Section 23.2)

23.50 (**a**) Using Werner's definition of valence, which property is the same as oxidation number, *primary valence* or *secondary valence*? (**b**) What term do we normally use for the other type of valence? (**c**) Why can NH_3 serve as a ligand but BH_3 cannot?

23.51 A complex is written as $NiBr_2 \cdot 6NH_3$. (**a**) What is the oxidation state of the Ni atom in this complex? (**b**) What is the likely coordination number for the complex? (**c**) If the complex is treated with excess $AgNO_3(aq)$, how many moles of AgBr will precipitate per mole of complex?

23.52 Indicate the coordination number and the oxidation number of the metal for each of the following complexes:

(**a**) $Na_2[Co(EDTA)]$

(**b**) $KMnO_4$

(**c**) $[Pt(NH_3)_4]Cl_2$

(**d**) $K_3Fe(CN)_6$

(**e**) $Rh(PPh_3)_3Cl$

(**f**) $Zn(C_2O_4)(NH_3)_2$

Common Ligands in Coordination Chemistry (Section 23.3)

23.53 For each of the following molecules or polyatomic ions, draw the Lewis structure and indicate if it can act as a monodentate ligand, a bidentate ligand, or is unlikely to act as a ligand at all: (**a**) ethylamine, $CH_3CH_2NH_2$, (**b**) trimethylphosphine, $P(CH_3)_3$, (**c**) carbonate, CO_3^{2-}, (**d**) ethane, C_2H_6.

23.54 Polydentate ligands can vary in the number of coordination positions they occupy. In each of the following, identify the polydentate ligand present and indicate the probable number of coordination positions it occupies:

(**a**) $Cr(EDTA)^-$

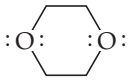
(**b**) $[Ni(C_2O_4)(H_2O)_2]Br_2$

(**c**) $[Ru(en)(NH_3)_4]Cl_3$

(**d**) $K_2[Fe(o\text{-}phen)(CN)_4]$

23.55 For each of the following pairs, identify the molecule or ion that is more likely to act as a ligand in a metal complex: (**a**) carbonic acid (H_2CO_3) or carbonate (CO_3^{2-}), (**b**) water (H_2O) or hydronium ion (H_3O^+), (**c**) phosphine (PH_3) or phosphoric acid (H_3PO_4).

23.56 True or false? The following ligand can act as a bidentate ligand.



Nomenclature and Isomerism in Coordination Chemistry (Section 23.4)

23.57 Write the formula for each of the following compounds, being sure to use brackets to indicate the coordination sphere:

(**a**) triamminetriaquachromium(III) nitrate

(**b**) dichloridobis(ethylenediamine)platinum(II)

(**c**) pentacarbonyliron(0)

(**d**) ammonium diaquabis(oxalato)Co(II)

(**e**) tris(bipyridyl)cobalt(III) sulfate

23.58 Write the names of the following compounds, using the standard nomenclature rules for coordination complexes:

(**a**) $[Ag(NH_3)_2]NO_3$

(**b**) $Hg[Co(SCN)_4]$

(**c**) $[Ru(PPh_3)_3Cl_3]$

(**d**) $[Co(NH_3)_5CO_3]_2SO_4$

23.59 Consider the following three complexes:

(Complex 1) $[Co(NH_3)_4Br_2]Cl$

(Complex 2) $[Pd(NH_3)_2(ONO)_2]$

(Complex 3) $[V(en)_2Cl_2]^+$,

Which of the three complexes can have (**a**) geometric isomers, (**b**) linkage isomers, (**c**) optical isomers, (**d**) coordination-sphere isomers?

23.60 A four-coordinate complex MA_2B_2 is prepared and found to have two different isomers. Is it possible to determine from this information whether the complex is square planar or tetrahedral? If so, which is it?

23.61 Determine if each of the following complexes exhibits geometric isomerism. If geometric isomers exist, determine how many there are. (**a**) tetrahedral $[Cd(H_2O)_2Cl_2]$, (**b**) square-planar $[IrCl_2(PH_3)_2]^-$, (**c**) octahedral $[Fe(o\text{-phen})_2Cl_2]^+$.

23.62 Determine if each of the following metal complexes is chiral and therefore has an optical isomer: (**a**) tetrahedral $[Zn(H_2O)_2Cl_2]$, (**b**) octahedral *trans*-$[Ru(bipy)_2Cl_2]$, (**c**) octahedral *cis*-$[Ru(bipy)_2Cl_2]$.

Color and Magnetism in Coordination Chemistry; Crystal-Field Theory (Sections 23.5 and 23.6)

23.63 (**a**) If a complex absorbs light at 610 nm, what color would you expect the complex to be? (**b**) What is the energy in joules of a photon with a wavelength of 610 nm? (**c**) What is the energy of this absorption in kJ/mol?

23.64 Identify each of the following coordination complexes as either diamagnetic or paramagnetic:

(**a**) $[CoBr(NH_3)_5]^{2+}$

(**b**) $[W(CN)_6]^{3-}$

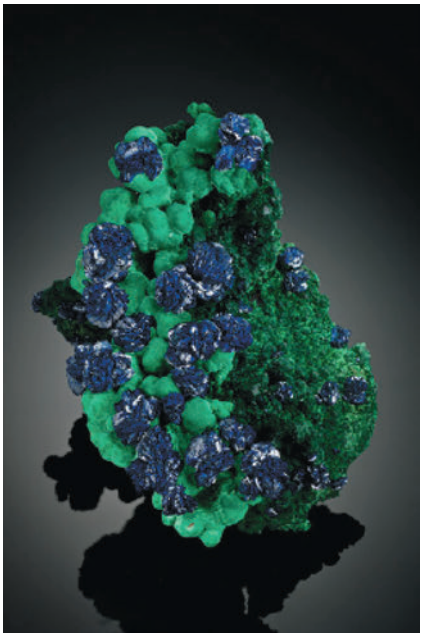
(**c**) $[VF_6]^{3-}$

(**d**) $[Rh(o\text{-phen})_3]^{3+}$

23.65 If the lobes of a given *d*-orbital point directly at the ligands, will an electron in that orbital have a higher or lower energy than an electron in a *d*-orbital whose lobes *do not* point directly at the ligands?

23.66 (**a**) Sketch a diagram that shows the definition of the *crystal-field splitting energy* (Δ) for an octahedral crystal-field. (**b**) What is the relationship between the magnitude of Δ and the energy of the *d-d* transition for a d^1 complex? (**c**) Calculate Δ in kJ/mol if a d^1 complex has an absorption maximum at 545 nm.

23.67 The colors in the copper-containing minerals malachite, which is green and has an empirical formula of $Cu_2CO_3(OH)_2$, and azurite, which is blue and has an empirical formula of $Cu_3(CO_3)_2(OH)_2$, come from a single *d-d* transition in each compound. The compounds are sometimes found together in nature as shown here. (**a**) What is the electron configuration of the copper ion in each mineral? (**b**) Based on their colors, in which compound would you predict the crystal-field splitting Δ is larger?



23.68 Give the number of (valence) *d* electrons associated with the central metal ion in each of the following complexes: (**a**) $[Pt(NH_3)_2Cl_2]Cl_2$, (**b**) $K_2[Cu(C_2O_4)_2]$, (**c**) $[Os(en)_3]Cl_3$, (**d**) $[Cr(EDTA)]SO_4$, (**e**) $[Cd(OH_2)_6]Cl_2$.

23.69 A classmate says, "A weak-field ligand usually means the complex is high spin." Is your classmate correct? Explain.

23.70 For each of the following metals, write the electronic configuration of the atom and its 2+ ion: (**a**) Mn, (**b**) Ru, (**c**) Rh. Draw the crystal-field energy-level diagram for the *d* orbitals of an octahedral complex, and show the placement of the *d* electrons for each 2+ ion, assuming a strong-field complex. How many unpaired electrons are there in each case?

23.71 Draw the crystal-field energy-level diagrams and show the placement of *d* electrons for each of the following: (**a**) $[Cr(OH_2)_6]^{2+}$ (four unpaired electrons), (**b**) $[Mn(H_2O)_6]^{2+}$ (a high-spin complex), (**c**) $[Ru(NH_3)_5(OH_2)]^{2+}$ (a low-spin complex), (**d**) $[IrCl_6]^{2-}$ (a low-spin complex), (**e**) $[Cr(en)_3]^{3+}$, (**f**) $[NiF_6]^{4-}$.

23.72 The complex $[Mn(NH_3)_6]^{2+}$ contains five unpaired electrons. Sketch the energy-level diagram for the *d* orbitals, and indicate the placement of electrons for this complex ion. Is the ion a high-spin or a low-spin complex?

Additional Exercises

23.73 The *Curie temperature* is the temperature at which a ferromagnetic solid switches from ferromagnetic to paramagnetic, and for nickel, the Curie temperature is 354 °C. Knowing this, you tie a string to two paper clips made of nickel and hold the paper clips near a permanent magnet. The magnet attracts the paper clips, as shown in the photograph on the left. Now you heat one of the paper clips with a cigarette lighter, and the clip drops (right photograph). Explain what happened.





23.74 Explain why the transition metals in Periods 5 and 6 have nearly identical radii in each group.

23.75 Based on the molar conductance values listed here for the series of platinum(IV) complexes, write the formula for each complex so as to show which ligands are in the coordination sphere of the metal. By way of example, the molar conductances of 0.050 *M* NaCl and $BaCl_2$ are 107 ohm^{-1} and 197 ohm^{-1}, respectively.

Complex	Molar Conductance (ohm^{-1})* of 0.050 *M* Solution
$Pt(NH_3)_6Cl_4$	523
$Pt(NH_3)_4Cl_4$	228
$Pt(NH_3)_3Cl_4$	97
$Pt(NH_3)_2Cl_4$	0
$KPt(NH_3)Cl_5$	108

*The ohm is a unit of resistance; conductance is the inverse of resistance.

23.76 (**a**) A compound with formula $RuCl_3 \cdot 5\ H_2O$ is dissolved in water, forming a solution that is approximately the same color as the solid. Immediately after forming the solution, the addition of excess $AgNO_3(aq)$ forms 2 mol of solid AgCl per mole of complex. Write the formula for the compound, showing which ligands are likely to be present in the coordination sphere. (**b**) After a solution of $RuCl_3 \cdot 5\ H_2O$ has stood for about a year, addition of $AgNO_3(aq)$ precipitates 3 mol of AgCl per mole of complex. What has happened in the ensuing time?

23.77 Sketch the structure of the complex in each of the following compounds and give the full compound name:

(**a**) *cis*-$[PtBrCl(NO_2)_2]^{2-}$

(**b**) $[Mn(CO)_3(C_6H_6)]^+$

(**c**) *cis*-$[CrCl_4)(OH_2)_2]^-$

(**d**) *trans*-$[Co(OH)(en)_2Cl]^+$

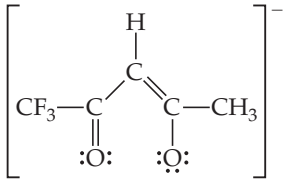
23.78 Does complex *d* in Exercise 23.77 have optical isomers?

23.79 The molecule *dimethylphosphinoethane* $[(CH_3)_2PCH_2CH_2P(CH_3)_2$, which is abbreviated dmpe] is used as a ligand for some complexes that serve as catalysts. A complex that contains this ligand is $Mo(CO)_4$(dmpe). (**a**) Draw the Lewis structure for dmpe, and compare it with ethylenediamine as a coordinating ligand. (**b**) What is the oxidation state of Mo in $Na_2[Mo(CN)_2(CO)_2$(dmpe)]? (**c**) Sketch the structure of the $[Mo(CN)_2(CO)_2$(dmpe)$]^{2-}$ ion, including all the possible isomers.

23.80 The square-planar complex $[Pt(en)Cl_2]$ only forms in one of two possible geometric isomers. Which isomer is not observed: *cis* or *trans*?

23.81 The acetylacetone ion forms very stable complexes with many metallic ions. It acts as a bidentate ligand, coordinating to the metal at two adjacent positions. Suppose that one of the CH_3 groups of the ligand is replaced by a CF_3 group, as shown here:

Trifluoromethyl acetylacetonate (tfac)



Sketch all possible isomers for the complex with three tfac ligands on cobalt(III). (You can use the symbol ↶ to represent the ligand.)

23.82 Which transition metal atom is present in each of the following biologically important molecules: (**a**) hemoglobin, (**b**) chlorophylls, (**c**) siderophores, (**d**) hemocyanine.

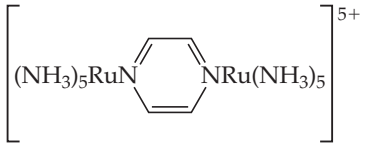
23.83 Carbon monoxide, CO, is an important ligand in coordination chemistry. When CO is reacted with nickel metal, the product is $[Ni(CO)_4]$, which is a toxic, pale yellow liquid. (**a**) What is the oxidation number for nickel in this compound? (**b**) Given that $[Ni(CO)_4]$ is a diamagnetic molecule with a tetrahedral geometry, what is the electron configuration of nickel in this compound? (**c**) Write the name for $[Ni(CO)_4]$ using the nomenclature rules for coordination compounds.

23.84 Some metal complexes have a coordination number of 5. One such complex is $Fe(CO)_5$, which adopts a *trigonal bipyramidal* geometry (see Figure 9.8). (**a**) Write the name for $Fe(CO)_5$, using the nomenclature rules for coordination compounds. (**b**) What is the oxidation state of Fe in this compound? (**c**) Suppose one of the CO ligands is replaced with a CN^- ligand, forming $[Fe(CO)_4(CN)]^-$. How many geometric isomers would you predict this complex could have?

23.85 Which of the following objects is chiral: (**a**) a pencil, (**b**) a computer keyboard, (**c**) a grand piano, (**d**) a molecular model of *cis*-$Fe(bipy)_2Cl_2$, (**e**) a piece of plane A4 paper?

23.86 The complexes $[CrBr_6]^{3-}$ and $[Cr(NH_3)_6]^{3+}$ are both known. (**a**) Draw the *d*-orbital energy-level diagram for octahedral Cr(III) complexes. (**b**) What gives rise to the colors of these complexes? (**c**) Which of the two complexes would you expect to absorb light of higher energy?

23.87 One of the more famous species in coordination chemistry is the Creutz–Taube complex:



It is named for the two scientists who discovered it and initially studied its properties. The central ligand is pyrazine, a planar six-membered ring with nitrogens at opposite sides. (**a**) How can you account for the fact that the complex, which has only neutral ligands, has an odd overall charge? (**b**) The metal is in a low-spin configuration in both cases. Assuming octahedral coordination, draw the *d*-orbital energy-level diagram for each metal. (**c**) In many experiments the two metal ions appear to be in exactly equivalent states. Can you think of a reason that this might appear to be so, recognizing that electrons move very rapidly compared to nuclei?

23.88 Solutions of $[Co(NH_3)_6]^{2+}$, $[Co(OH_2)_6]^{2+}$ (both octahedral), and $[CoCl_4]^{2-}$ (tetrahedral) are colored. One is pink, one is blue, and one is yellow. Based on the spectrochemical series and remembering that the energy splitting in tetrahedral complexes is normally much less than that in octahedral ones, assign a color to each complex.

23.89 Oxyhemoglobin, with an O_2 bound to iron, is a low-spin Fe(II) complex; deoxyhemoglobin, without the O_2 molecule, is a high-spin complex. (**a**) Assuming that the coordination environment about the metal is octahedral, how many unpaired electrons are centered on the metal ion in each case? (**b**) What ligand is coordinated to the iron in place of O_2 in deoxyhemoglobin? (**c**) Explain in a general way why the two forms of hemoglobin have different colors (hemoglobin is red, whereas deoxyhemoglobin has a bluish cast). (**d**) A 15-minute exposure to air containing 400 ppm of CO causes about 10% of the hemoglobin in the blood to be converted into the carbon monoxide complex, called carboxyhemoglobin. What does this suggest about the relative equilibrium constants for binding of carbon monoxide and O_2 to hemoglobin? (**e**) CO is a strong-field ligand. What color might you expect carboxyhemoglobin to be?

23.90 Consider the tetrahedral anions VO_4^{3-} (orthovanadate ion), CrO_4^{2-} (chromate ion), and MnO_4^- (permanganate ion). (**a**) These anions are *isoelectronic*. What does this statement mean? (**b**) Would you expect these anions to exhibit *d-d* transitions? Explain. (**c**) As mentioned in "A Closer Look" on charge-transfer color, the violet color of MnO_4^- is due to a *ligand-to-metal charge transfer* (LMCT) transition. What is meant by this term? (**d**) The LMCT transition in MnO_4^- occurs at a wavelength of 565 nm. The CrO_4^{2-} ion is yellow. Is the wavelength of the LMCT transition for chromate larger or smaller than that for MnO_4^-? Explain. (**e**) The VO_4^{3-} ion is colorless. Do you expect the light absorbed by the LMCT to fall in the UV or the IR region of the electromagnetic spectrum? Explain your reasoning.

23.91 Given the colors observed for VO_4^{3-} (orthovanadate ion), CrO_4^{2-} (chromate ion), and MnO_4^- (permanganate ion) (see Exercise 23.90), what can you say about how the energy separation between the ligand orbitals and the empty *d* orbitals changes as a function of the oxidation state of the transition metal at the center of the tetrahedral anion?

23.92 The blue-green color of turquoise is due to the presence of Cu(II) ions at octahedral sites which is coordinated with OH^- and H_2O. Assuming Cu(II) ions adopt an octahedral

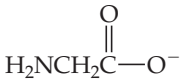
geometry, draw the crystal-field splitting diagram for Cu(II) in this environment. Suppose that the turquoise crystal is subjected to high pressure. What do you predict for the variation in the wavelength of absorption of the turquoise as a function of pressure? Explain.

23.93 In 2001, chemists at State University of New York-Stony Brook succeeded in synthesizing the complex *trans*-$[Fe(CN)_4(CO)_2]^{2-}$, which could be a model of complexes that may have played a role in the origin of life. (**a**) Sketch the structure of the complex. (**b**) The complex is isolated as a sodium salt. Write the complete name of this salt. (**c**) What is the oxidation state of Fe in this complex? How many *d* electrons are associated with the Fe in this complex? (**d**) Would you expect this complex to be high spin or low spin? Explain.

23.94 When Alfred Werner was developing the field of coordination chemistry, it was argued by some that the optical activity he observed in the chiral complexes he had prepared was due to the presence of carbon atoms in the molecule. To disprove this argument, Werner synthesized a chiral complex of cobalt that had no carbon atoms in it, and he was able to resolve it into its enantiomers. Design a cobalt(III) complex that would be chiral if it could be synthesized and that contains no carbon atoms. (It may not be possible to synthesize the complex you design, but we will not worry about that for now.)

23.95 Generally speaking, for a given metal and ligand, the stability of a coordination compound is greater for the metal in the +3 rather than in the +2 oxidation state (for metals that form stable +3 ions in the first place). Suggest an explanation, keeping in mind the Lewis acid–base nature of the metal–ligand bond.

23.96 Many trace metal ions exist in the blood complexed with amino acids or small peptides. The anion of the amino acid glycine (gly),



can act as a bidentate ligand, coordinating to the metal through nitrogen and oxygen atoms. How many isomers are possible for (**a**) $[Zn(gly)_2]$ (tetrahedral), (**b**) $[Pt(gly)_2]$ (square planar), (**c**) $[Co(gly)_3]$ (octahedral)? Sketch all possible isomers. Use the symbol  to represent the ligand.

23.97 The coordination complex $[Cr(CO)_6]$ forms colorless, diamagnetic crystals that melt at 90 °C. (**a**) What is the oxidation number of chromium in this compound? (**b**) Given that $[Cr(CO)_6]$ is diamagnetic, what is the electron configuration of chromium in this compound? (**c**) Given that $[Cr(CO)_6]$ is colorless, would you expect CO to be a weak-field or strong-field ligand? (**d**) Write the name for $[Cr(CO)_6]$ using the nomenclature rules for coordination compounds.

Integrative Exercises

23.98 Metallic elements are essential components of many important enzymes operating within our bodies. *Carbonic anhydrase*, which contains Zn^{2+} in its active site, is responsible for rapidly interconverting dissolved CO_2 and bicarbonate ion, HCO_3^-. The zinc in carbonic anhydrase is tetrahedrally coordinated by three neutral nitrogen-containing groups and a water molecule. The coordinated water molecule has a pK_a of 7.5, which is crucial for the enzyme's activity. (**a**) Draw the active site geometry for the Zn(II) center in carbonic anhydrase, just writing "N" for the three neutral nitrogen ligands from the protein. (**b**) Compare the pK_a of carbonic anhydrase's active site with that of pure water; which species is more acidic? (**c**) When the coordinated water to the Zn(II) center in carbonic anhydrase is deprotonated, what ligands are bound to the Zn(II) center? Assume the three nitrogen ligands are unaffected. (**d**) The pK_a of $[Zn(H_2O)_6]^{2+}$ is 10. Suggest an explanation for the difference between this pK_a and that of carbonic anhydrase. (**e**) Would you expect carbonic anhydrase to have a deep color, like hemoglobin and other metal-ion-containing proteins do? Explain.

23.99 Two different compounds have the formulation $CoBr(SO_4) \cdot 5\,NH_3$. Compound A is dark violet, and compound B is red-violet. When compound A is treated with $AgNO_3(aq)$, no reaction occurs, whereas compound B reacts with $AgNO_3(aq)$ to form a white precipitate. When compound A is treated with $BaCl_2(aq)$, a white precipitate is formed, whereas compound B has no reaction with $BaCl_2(aq)$. (**a**) Is Co in the same oxidation state in these complexes? (**b**) Explain the reactivity of compounds A and B with $AgNO_3(aq)$ and $BaCl_2(aq)$. (**c**) Are compounds A and B isomers of one another? If so, which category from Figure 23.19 best describes the isomerism observed for these complexes? (**d**) Would compounds A and B be expected to be strong electrolytes, weak electrolytes, or nonelectrolytes?

23.100 An iron complex formed from a solution containing hydrochloric acid and bipyridine is purified and analyzed. It contains 9.38% Fe, 60.53% carbon, 4.06% hydrogen, and 14.12% nitrogen by mass. The remainder of the compound is chlorine. An aqueous solution of the complex has about the same electrical conductivity as an equimolar solution of $K_2[CuCl_4]$. Write the formula of the compound, using brackets to denote the iron and its coordination sphere.

23.101 The $E°$ values for two low-spin iron complexes in acidic solution are as follows:

$$[Fe(o\text{-phen})_3]^{3+}(aq) + e^- \rightleftharpoons [Fe(o\text{-phen})_3]^{2+}(aq) \qquad E° = 1.12\ V$$

$$[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq) \qquad E° = 0.36\ V$$

(**a**) Is it thermodynamically favorable to reduce both Fe(III) complexes to their Fe(II) analogs? Explain. (**b**) Which complex, $[Fe(o\text{-phen})_3]^{3+}$ or $[Fe(CN)_6]^{3-}$, is more difficult to reduce? (**c**) Suggest an explanation for your answer to (b).

23.102 A platinum complex formed from a solution containing chloride ion and ammonia is found on elemental analysis to contain 23.63% chlorine, 9.34% nitrogen, 2.02% hydrogen by mass. The compound is slightly soluble in several organic solvents; its solutions in water or alcohol do not conduct electricity. It is found experimentally to have a net dipole moment. Write the chemical formula of this platinum complex, and indicate its probable structure.

23.103 (**a**) In early studies it was observed that when the complex $[Co(NH_3)_4Br_2]Br$ was placed in water, the electrical conductivity of a 0.05 *M* solution changed from an initial value of 191 ohm^{-1} to a final value of 374 ohm^{-1} over a period of an hour or so. Suggest an explanation for the observed results. (See Exercise 23.75 for relevant comparison data.) (**b**) Write a balanced chemical equation to describe the reaction. (**c**) A 500 mL solution is made up by dissolving 3.87 g of the complex. As soon as the solution is formed, and before any change in conductivity has occurred, a 25.00 mL portion of the solution is titrated with 0.0100 *M* $AgNO_3$ solution. What volume of $AgNO_3$ solution do you expect to be required to precipitate the free $Br^-(aq)$? (**d**) Based on the response you gave to part (b), what volume of $AgNO_3$ solution would be required to titrate a fresh 25.00 mL sample of $[Co(NH_3)_4Br_2]Br$ after all conductivity changes have occurred?

23.104 The total concentration of Ca^{2+} and Mg^{2+} in a sample of hard water was determined by titrating a 0.100 L sample of the water with a solution of $EDTA^{4-}$. The $EDTA^{4-}$ chelates the two cations:

$$Mg^{2+} + [EDTA]^{4-} \longrightarrow [Mg(EDTA)]^{2-}$$
$$Ca^{2+} + [EDTA]^{4-} \longrightarrow [Ca(EDTA)]^{2-}$$

It requires 31.5 mL of 0.0104 *M* $[EDTA]^{4-}$ solution to reach the end point in the titration. A second 0.100 L sample was then treated with sulfate ion to precipitate Ca^{2+} as calcium sulfate. The Mg^{2+} was then titrated with 18.7 mL of 0.0104 *M* $[EDTA]^{4-}$. Calculate the concentrations of Mg^{2+} and Ca^{2+} in the hard water in mg/L.

23.105 Carbon monoxide is toxic because it binds more strongly to the iron in hemoglobin (Hb) than does O_2, as indicated by these approximate standard free-energy changes in blood:

$$Hb + O_2 \longrightarrow HbO_2 \quad \Delta G^\circ = -70\ kJ$$
$$Hb + CO \longrightarrow HbCO \quad \Delta G^\circ = -80\ kJ$$

Using these data, estimate the equilibrium constant at 298 K for the equilibrium

$$HbO_2 + CO \rightleftharpoons HbCO + O_2$$

23.106 The value of Δ for the $[MoI_6]^{3-}$ complex is 198.58 kJ/mol. Calculate the expected wavelength of the absorption corresponding to promotion of an electron from the lower energy to the higher-energy *d*-orbital set in this complex. Should the complex absorb in the visible range?

23.107 A Zn electrode is immersed in a solution that is 1.00 *M* in $[Zn(NH_3)_4]^{2+}$ and 1.00 *M* in NH_3. When the cathode is a standard hydrogen electrode, the emf of the cell is found to be +1.04 V. What is the formation constant for $[Zn(NH_3)_4]^{2+}$?

Design an Experiment

Following a procedure found in a scientific paper, you go into the lab and attempt to prepare crystals of dichlorobis(ethylenediamine) cobalt(III) chloride. The paper states that this compound can be made by reacting $CoCl_2 \cdot 6\,H_2O$, an excess of ethylenediamine, O_2 from the air (which acts as an oxidizing agent), water, and concentrated hydrochloric acid. At the end of the reaction, you filter off the solution and are left with a green, crystalline product. (**a**) What experiment(s) could you perform to confirm that you have prepared $[CoCl_2(en)_2]Cl$ and not $[Co(en)_3]Cl_3$? (**b**) How could you verify that cobalt was present as Co^{3+} and determine the spin state of the cobalt complex in your product? (**c**) How many geometric isomers exist for $[CoCl_2(en)_2]Cl$? How could you determine if your product contains a single geometric isomer or a mixture of geometric isomers? (**d**) If the product does contain a single geometric isomer how would you determine which one was present? (*Hint: You may find the information in Table 23.3 helpful.*)

24

THE CHEMISTRY OF ORGANIC COMPOUNDS

WHAT'S AHEAD

24.1 General Characteristics of Organic Molecules
24.2 An Introduction to Hydrocarbons
24.3 Structures of Alkanes
24.4 Alkane Nomenclature
24.5 Cycloalkanes
24.6 Organic Functional Groups
24.7 Reactions of Alkanes

24.1 General Characteristics of Organic Molecules



We are all familiar with how chemical substances can influence our health and behavior. Aspirin, also known as acetylsalicylic acid, relieves aches and pains. The caffeine that is in coffee and tea and the ethanol that is in wine and beer are well-known molecules that, at proper doses, give us pleasure. Spices contain a host of molecules such as capsaicin (in chili peppers) and vanillin (in the vanilla bean). Other plant-derived compounds include quinine, for treating malaria, and taxol, for treating many cancers. All of these compounds are based on carbon.

Over 20 million carbon-containing compounds are known, and approximately 90% of the new compounds synthesized each year contain carbon. The study of compounds of carbon constitutes a branch of chemistry called organic chemistry.

The term organic chemistry arose from the eighteenth-century belief that organic compounds could only be formed by living systems. This idea was disproved in 1828 when the German chemist Friedrich Wöhler synthesized urea (H_2NCONH_2), an organic substance found in the urine of mammals, by heating the inorganic substance ammonium cyanate (NH_4OCN).

By the end of this section, you should be able to:

- Appreciate the general structure of organic molecules

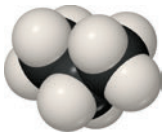
What is it about carbon that leads to the tremendous diversity of its compounds and allows them to play such a diverse role in biology and industry? Let's consider some general features of organic molecules and, as we do so, review principles we learned in earlier chapters.

The Structure of Organic Molecules

Because carbon has four valence electrons ([He]$2s^2 2p^2$), it forms four bonds in virtually all its compounds. When all four bonds are single bonds, the electron pairs are disposed in a tetrahedral arrangement. In the hybridization model, the carbon 2*s* and 2*p* orbitals are then sp^3 hybridized.

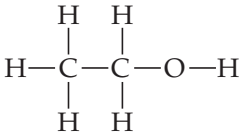
Although it is only a model, this approach has been used widely to describe qualitatively both structure and reactivity of organic compounds. When there is one double bond, the arrangement is trigonal planar (and modelled as sp^2 hybridization). With a triple bond, it is linear (and modelled as *sp* hybridization). Examples are shown in **Figure 24.1**.

Almost every organic molecule contains C—H bonds. Because the valence shell of H can hold only two electrons, hydrogen forms only one covalent bond. As a result, hydrogen atoms are always located on the surface of organic molecules whereas the C—C bonds form the backbone, or skeleton, of the molecule, as in the propane molecule:

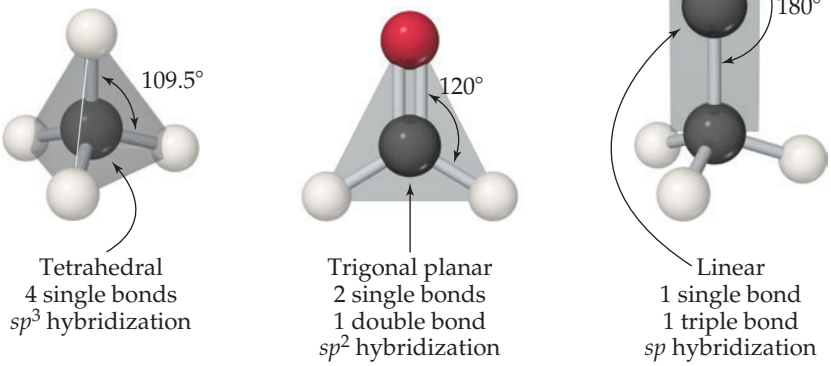


The Stabilities of Organic Molecules

Carbon forms strong bonds with a variety of elements, especially H, O, N and the halogens. Carbon also has an exceptional ability to bond to itself, forming a variety of molecules made up of chains or rings of carbon atoms. Most reactions with low or moderate activation energy begin when a region of high electron density on one molecule encounters a region of low electron density on another molecule. The regions of high electron density may be due to the presence of a multiple bond or to the more electronegative atom in a polar bond. Because of their strength and lack of polarity, both C—C single bonds and C—H bonds are relatively unreactive and form a stable base for the organic molecule. To understand the implications of these facts better, consider ethanol:



▼ Figure 24.1 Carbon geometries. The three common geometries around carbon are tetrahedral as in methane (CH_4), trigonal planar as in formaldehyde (CH_2O) and linear as in acetonitrile (CH_3CN). Notice that in all cases each carbon atom forms four bonds.



The differences in the electronegativity values of C (2.5) and O (3.5) and of O and H (2.1) indicate that the C—O and O—H bonds are quite polar while the C—H bond is only slightly polar and the C—C bond is non-polar. Thus many reactions of ethanol involve the C—O and O—H bonds while the hydrocarbon portion of the molecule remains intact. A group of atoms such as the C—O—H group, which determines how an organic molecule reacts (in other words, how the molecule *functions*), is called a **functional group**. As we progress through the chapter we will see that the functional group is the center of reactivity in an organic molecule.

Self-Assessment Exercise

24.1 Consider the following average bond enthalpies: C—C (348 kJ/mol), N—N (163 kJ/mol), O—O (146 kJ/mol), S—S (266 kJ/mol). Which element is most likely to form stable compounds containing chains of atoms of that element?

(a) Carbon
(b) Nitrogen
(c) Oxy

Exercises

24.2 List five elements that are commonly found in organic compounds. Which ones are more electronegative than carbon?

24.3 Organic compounds containing C—O and C—Cl bonds are more reactive than simple alkane hydrocarbons. Considering the comparative values of C—H, C—C, C—O and C—Cl bond energies (Table 8.4), why is this so?

Answers to Self-Assessment Exercise

24.1 (a)

24.2 | An Introduction to Hydrocarbons



One of the most important issues of our time is global warming. The sun heats the surface of the Earth during daytime and energy is radiated back into space at night. Nitrogen and oxygen, which make up 99% of our atmosphere, are transparent to infrared radiation and allow this heat loss to occur. However, other gases, most notably water vapor, methane, and carbon dioxide, absorb infrared radiation, trapping the heat in the atmosphere. These are called greenhouse gases. Since the industrial revolution, there has been a 50% increase in the amount of carbon dioxide released into the atmosphere with a consequent warming of the planet. As our standard of living rises, our demand for energy increases. In 2018, fossil fuels (coal, oil, and gas) accounted for 80% of the world's energy production. Mitigation strategies include switching to renewable energy sources, increasing energy efficiency in power production, transportation and manufacturing, and capturing greenhouse gases from the atmosphere. We all have a role to play in reducing our 'carbon footprint' and understanding some of the chemistry behind many of our modern materials can inform our choices. Organic chemistry plays a major part in this and we examine the basics of it over the next nine chapters.

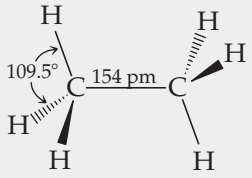
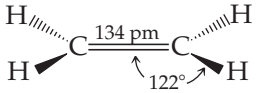
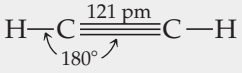
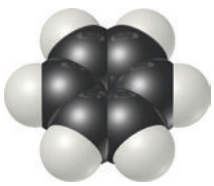
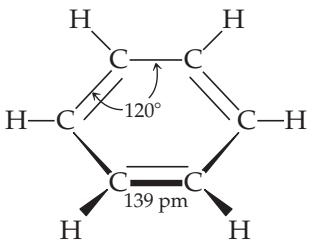
By the end of this section, you should be able to:

- Understand the general composition of the simplest of organic molecules, the hydrocarbons.
- Appreciate the link between molecular weight and a physical property such as melting point.

Because carbon compounds are so numerous, it is convenient to organize them into families that have structural similarities. Compounds that contain *only* carbon and hydrogen are called **hydrocarbons**. The key structural feature of hydrocarbons (and of most organic substances) is the presence of stable carbon–carbon bonds. Carbon is the only element capable of forming stable, extended chains of atoms bonded through single, double or triple bonds.

Hydrocarbons can be divided into four types, depending on the kinds of carbon–carbon bonds in the molecules. Table 24.1 shows an example of each type.

TABLE 24.1 The four hydrocarbon types

Type	Classification	Example			
Alkane	Saturated	Ethane	CH_3CH_3		
Alkene	Unsaturated	Ethene	$CH_2{=}CH_2$		
Alkyne	Unsaturated	Ethyne	$CH{\equiv}CH$		
Aromatic	Unsaturated	Benzene	C_6H_6		

These hydrocarbons are either *aliphatic* (from the Greek work *aleiphar*, meaning oil; these include alkanes, alkenes, and alkynes) or *aromatic*, and are classified as either saturated or unsaturated. In this chapter, we will explore aliphatic hydrocarbons that are **saturated** (that is, all carbons are bound to four other atoms and there are no double or triple bonds). Such hydrocarbons are called **alkanes**. We will look at the other classes of hydrocarbons in subsequent chapters.

Alkanes

The three simplest alkanes, which contain one, two and three carbon atoms, are methane (CH_4), ethane (C_2H_6) and propane (C_3H_8), respectively. These are illustrated in Table 24.2.

The names of the first 10 *straight-chain* alkanes are given in Table 24.3. You will notice that each aliphatic alkane has a name that ends in *-ane*. This suffix is true of all alkanes as it denotes this class of organic compounds. Alkanes longer than those described in Table 24.3 can be made by adding further CH_2 groups to the skeleton of the molecule.

TABLE 24.2 The simplest alkanes

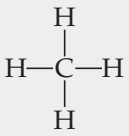
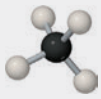
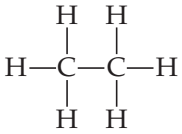
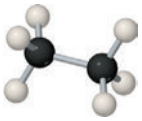
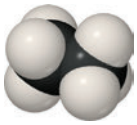
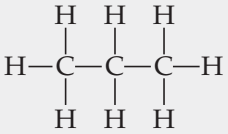
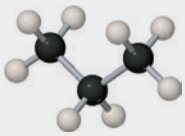
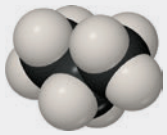
Common name	Structural formula	Condensed structural formula	Ball-and-stick model	Space-filling representation
Methane		CH_4		
Ethane		CH_3CH_3		
Propane		$CH_3CH_2CH_3$		

TABLE 24.3 First 10 members of the straight-chain alkane series

Name	Molecular formula	Condensed structural formula	Boiling point (°C)
Methane	CH_4	CH_4	−161
Ethane	C_2H_6	CH_3CH_3	−89
Propane	C_3H_8	$CH_3CH_2CH_3$	−44
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	−0.5
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	36
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	68
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	98
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	125
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	151
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	174

Notice the trend within the molecular formulas in the second column of Table 24.3. For n carbon atoms ($n = 1, 2, 3 \ldots$) there are $(2n + 2)$ hydrogen atoms, so alkanes have the general formula:

$$C_nH_{2n+2} \qquad [24.1]$$

The condensed structural formula reveals the way in which atoms are bonded to one another but does not require us to draw in all the bonds. It is one of the most useful ways of representing organic molecules.

Applications and Physical Properties of Alkanes

Alkanes are very important in our society, whether they are gaseous, liquid or solid. Many of their common applications, illustrated in **Figure 24.2**, will be familiar to you. Methane, a colorless and odorless gas, is the major component of natural gas and is used for home heating and in gas stoves and water heaters. Propane is the major component of the bottled gas used for home heating and cooking in areas where natural gas is not available. Butane is used in disposable lighters and in fuel canisters for gas camping stoves and lanterns. Alkanes with 5–12 carbon atoms per molecule (C_5—C_{12}) are found in petrol. This difference in application between different groups of alkanes is a result of their physical properties, such as boiling point (bp) and melting point (mp), which determine whether the alkane is a solid, liquid or gas at room temperature.

Homologous Series

An *n*-alkane, sometimes called a "*normal*-alkane" is an alkane in which all of the carbon atoms are linked in one continuous chain. A series of compounds, like the *n*-alkanes, that differ only by the number of methine (–CH_2–) units is called a **homologous series**. Compounds in such a series possess similar chemical properties and show a gradation in physical properties as a result of increase in molecular size and mass (Table 24.3). The individual members of this series are called *homologues*. For example, pentane, decane, and octane are homologues. Physical properties in a homologous series, such as melting and boiling points or density, tend to increase smoothly with an increasing number of carbon atoms.

The difference in melting points and boiling points of hydrocarbons, including alkanes, result from *dispersion forces*. The larger the alkane molecules are, the more extensive these dispersion forces become. Hence, hydrocarbons tend to become less volatile with increasing molar mass. As a result, hydrocarbons of very low molecular weight, such as C_2H_6 (bp = −89 °C), are gases at room temperature; those of moderate molecular weight, such as C_6H_{14} (bp = 68 °C), are liquids; and those of high molecular weight, such as $C_{22}H_{46}$ (mp = 44 °C), are solids.

Hydrocarbon molecules such as alkanes are relatively nonpolar because carbon and hydrogen do not differ greatly in their electronegativities. Thus, alkanes dissolve readily in nonpolar solvents but are almost completely insoluble in water.

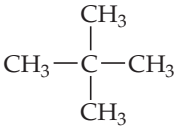


(a) (b) (c)

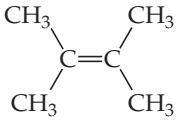
▶ **Figure 24.2 Applications of alkanes.** Alkanes are very important in our modern society, whether gaseous, liquid or solid. (a) Methane is used as a source of heat. (b) Butane is commonly used in lighter fluid. (c) Candles are traditionally made from waxes, which are long-chain alkanes.

Self-Assessment Exercises

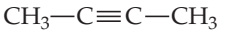
24.4 Which of the following structures represents a saturated aliphatic hydrocarbon?



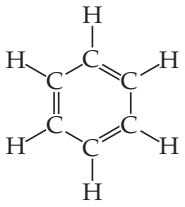
(a)



(b)



(c)



(d)

24.5 Which condensed structural formula represents the substance with the highest melting point?

(a) $CH_3CH_2CH_3$
(b) $CH_3CH_2CH_2CH_2CH_3$
(c) $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Exercises

24.6 What can we tell about a compound when we know the empirical formula? What additional information is conveyed by the molecular formula? By the structural formula? Explain in each case using CH_2 as an empirical formula.

24.7 **(a)** What is a hydrocarbon? **(b)** Are all alkanes hydrocarbons? **(c)** Write the structural formula for propane (C_3H_8). **(d)** Butane is an alkane containing four carbon atoms in a line. Write a structural formula for this compound and determine its molecular and empirical formulas.

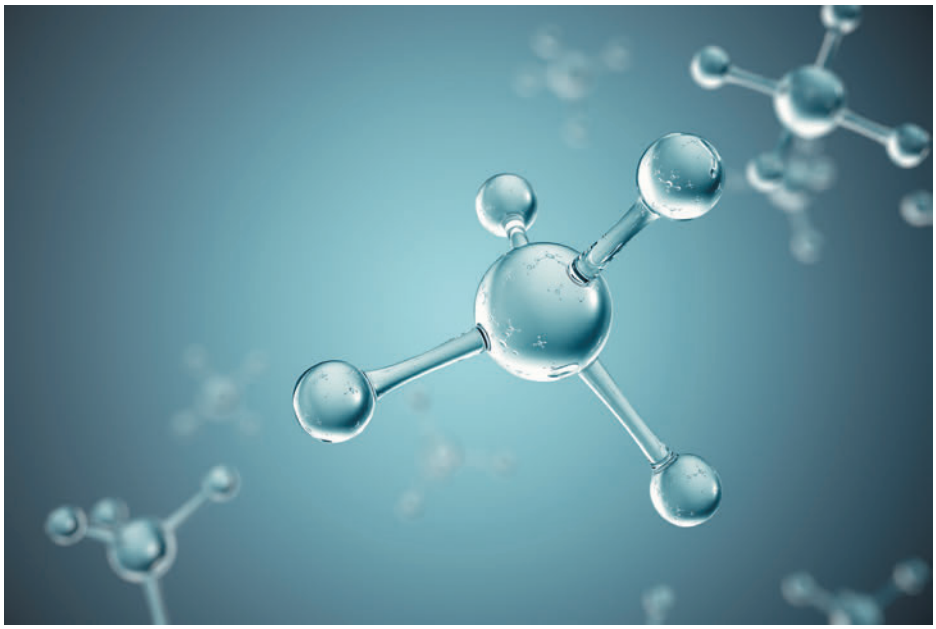
24.8 **(a)** What ending is used for the names of alkanes? **(b)** *Undecane* is an alkane with all its 11 carbon atoms in one chain. It is used as an attractant to cockroaches. Write a structural formula for this compound and determine its molecular and empirical formulas.

24.9 Rank the following in order of the strength of the London dispersion forces between two or more molecules of the same compound: $CH_3(CH_2)_4CH_3$ (hexane); CH_3CH_2OH (ethanol); $CH_3(CH_2)_{13}CH_2COOH$ (palmitic acid).

Answers to Self-Assessment Exercises

24.4 (a) **24.5** (c)

24.3 Structures of Alkanes



So much of understanding in chemistry is based on a blend of the macroscopic, the microscopic, and the symbolic. This is particularly true as we investigate the structure of alkanes. For example, we may seek to explain trends in the boiling points of alkanes. Our starting point is the macroscopic—our observation of the temperature of a boiling liquid. This depends on the microscopic—the type, number, and arrangement of atoms that constitute the alkane; and is aided by the symbolic—how we represent the atoms and the bonding between them.

CHEMISTRY AND LIFE Petroleum Products

Petroleum, also called crude oil, is a complex mixture of organic compounds, mainly hydrocarbons, with smaller quantities of other organic compounds containing nitrogen, oxygen or sulfur. The usual first step in the refining of petroleum is to separate it on the basis of boiling point as shown in **Table 24.4**. Because petrol is the most commercially important of these separated mixtures, called *fractions*, various processes are used to maximize its yield.

Petrol is a blend of volatile hydrocarbons containing alkanes. In a car engine a mixture of air and petrol vapor is compressed by a piston and then ignited by a spark plug. The burning of petrol vapor should create a strong, smooth expansion of gas, forcing the piston outward and imparting force along the drive shaft of the engine. If the petrol vapor burns too rapidly, the piston receives a single hard slam rather than a strong, smooth push. The result is a "knocking" or "pinging" sound and a reduction in the efficiency with which energy produced by the combustion is converted to work.

The octane number of a petrol blend (**Figure 24.3**) is a measure of its resistance to knocking. Petrols with a high octane number burn more smoothly and are thus more effective fuels. The octane number of unleaded petrol is obtained by comparing its knocking characteristics with those of 2,2,4-trimethylpentane (also known as isooctane) and heptane. 2,2,4-Trimethylpentane is assigned an octane number of 100, and heptane is assigned zero. Petrol with the same knocking characteristics as a mixture of 90% isooctane and 10% heptane has an octane rating of 90.

The petrol obtained directly from fractionation of petroleum contains mainly straight-chain hydrocarbons and has an octane number of around 50. It is therefore subjected to processes such as *cracking*, which convert the straight-chain alkanes into more desirable branched-chain and aromatic hydrocarbons (**Figure 24.4**). Cracking is also used to convert some of the less volatile kerosene and fuel-oil fractions into compounds with lower molecular weights that are suitable for use as motor fuel. The octane rating of petrol is also increased by adding aromatic compounds such as toluene ($C_6H_5CH_3$) and oxygenated hydrocarbons such as ethanol (CH_3CH_2OH).



▲ **Figure 24.3 Octane rating.** The octane rating of petrol measures its resistance to knocking when burned in an engine. The octane rating of this petroleum product is 89, as shown on the face of the pump.



▲ **Figure 24.4 Fractional distillation.** Petroleum is separated into fractions by distillation and subjected to catalytic cracking in a refinery.

TABLE 24.4 Hydrocarbon fractions from petroleum

Fraction	Carbon-chain lengths	Boiling-point range (°C)	Uses
Gas	C_1 to C_5	−160 to 30	Gaseous fuel, production of H_2
Petrol	C_5 to C_{12}	30 to 200	Motor fuel
Kerosene, fuel oil	C_{12} to C_{18}	180 to 400	Diesel fuel, furnace fuel, cracking
Lubricants	C_{16} and up	350 and up	Lubricants
Paraffins	C_{20} and up	Low melting solids	Candles
Asphalt	C_{36} and up	Gummy residues	Surfacing roads

By the end of this section, you should be able to

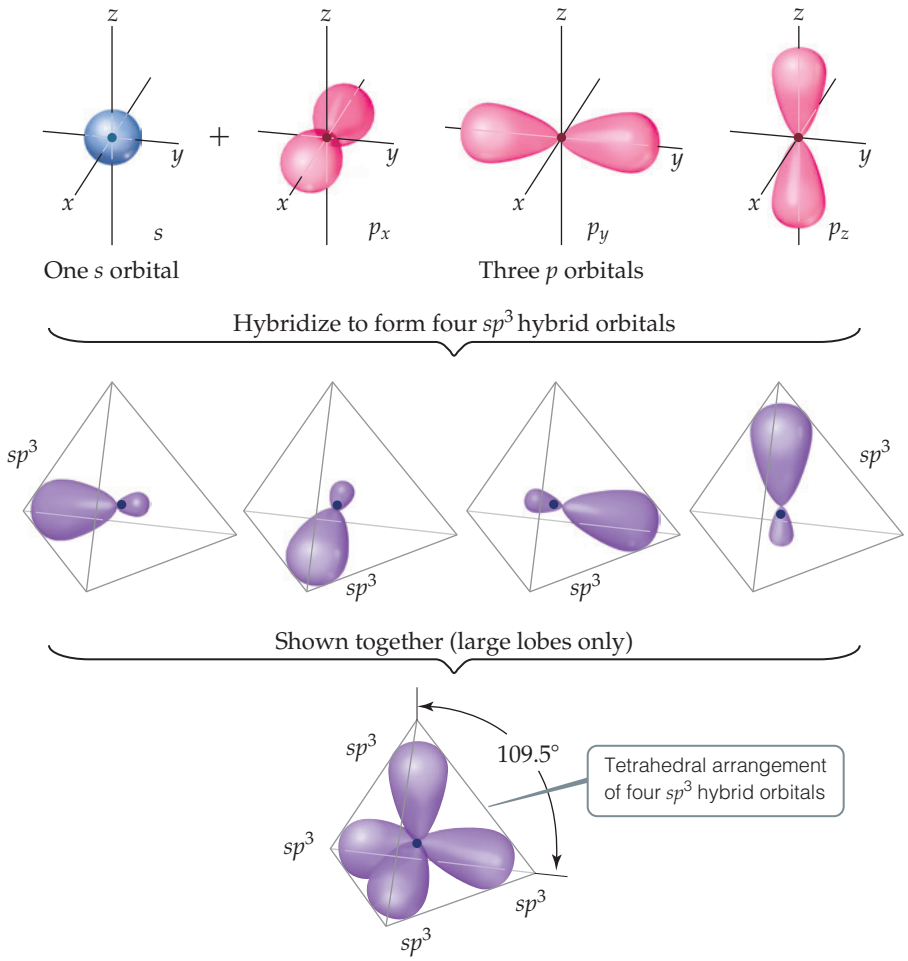
- Identify conformational isomers and recognize they are associated with different relative energies.
- Understand that alkanes with four or more carbon atoms give rise to constitutional isomers.

Recall that earlier in the text we described hybridization as the process of mixing atomic orbitals in a mathematical operation. The newly formed orbitals, called *hybrid orbitals,* are based on the atomic orbitals that constitute them (**Figure 24.5**). Hybridization and valence-bond theory are used predominantly by organic chemists to describe the bonding outcomes for carbon. In essence, the hybrid orbitals are defined by the geometry of the bonds formed by carbon that influence the overall shape and structure of the molecule. Any carbon bearing four single bonds must be tetrahedral and, hence, sp^3 hybridized.

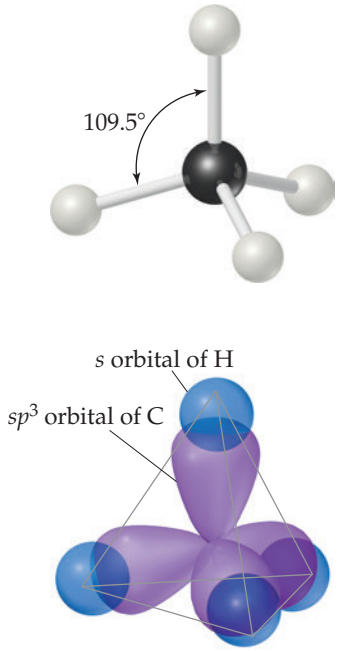
The tetrahedral geometry leads to bond angles of 109.5°, which is the largest possible separation for the four one-electron sp^3 hybrid orbitals in free space. By way of example, the three-dimensional structure of methane can be represented as shown in **Figure 24.6**.

A covalent bond that is formed by the end-to-end interaction of two one-electron orbitals (either atomic, hydridized or a mixture of both), as described in Figure 24.6, is called a sigma (σ) bond.

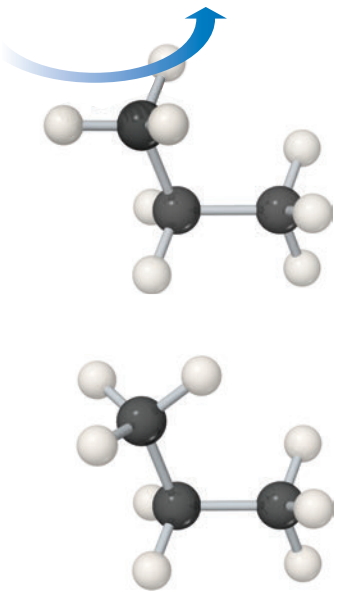
Go Figure How many atomic orbitals contribute to form the four sp^3 hybrid orbitals?



▲ **Figure 24.5 Formation of sp^3 hybrid orbitals.** One *s* orbital and three *p* orbitals can hybridize to form four equivalent sp^3 hybrid orbitals. The large lobes of the hybrid orbitals point towards the corners of a tetrahedron.



▲ **Figure 24.6 Bonds about carbon in methane.** This tetrahedral molecular geometry is found around all carbons in alkanes.



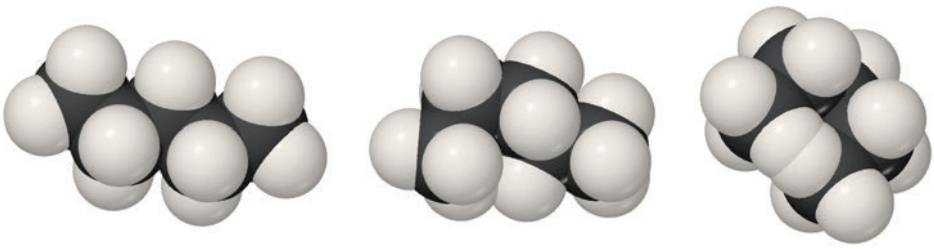
▲ **Figure 24.7 Rotation about a C–C bond occurs easily and rapidly in all alkanes.**

Alkane Shape and Conformations

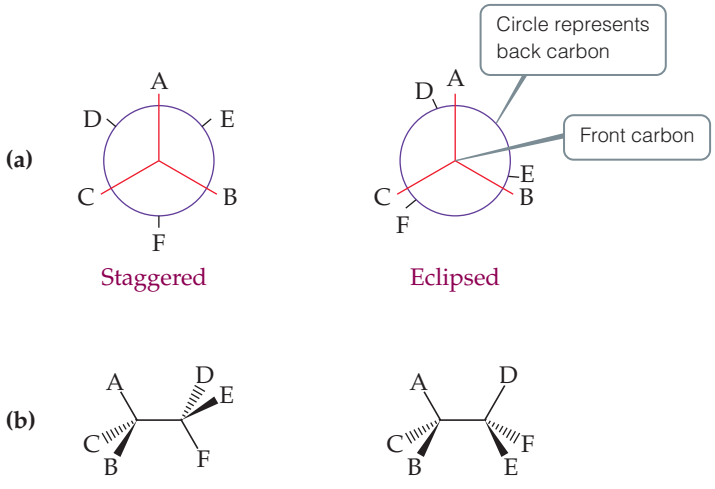
Although organic molecules are drawn in a static way, remember that they are always dynamic. One of the properties of alkanes is their ability to change shape continuously (Figure 24.7). The three-dimensional arrangement of atoms in a molecule that results from rotation about a single bond is known as a **conformation**. When different conformations of a molecule are compared, they are said to be **isomers** of the same structure. Isomers are two or more compounds with the same molecular formula but different three-dimensional structure. Figure 24.8 illustrates some of the **conformational isomers** (or *conformers*) of pentane. The **Newman projection** shown in Figure 24.9 is a useful way of viewing a molecule and for gaining an idea of its energy relative to other possible conformers. Newman projections are derived by imagining you are looking along the carbon–carbon bond being rotated and comparing the positions of the three groups attached to the front carbon atom with those attached to the back carbon atom.

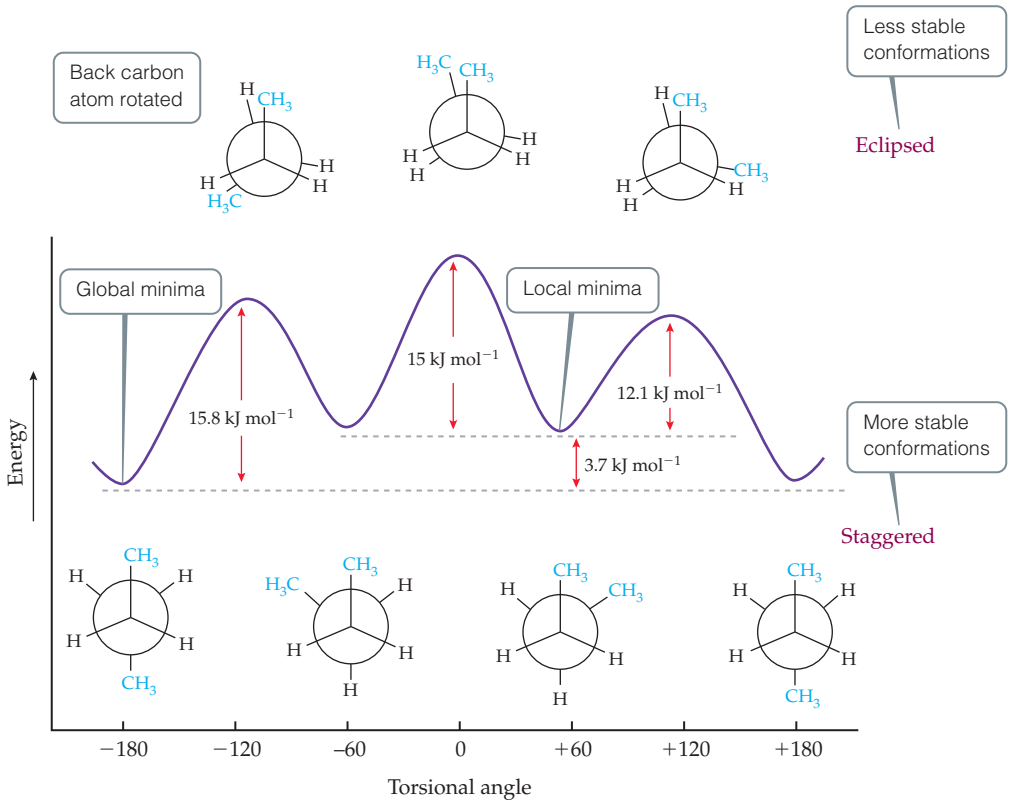
The number of conformational isomers within alkanes containing two or more carbon atoms is infinite because of free rotation about any of the carbon–carbon bonds. Each conformer, however, has a certain amount of energy associated with it. In this regard, there are two conformational isomers that are readily identifiable and usually represent the low and high energy forms. They are called **staggered** and **eclipsed**, and they define the energetic limits of all conformations. Often, a **Newman projection** is used to represent conformers. Here, the two bonded carbon atoms about which rotation will occur are imagined superimposed on one another with the front carbon atom represented as a point and the back carbon atom represented as a circle from which the other bonds associated with these carbon atoms radiate (Figures 24.9 and 24.10). Staggered conformations represent the lowest energy conformation, whereas eclipsed conformations are higher in energy. The difference in energy between the two states is due to added *non-bonded interaction* strain in the eclipsed conformation. This strain is derived from both **steric** (van der Waals interactions) and *torsional* effects, which are a resistance to twisting of the bonds. The magnitude depends on how close neighboring groups become and on the size of the two neighboring groups. For example, hydrogen atoms on adjacent carbons, as in ethane, have minimal but still measurable strain (approximately 12.1 kJ/mol separates the low and high energy conformers).

▶ **Figure 24.8 Conformers of pentane.** Rotation about carbon–carbon single bonds can result in noticeable changes in molecular shape.



▶ **Figure 24.9 (a) Newman projection.** In the staggered representation the groups attached to the adjacent carbon atoms are arranged as far apart as possible. The eclipsed conformation causes the groups on the adjacent carbon atoms to align one behind the other. By convention, the groups are drawn slightly offset so all may be seen. **(b) Sawhorse representation.** Here the molecule is represented from the side with the bond being rotated viewed as horizontal.





◀ Figure 24.10 Relative energy differences between staggered and eclipsed conformations of butane. Newman projections are used to illustrate the different conformers upon rotation about the C2—C3 bond.

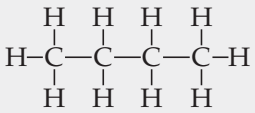
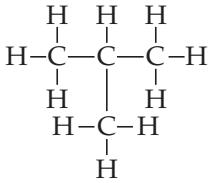
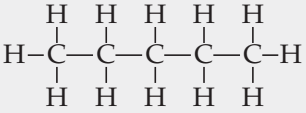
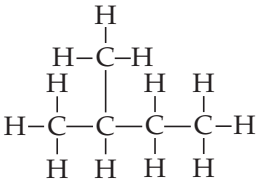
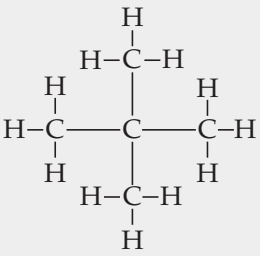
With larger groups, such as bromo, iodo or methyl groups, the strain, and, hence, energy difference, is larger. The vast majority of bonds in acyclic aliphatic alkanes are found in a staggered conformation. The eclipsed conformation represents the activation barrier between two staggered conformations.

Let's now investigate the strain effects for rotation about C2—C3 in butane (Figure 24.10). We will consider the staggered conformation of butane with the lowest energy as a useful starting point. This would be the case where the two methyl (CH_3) groups that terminate the butane chain are as far apart as possible. Make sure at this point that you can identify that this is a Newman projection for butane. Rotation about C2—C3 by 60° yields the first eclipsed conformer. Non-bonding interactions between the methyl groups and hydrogen atoms on the adjacent carbon atom in this eclipsed form strain the molecule making it a slightly less stable arrangement of atoms (by 15.8 kJ/mol) and giving a higher-energy conformer. A further rotation of 60° relieves the strain somewhat but, in doing so, the two methyl groups are able to interact weakly making it less stable by 3.7 kJ/mol than the staggered conformer we started with, so that a *local* energy minimum is reached. Rotation of the C2—C3 bond by another 60° causes the two methyl groups to interact strongly, forming the conformer with the highest relative energy (15.8 kJ/mol above our starting point). Note that, although the hydrogen atoms also contribute to the overall energy, it is the methyl interactions that dominate in this case. Any further rotation from this point mirrors the structures that have already been discussed. Finally, the methyl groups are again opposed, resulting once more in the orientation that yields the minimum energy conformation (sometimes referred to as the *global* minimum).

Constitutional/Structural Isomers

The alkanes listed in Table 24.3 are *straight-chain aliphatic hydrocarbons* because all the carbon atoms are joined in a continuous chain. Alkanes consisting of four or more carbon atoms can also have branched chains and are called *branched-chain alkanes*. **Table 24.5** shows space-filling models, full structural formulas and condensed structural formulas for all the possible structures of alkanes containing four or five carbon atoms. Note that the molecular formula for a branched alkane *is the same* as for a straight-chain alkane with the same number of carbon atoms.

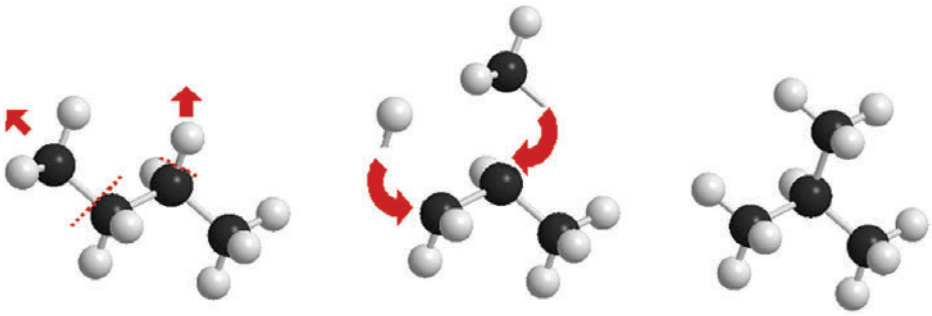
TABLE 24.5 Isomers of C_4H_{10} and C_5H_{12}

Systematic name (common name)	Structural formula	Condensed structural formula	Space-filling model	Melting point (°C)	Boiling point (°C)
Butane (*n*-butane)		$CH_3CH_2CH_2CH_3$		−138 °C	−0.5 °C
2-Methylpropane (isobutane)		$CH_3{-}CH(CH_3){-}CH_3$		−159 °C	−12 °C
Pentane (*n*-pentane)		$CH_3CH_2CH_2CH_2CH_3$		−130 °C	+36 °C
2-Methylbutane (isopentane)		$CH_3{-}CH(CH_3){-}CH_2{-}CH_3$		−160 °C	+28 °C
2,2-Dimethylpropane (neopentane)		$C(CH_3)_4$		−16 °C	+9 °C

As we saw in Chapter 23, compounds with the same molecular formula but with different bonding arrangements (and hence different structures) are called **structural** or **constitutional isomers**).

This is easily envisaged if you think of alkanes as a series of building blocks made up of C, CH, CH_2 and CH_3 groups. Figure 24.11 demonstrates the principle. Converting one constitutional isomer into another requires the breaking and making of bonds (unlike conformational isomers). Consequently, constitutional isomers are not easily interconverted at room temperature and may be separated from one another.

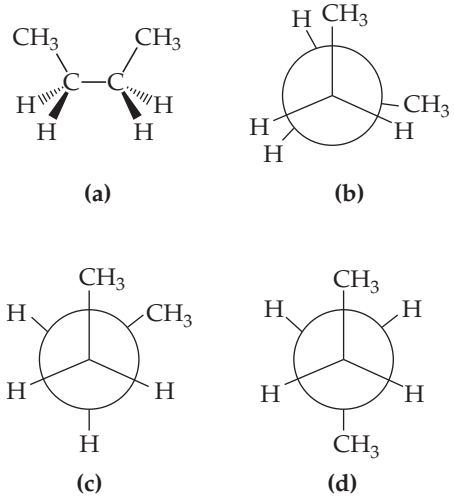
Constitutional isomers of a given alkane differ slightly from one another in physical properties. Note the melting and boiling points of the constitutional isomers of butane and pentane given in Table 24.5. These melting and boiling points are a measure of the energy needed to overcome weak and favourable interactions that give rise to the solid or liquid properties, respectively. The variation in melting and boiling points for a set of constitutional isomers is a result of the subtleties of molecular interactions. The number of possible constitutional isomers increases rapidly with the number of carbon atoms in the alkane. There are 18 possible constitutional isomers with the molecular formula C_8H_{18}, for example, and 75 possible isomers with the molecular formula $C_{10}H_{22}$.



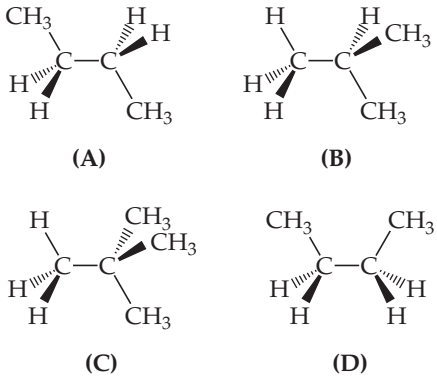
◀ **Figure 24.11 Constitutional isomers of butane.** If we were to remove a terminal (end) carbon unit in butane and attach it to the middle remaining carbon, a structure different from the initial straight chain of butane would be obtained. The connectivity changes, but the molecular formula is exactly the same. There are still four carbons within the molecule and, if we were to complete the structure again, there would still be 10 hydrogens to include. The two structures differ not only in their shape but also in their physical and chemical properties.

Self-Assessment Exercises

24.10 Which structure represents the lowest energy conformation of butane, C_4H_{10}?



24.11 What is the relationship between the following pairs of structures?



(a) Structures **A** and **B** are constitutional isomers.
(b) Structures **A** and **C** are conformational isomers.
(c) Structures **A** and **D** are constitutional isomers.

Exercises

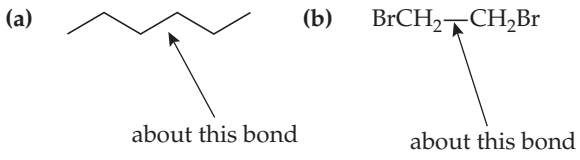
24.12 Draw representations of the following orbitals: s, p_x, p_y, p_z. How do they relate to an sp^3 hybrid orbital?

24.13 How many constitutional isomers are possible for hexane (C_6H_{14})? Draw them.

24.14 Distinguish between constitutional and conformational isomers using butane as an example.

24.15 Draw Newman projections for the most stable and least stable conformers of propane.

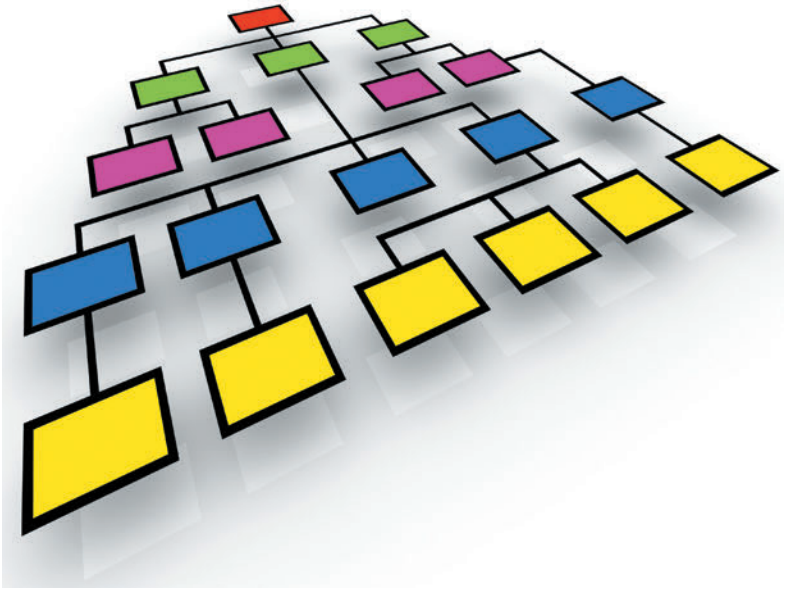
24.16 Using Newman projections, draw the most stable staggered form of the following compounds:



Answers to Self-Assessment Exercises

24.10 (d) **24.11** (a)

24.4 | Alkane Nomenclature



We can imagine a hierarchy of information which gives increasing detail about a substance—the empirical formula being the most basic bit of information all the way up to a name that uniquely describes a compound.

The need for a common "language" to name molecules was recognized early in the history of organic chemistry. In 1892, the International Union of Chemistry met in Geneva, Switzerland, to formulate a set of rules for systematically naming organic substances. Since that time, the task of updating the rules for naming all compounds has fallen to the International Union of Pure and Applied Chemistry (IUPAC). Chemists everywhere, regardless of their nationality or political affiliation, subscribe to a common system for naming compounds. This naming process, called **nomenclature**, provides a systematic way to define unambiguously which atoms are bonded to one another within a molecule and to be able to communicate the structure of a compound in writing.

By the end of this section, you should be able use systematic nomenclature to:

- Convert between the name and structure of a simple alkane.

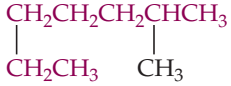
Constitutional isomerism complicates how we might describe organic molecules since a description based solely on molecular formulas is not nearly enough. Apart from ethane and propane, a number of different structures can be obtained from the same molecular formula. All of this means that we need a systematic means of naming organic compounds.

The IUPAC names for the isomers of butane and pentane are given in Table 24.5. These names, as well as those of other organic compounds, have three parts to them:

Prefix – Parent – Suffix

The following steps summarize the procedures used to arrive at the names of alkanes, all of which end with the suffix *-ane*. The prefix relates to the number, type and position of substituents (for example, the prefix 2,3-dibromo would indicate the compound contains two bromine atoms attached at positions 2 and 3). The parent name indicates the number of carbon atoms within the longest chain (for example, *eth* = two carbons, *pent* = five carbons). We use a similar approach to writing the names of other organic compounds and we develop a further understanding of organic nomenclature in Chapters 25–31.

In order to understand the steps to derive an appropriate nomenclature, let's examine how we would name the following compound:

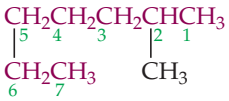


1. ***Find the longest continuous chain of carbon atoms and use the name of this chain (Table 24.3) as the base name of the compound.***

   Because this compound's longest chain is made up of seven C atoms (colored), it is named a substituted heptane (see Table 24.3). Groups attached to the main chain are called *substituents* because they are in substitution of a hydrogen atom on the main chain.

2. ***Number the carbon atoms in the longest chain, beginning with the end of the chain that is nearest to a substituent.***

   In our example, we number the C atoms from the right because that places the CH_3 substituent on the second C atom of the chain; if we number from the lower left, the CH_3 would be on the sixth C atom. The chain is numbered from the end that gives the lowest combined number for all substituent positions.



3. ***Name and give the location of each substituent group.***

   A substituent group that is formed by removing a hydrogen atom from an alkane is called an **alkyl group**. We have already been informally introduced to this nomenclature. Alkyl groups are named by replacing the *-ane* ending of the alkane name with *-yl*. Table 24.6 lists the three simplest alkyl groups.

   The name of our example is 2-methylheptane. Note the hyphen after the number. Note also that there is *no* space, comma or hyphen between methyl and heptane. The name should also allow you to draw the structure using these same three simple steps.

4. ***Where two or more substituents are present, list them in alphabetical order, ignoring multiplying prefixes.***

   Where there are two or more of the same substituent, the number of substituents of that type is indicated by a prefix: *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five)

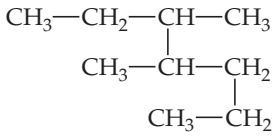
TABLE 24.6 Naming simple alkyl substituents

Substituent	Substituent name
CH_3	*methyl*
CH_3CH_2	*ethyl*
$CH_3CH_2CH_2$	*propyl*

Sample Exercise 24.1

Naming alkanes

Give the systematic name for the following alkane

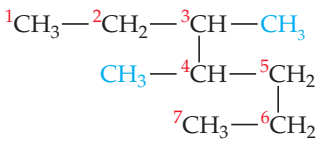


SOLUTION

Analyze We are given the condensed structural formula of an alkane and asked to give its name.

Plan Because the hydrocarbon is an alkane, its name ends in *-ane*. The name of the parent hydrocarbon is based on the longest continuous chain of carbon atoms. Branches are alkyl groups, named after the number of C atoms in the branch and located by counting C atoms along the longest continuous chain.

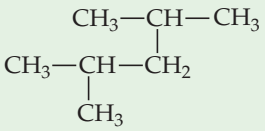
Solve The longest continuous chain of C atoms extends from the upper left CH_3 group to the lower left CH_3 group and is seven C atoms long:



The parent compound is thus heptane. There are two methyl groups branching off the main chain. Hence this compound is a dimethylheptane. To specify the location of the two methyl groups, we must number the C atoms from the end that gives the lower two numbers to the carbons bearing side chains. This means that we should start numbering at the upper left carbon. There is a methyl group on C3 and one on C4. The compound is thus 3,4-dimethylheptane.

Practice Exercise

Name the following alkane:



Sample Exercise 24.2

Writing condensed structural formulas

Write the condensed structural formula for 3-ethyl-2-methylpentane.

SOLUTION

Analyze We are asked to draw the molecular structure of an organic compound from its systematic name.

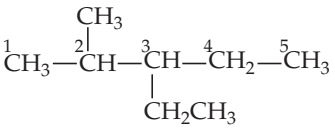
Plan First we need to determine the classification of the organic compound, then work backwards from the parent compound, adding in functionality and side groups.

Solve Because the compound's name ends in *-ane*, it is an alkane, meaning that all the carbon–carbon bonds are single bonds. The parent hydrocarbon is pentane, indicating five C atoms (Table 24.3). There are two alkyl groups specified, an ethyl group (two carbon atoms, C_2H_5) and a methyl group (one carbon atom, CH_3). Counting from left to right along the five-carbon chain, the ethyl group will be attached to the third C atom and the methyl group will be attached to the second C atom.

We begin by writing a string of five C atoms attached to each other by single bonds. These represent the backbone of the parent pentane chain:

C—C—C—C—C

We next place a methyl group on the second C and an ethyl group on the third C atom of the chain. Hydrogens are then added to all the other C atoms to make the four bonds to each saturated carbon, giving the following condensed structure:



The formula can be written even more concisely in the following style:

$$CH_3CH(CH_3)CH(CH_2CH_3)_2$$

In this formula the branching alkyl groups are indicated in parentheses.

Practice Exercise

Write the condensed structural formula for 2,3-dimethylhexane.

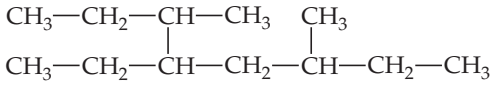
and so on. The position of each substituent is separated by a comma (for example, 2,3-dibromopentane). In the case where substituents are different, each prefix is separated from the next by a hyphen. Substituents are also listed alphabetically (ethyl, methyl, propyl and so on). Notice how the following example is named (and numbered):



for numbering because *4-ethyl-2,5-dimethylheptane* gives a lower numbering than *4-ethyl-3,6-dimethylheptane* does.

Self-Assessment Exercise

24.17 What is the systematic name of the following structure?



(a) 3-butyl-5-methylheptane
(b) 3-methyl-5-butylheptane
(c) 4-ethyl-3,6-dimethyloctane
(d) 5-ethyl-3,6-dimethyloctane

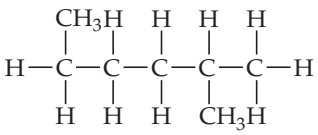
Exercises

24.18 What is the chemical formula of the propyl group?

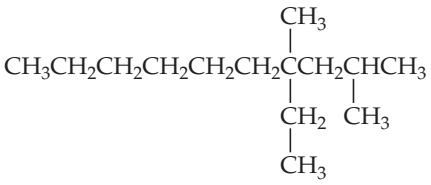
24.19 Draw all possible isomers of C_5H_{12}. Systematically name each compound.

24.20 Draw the structural formula or give the IUPAC name, as appropriate, for the following:

(a)



(b)



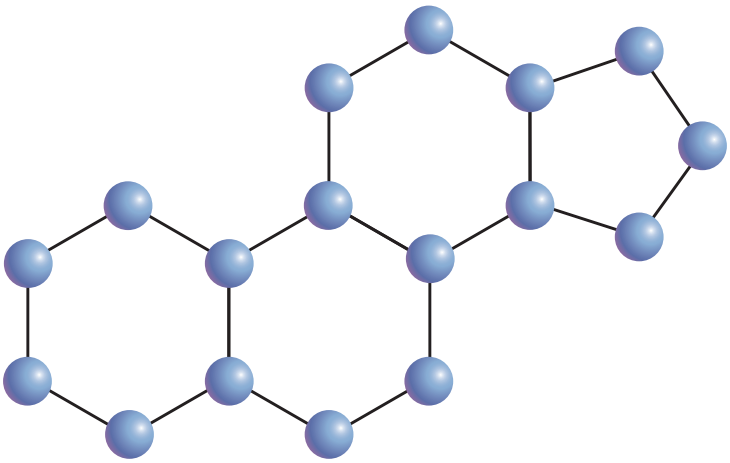
(c) 3-methylhexane
(d) 4-ethyl-2,2-dimethyloctane
(e) methylcyclohexane

24.21 What do ethane, ethanol, and ethylene have in common with respect to their nomenclature? What can you infer about the number of carbon atoms in each compound?

Answers to Self-Assessment Exercise

24.17 (c)

24.5 | Cycloalkanes



Gonane

We saw in Section 24.3 that we don't need many carbon atoms before it is possible to arrange them in a number of different ways, called constitutional isomers. Another way to arrange a chain of carbon atoms is in a ring, called a cyclic compound. For a given number of carbon atoms, the formula of the chain form and the ring form differ in the number of hydrogen atoms present, so the two forms are not classed as isomers but are distinct compounds, albeit closely related ones. The structure of gonane, with four rings fused together, is the core structure on which steroids are built, which are essential for many regulation and growth processes in living cells. By the end of this section, you should be able to

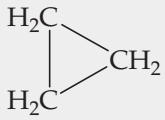
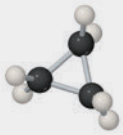
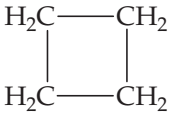
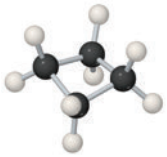
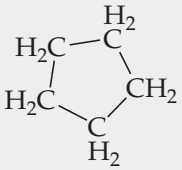
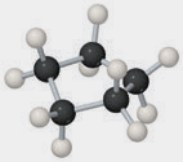
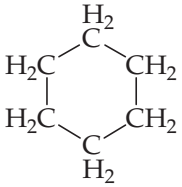
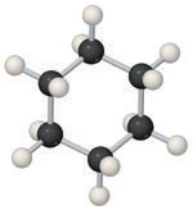
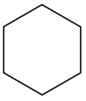
- Interpret a line drawing of a cyclic structure
- Recognize the difference between the two major conformations of cyclohexane

Hydrocarbons can form not only straight and branched chains but also rings, or cycles. Alkanes with this latter form of structure are called **cycloalkanes**. Cycloalkanes are formed by the loss of two C—H bonds and the formation of a C—C bond from the equivalent aliphatic alkane structure. As such, the general molecular formula for a cycloalkane differs from that of an alkane by two hydrogen atoms.

$$C_nH_{2n} \qquad [24.2]$$

Table 24.7 illustrates a few simple cycloalkanes. Cycloalkanes containing from three to more than 30 carbon atoms are known. The most common forms contain five- (cyclopentane) and six- (cyclohexane) membered rings. Hydrocarbon rings containing fewer than five carbon atoms are strained because the C—C—C bond angle in these

TABLE 24.7 Cycloalkanes

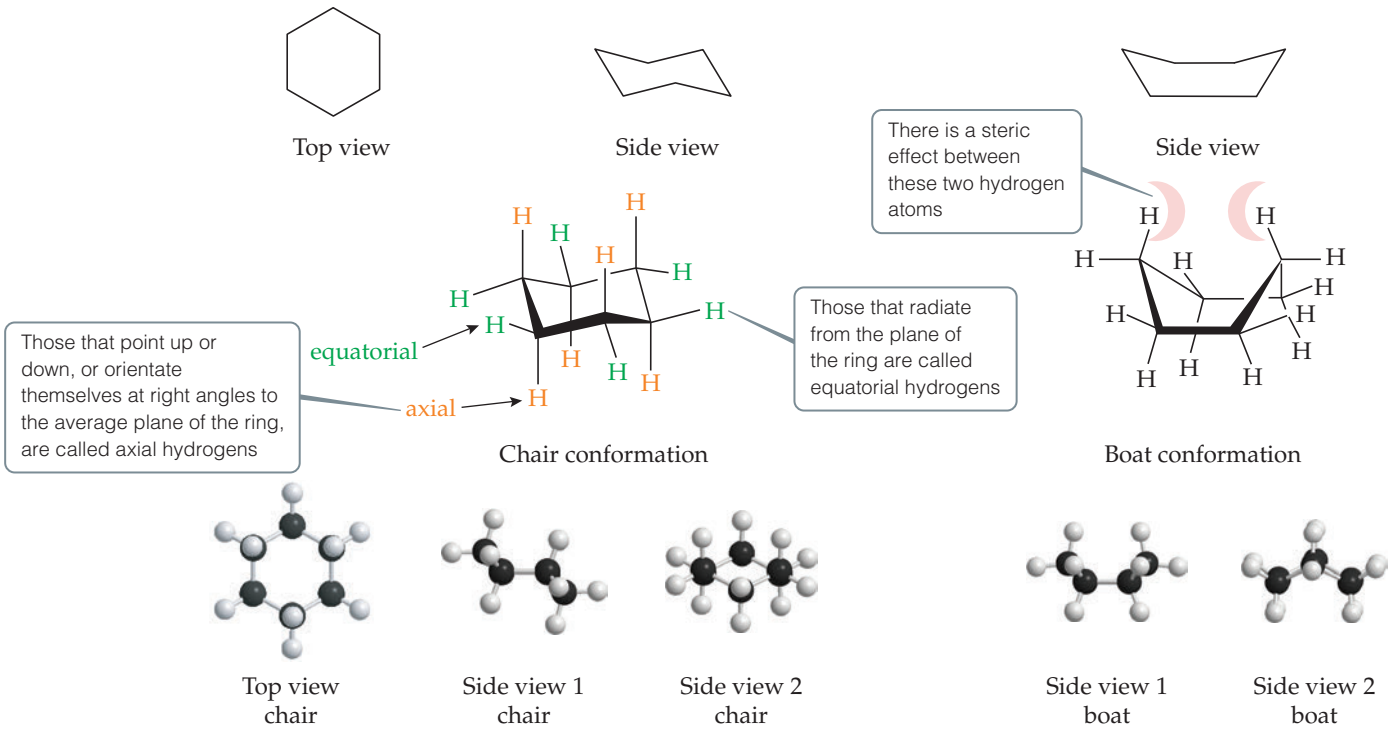
Cycloalkane	Structural formula	Ball-and-stick representation	Line drawing
Cyclopropane			
Cyclobutane			
Cyclopentane			
Cyclohexane			

smaller rings must be much less than the 109.5° angle expected for an sp^3 hybridized atom. The amount of *ring strain* increases as the ring size gets smaller than that for cyclohexane. In cyclopropane, which has the shape of an equilateral triangle, the angle is only 60°; as a result, this molecule is much more reactive than propane, its straight-chain analogue.

Apart from model and structural formula representations, Table 24.7 also demonstrates how cycloalkane structures can be drawn as simple polygons in which each corner of the polygon represents a CH_2 group and each side represents a C—C single bond. The hydrogen atoms are still present in this *line drawing* representation—we just don't include them in the drawing. When using this representation for cycloalkanes, however, remember that you are drawing a three-dimensional structure in two dimensions and that, as a consequence, geometric subtleties are lost. In fact, cycloalkane rings with four or more carbons are not planar.

To illustrate this point, consider the structure of cyclohexane as shown in **Figure 24.12**. Looking at the structure from the top certainly gives the same hexagonal shape as represented by a line drawing. However, the view from any side tells a different and more complicated story. Two major conformations for cyclohexane are known, and they both allow bond angles of about 109.5° to be realized. The **chair conformation** is the more stable of the two types of conformers. It is called a chair structure because of its resemblance to a chair. In this case, the hydrogen atoms adopt one of two orientations. Those that point up or down, or orientate themselves at right angles to the average plane of the ring, are called **axial hydrogens**; those that radiate from the plane of the ring are called **equatorial hydrogens**. Substituents at these positions are also described in the same way. Note that

Go Figure In which conformation of cyclohexane are neighboring hydrogens staggered and in which are they eclipsed?



▲ **Figure 24.12** **Conformations of cyclohexane.**

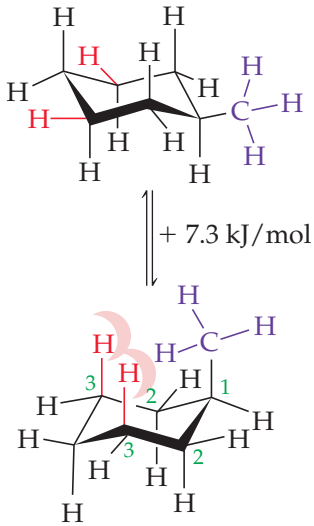
all bonds on adjacent carbons in cyclohexane are staggered, implying that in any given hemisphere the hydrogens alternate between axial and equatorial.

The less stable of the two forms (by about 30 kJ/mol) is described as the **boat conformation**. Its relative instability is caused by the non-bonding interactions generated by the close proximity of the two hydrogen atoms on C1 and C4 that overhang the ring system in this conformation (Figure 24.12), and by the eclipsing of hydrogens along the C2–C3 and C5–C6 bonds.

Now let's consider the effect of placing a single substituent on a cyclohexane ring. The substituent has two possible orientations, axial or equatorial. The two conformers do interconvert but the equatorial conformation is preferred because the methyl group experiences destabilising **1,3-diaxial interactions** with the other two axial hydrogens on that face (**Figure 24.13**) if it is axial. These types of interactions are minimized in the equatorial conformation as the methyl group and, more importantly, the hydrogen atoms on that methyl group point away from the ring system.

We do not need to number the position of the substituent for a cycloalkane with only one substituent, nor do we need to define the conformation as either *ax* (for axial) or *eq* (for equatorial). For example, both structures in Figure 24.13 are called methylcyclohexane, as this name is suitable enough to avoid ambiguity.

The concept of geometrical isomerism was introduced in Section 23.4 for coordination compounds. We will investigate the concept of *geometrical isomerism* in cycloalkanes in Chapter 25. Geometrical isomers occur in cycloalkanes when two or more substituents are found around the ring in axial, equatorial or both positions. Geometrical isomers differ in their physical properties and spatial orientation.



▲ **Figure 24.13** **1,3-Diaxial repulsion.** Substituents placed in an axial conformation interact strongly with the two axial hydrogens (red), destabilising this conformer relative to the equivalent equatorial conformer.

Self-Assessment Exercises

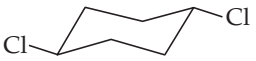
24.22 What is the molecular formula of the following structure?



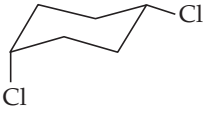
(a) C_6H_{14} **(b)** C_7H_{14} **(c)** C_7H_{16} **(d)** C_8H_{16}

24.23 Which structure represents the most stable conformer of 1,4-dichlorocyclohexane?

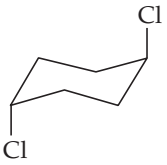
(a)



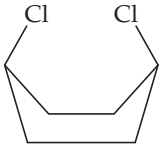
(b)



(c)



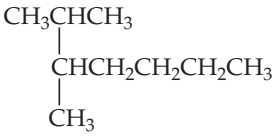
(d)



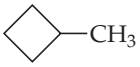
Exercises

24.24 Name the following compounds systematically:

(a)



(b)

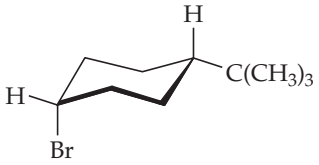


(c)

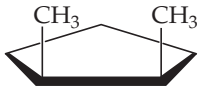


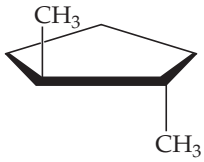
24.25 **(a)** Draw line drawings for cyclopentane and cyclobutane. **(b)** Which of the two cycloalkanes has the higher ring strain? Why?

24.26 **(a)** 1-Bromo-4-*tert*-butylcyclohexane exists almost entirely in the conformation shown. Explain why based on the relative size of the two groups. **(b)** Label the Br and $C(CH_3)_3$ groups as axial or equatorial.



24.27 Of these two disubstituted cyclic compounds, indicate which would experience the fewest non-bonding interactions, and hence would be lower in energy.

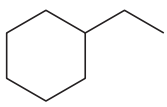




24.28 **(a)** Draw the structure of cyclohexane in the chair conformation including hydrogen atoms. Highlight those hydrogens that are axial and those that are equatorial. **(b)** Draw a 1,2-disubstituted cyclohexane in the chair conformation with your choice of alkyl substituents in axial positions. Now flip the structure to the other chair conformation. What do you notice about the position of the two substituents? Are both substituents axial, or equatorial, or is there one of each? Is this general? Explain. **(c)** Systematically name the structure you drew in part (b).

24.29 **(a)** Provide the molecular formula and systematic name for the following structures. **(b)** Draw the structure of a constitutional isomer for each. **(c)** Why is it unnecessary to name the two conformers of methylcyclohexane as two distinct molecules?

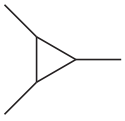
(a)



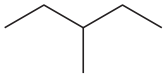
(b)



(c)



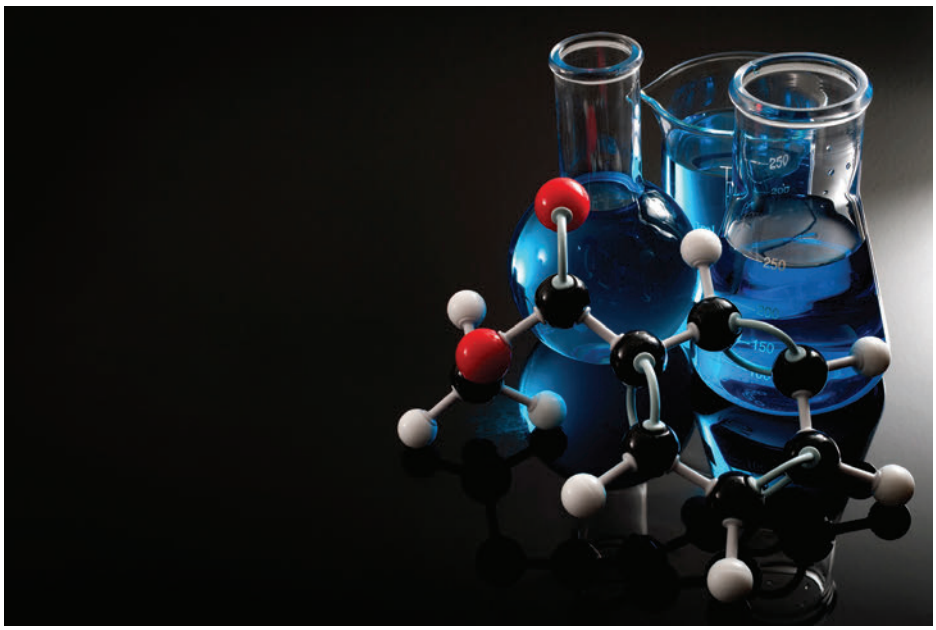
(d)



Answers to Self-Assessment Exercises

24.22 (b) **24.23** (a)

24.6 | Organic Functional Groups



The wealth of variety in organic chemistry results from the combination of a vast number of ways that carbon chains and rings may be constructed, punctuated by a selection of functional groups. These form the reactive part of the molecule and are given special attention, rather like an ace in a card game. By the end of this section, you should

- Be able to identify the common functional groups present in organic molecules.

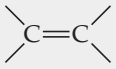
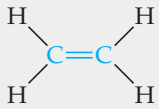
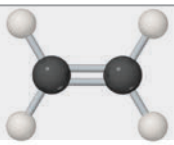
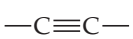
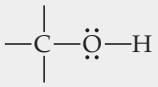
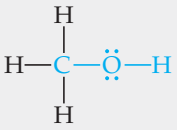
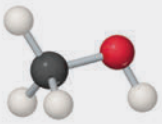
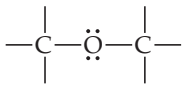
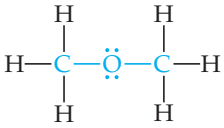
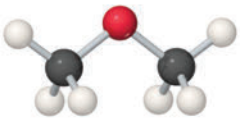
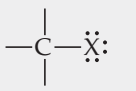
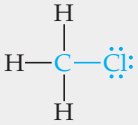
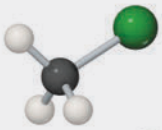
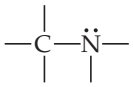
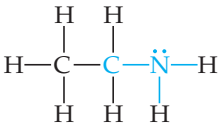
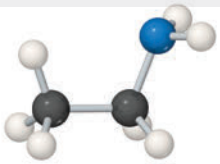
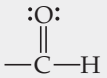
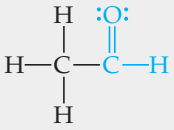
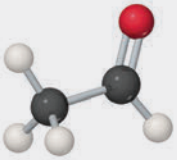
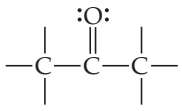
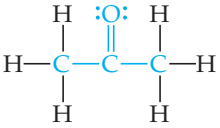
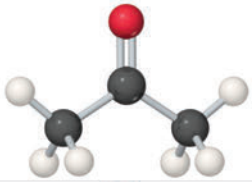
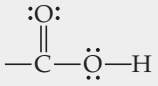
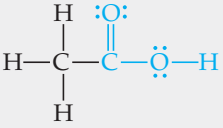
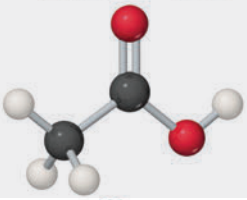
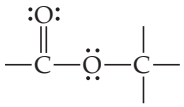
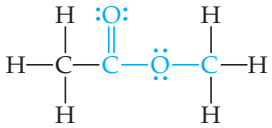
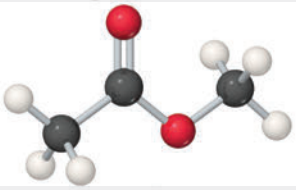
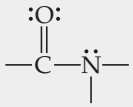
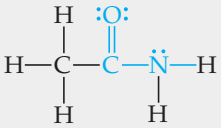
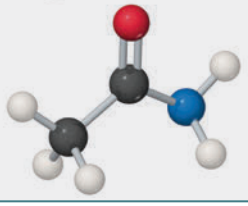
The reactivity of organic compounds can be attributed to particular atoms or groups of atoms within the molecule. A site of reactivity in an organic molecule is called a **functional group** because it characteristically controls how the molecule behaves, or functions under a given set of conditions. Functional groups define both the reactivity and class descriptions of organic molecules. As we will see in, the presence of carbon–carbon double or triple bonds in a hydrocarbon will markedly increase that compound's reactivity. Furthermore, these two functional groups undergo similar yet characteristic reactions. The same is true of other functional groups. Each distinct kind of functional group often undergoes the same kinds of reactions, regardless of the size and complexity of the molecule. Thus the chemistry of an organic compound is largely determined by the functional groups it contains.

Table 24.8 lists the most common functional groups and gives examples of each. Notice that, in addition to carbon–carbon double bonds or carbon–carbon triple bonds, there are also many functional groups that contain elements other than just C and H. In fact, many of the functional groups found within organic molecules contain other non-metals such as O and N. In later chapters we examine the structure and chemical properties of important functional groups containing oxygen, that is, alcohols and ethers (Chapter 27), aldehydes and ketones (Chapter 28), carboxylic acids and esters (Chapter 29) and those containing nitrogen, such as amines and amides (Chapter 31).

Alkane groups constitute the less reactive portions of any compound and so are typically abbreviated to the symbol "R". In describing the general features of organic compounds, chemists often use the designation R to represent any structural group: methyl, ethyl, propyl and so on (**Figure 24.14**); or, in fact, to represent a collective of atoms that do not participate in the reaction of interest. Alkanes, for example, which contain no functional group, are represented as R—H. **Alcohols**, which contain —OH, the alcohol functional group, are represented as R—OH. If two or more different structural groups are present in a molecule, we designate them R, R′, R″ and so forth.

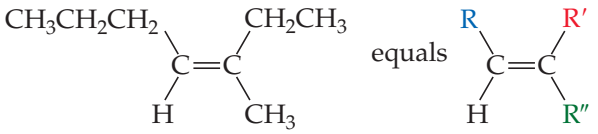
In organic chemistry, a **heteroatom** is defined as an atom other than hydrogen or carbon. Of the different types of heteroatoms associated with a hydrocarbon skeleton,

TABLE 24.8 Common functional groups

Functional group	Compound type	Suffix or prefix	Example: Structural formula	Example: Ball-and-stick model	Example: Systematic name (Common name)
	Alkene	*-ene*			Ethene (Ethylene)
	Alkyne	*-yne*			Ethyne (Acetylene)
	Alcohol	*-ol*			Methanol (Methyl alcohol)
	Ether	*ether*			Dimethyl ether
 (X = halogen)	Haloalkane	*halo-*			Chloromethane (Methyl chloride)
	Amine	*-amine*			Ethylamine
	Aldehyde	*-al*			Ethanal (Acetaldehyde)
	Ketone	*-one*			Propanone (Acetone)
	Carboxylic acid	*-oic acid*			Ethanoic acid (Acetic acid)
	Ester	*-oate*			Methyl ethanoate (Methyl acetate)
	Amide	*-amide*			Ethanamide (Acetamide)

$CH_3CH_2CH_2OH$ equals R—OH when R=$CH_3CH_2CH_2$

CH_3OH equals R′—OH when R′=CH_3



where R = $CH_3CH_2CH_3$
R′ = CH_2CH_3
R″ = CH_3

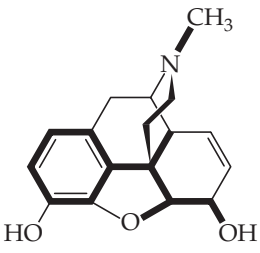
◀ **Figure 24.14** **The generalizations of organic chemistry.**

oxygen is the most prevalent. For oxygen to be added to a hydrocarbon, oxidation must occur. Because our atmosphere contains approximately 21% oxygen, oxidation reactions are always happening, and not only in the process of rusting. Carbon dioxide, water and most free radicals contain oxygen. Simple molecules containing oxygen, such as alcohols, are easily transformed into alkenes, haloalkanes, ethers, aldehydes and ketones and carboxylic acids and their derivatives. For the rest of this chapter we will investigate some of the common reactions used to functionalize alkanes.

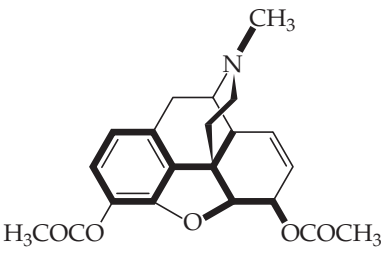
CHEMISTRY AND LIFE Structure–Activity Relationships

Medicinal chemistry research to find the best molecule to elicit a particular response in the body often involves "structure-activity" relationships. This requires synthesizing a range of similar molecules and testing them to see if a small structural difference makes them more or less active in a particular cell culture. Sometimes, molecules that at first sight look different, may adopt a similar shape when twisted into a particular conformation. The advent of sophisticated 3-D modeling of structures has helped identify similarities between molecules.

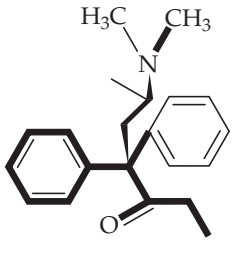
Each of the following molecules has a similar structural element highlighted in bold. Morphine is extracted from the opium poppy and is used in the management of extreme pain. It works by acting on the central nervous system, blocking pain but allowing most nerve activity to continue. One side effect of its use is drowsiness. Indeed, the name morphine is derived from Morpheus, the Greek god of dreams. The conversion of the alcohol functional groups into ester groups generates the compound heroin. This compound has been used as a recreational drug as it gives the user a feeling of euphoria. However, it is also devastatingly addictive and users quickly become physically dependent on it. Methadone is prescribed as a way of regulating, and ultimately reducing, heroin addiction. It is an *agonist*, which means that it binds to the opioid receptors in the brain and causes a response similar to that of heroin but one that is easier to control. In the case of a heroin overdose, an *antagonist*, naloxone, is used. This molecule binds strongly to the opioid receptors, displacing heroin, but does not cause any opioid response, so reversing the effect of the heroin. It is likely to precipitate withdrawal symptoms such as chills, sweating, stiffness, cramps, and anxiety.



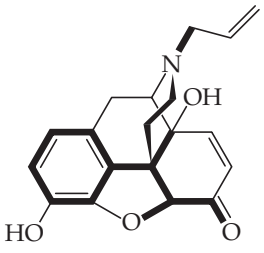
Morphine



Heroin



Methadone



Naloxone

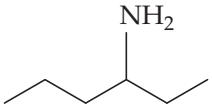
Self-Assessment Exercise

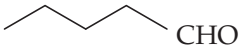
24.30 Identify the functional groups in morphine

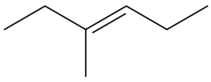
(a) alkene, amide, ether, ketone
(b) alcohol, alkyne, amine, ketone
(c) aldehyde, alkene, amide, ether
(d) alcohol, alkene, amine, ether

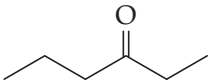
Exercises

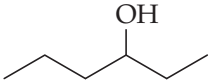
24.31 Circle the functional groups in each of the following compounds:

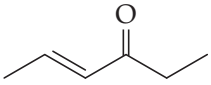
(a) 

(b) 

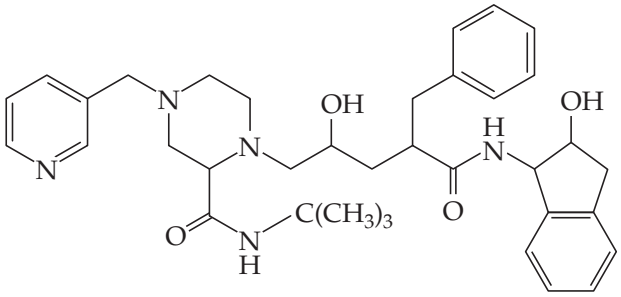
(c) 

(d) 

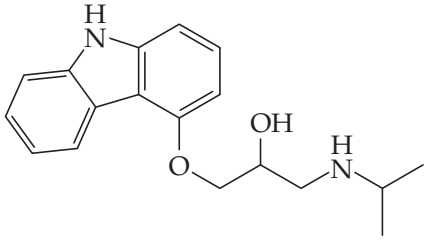
(e) 

(f) 

24.32 Indinavir is a HIV protease inhibitor. Identify the following functional groups and the number of each present in the structure of Indinavir: **(a)** alcohol; **(b)** amide; **(c)** amine.



24.33 Carazolol is an antihypertensive drug. Identify the following functional groups and the number of each present in the structure Carazolol: **(a)** alcohol; **(b)** ether; **(c)** amine.



Answers to Self-Assessment Exercise

24.30 (d)

24.7 Reactions of Alkanes



The starting point for many of the manufactured materials that surround us is a combination of crude oil and natural gas that feeds the petrochemical industry. Here, it is transformed into a myriad of products that ultimately end up as polymers, plastics, synthetic fibres, solvents, glues, pharmaceuticals, paints, and fertilizers to name just a few items. In 2020, the industry was estimated to be worth USD 476 billion. While the processes used

in the industry may be rather different to those in the research laboratory, in both cases, the basic type of reactions are the same and involve the dozen functional groups that are the foundation of organic chemistry. By the end of this section, you should

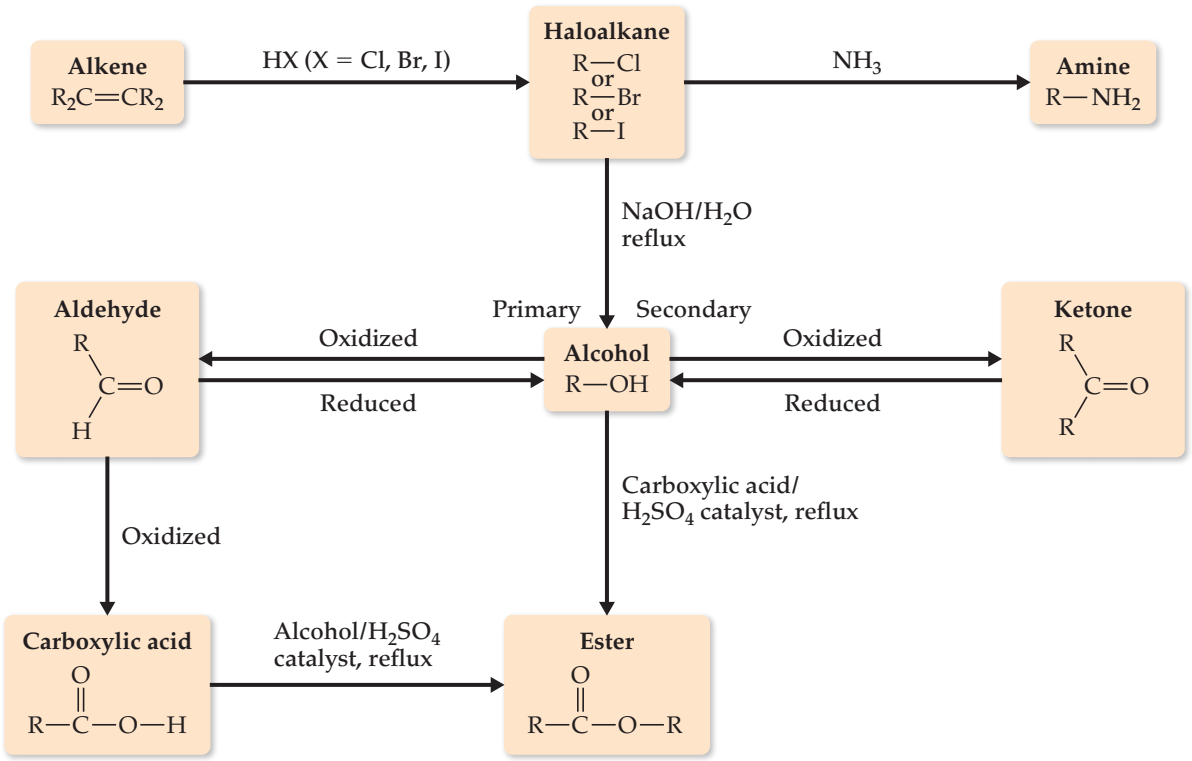
- Be able to identify primary, secondary, and tertiary carbon and hydrogen atoms
- Understand the mechanism of a free-radical polymerization reaction

Alkanes contain only C—C and C—H bonds and as a result are relatively unreactive. At room temperature, for example, alkanes do not react with any common acids, bases or strong oxidizing agents, and they are not even attacked by boiling nitric acid. Their low chemical reactivity is due primarily to the strength and lack of polarity of both C—C and C—H single bonds. The whole basis of organic chemistry—that is, converting one functional group into another by making or breaking bonds, leading to the formation of new compounds (**Figure 24.15**)—would fall apart if C—H and C—C bonds reacted under mild conditions. Essentially, organic molecules are composed of an inert hydrocarbon framework punctuated by functional groups, which are the reactive parts of the molecule. Functional groups not only define the reactivity but also the classes of organic molecules.

The following chapters show that hydrocarbons can be modified to impart greater reactivity by introducing unsaturation into the carbon–carbon framework and by attaching other reactive functional groups to the hydrocarbon backbone.

Combustion

Alkanes are not completely inert, however. Their relative high stability means that either harsh reaction conditions or the use of highly reactive reagents is needed to initiate a chemical reaction. One of the most commercially important reactions of alkanes is their **combustion** reaction in air, which is the basis of their use as fuels. The complete combustion of an alkane in the presence of oxygen *always* generates carbon dioxide and water



▲ **Figure 24.15 Functional group interconversion.** Functional groups are atoms or groups of atoms within a molecule that show a characteristic set of chemical properties. Some of the more common functional groups and their interconversion are shown. The functional group is the center of reactivity in an organic molecule. R = general representation for the rest of the molecule. *Note that the basic hydrocarbon framework is unchanged in these reactions.*



▲ **Figure 24.16 Combustion.** Ignition of a mixture of oxygen with flammable gases such as hydrogen or methane can have explosive consequences.

as the products of the reaction. For example, the balanced equation for the complete combustion of ethane is:

$$2\,C_2H_6(g) + 7\,O_2(g) \rightarrow 4\,CO_2(g) + 6\,H_2O(l) \quad \Delta H = -2855\ kJ \qquad [24.3]$$

The reaction of any organic molecule with oxygen is another example of an **oxidation** reaction. We investigate these types of reactions in the context of organic chemistry in greater detail in Chapter 28.

We know from calorimetric measurements that the reaction of a simple alkane such as methane (CH_4) with oxygen is highly exothermic (Section 14.4). Indeed, the combustion of methane (which is the major component of natural gas) keeps many of our homes warm during the winter months. Although the reactions of alkanes with oxygen are exothermic, most alkanes are stable indefinitely at room temperature in the presence of air because the activation energy required for combustion is large. This activation barrier is usually overcome by heat generated from a flame or spark, typically with explosive consequences (**Figure 24.16**).

Classification of C and H

An important skill to develop in organic chemistry is the ability to recognize which functional group within a molecule will react under a given set of conditions. This ability allows the organic chemist to synthesize very complex molecules. Sometimes, however, there is a choice of positions within a molecule at which reaction is likely to occur. This is as valid with simple organic molecules, like alkanes, as it is for highly complex molecular structures. Before going on to discuss one of the few important reactions of the alkanes, we need to have a way of distinguishing between the different kinds of carbons that appear. These classifications are important whenever we are trying to recognize which functional group or part of a molecule will react.

The classification used to distinguish between types of hydrogens and carbons and the appropriate symbolism is:

Primary (1°) carbon: a carbon atom bonded to one other carbon atom
1° H: a hydrogen bonded to a 1° carbon
Secondary (2°) carbon: a carbon atom bonded to two other carbon atoms
2° H: a hydrogen atom bonded to a 2° carbon
Tertiary (3°) carbon: a carbon bonded to three other carbon atoms
3° H: a hydrogen atom bonded to a 3° carbon
Quaternary (4°) carbon: a carbon bonded to four other carbon atoms

Sample Exercise 24.3

Oxidation of alkanes

Write the equation for the complete combustion of 2-methylpropane.

SOLUTION

Analyze We are asked to react an alkane with oxygen under conditions that give the complete combustion products, namely CO_2 and H_2O.

Plan Write the molecular formula for 2-methylpropane and the reagent molecular oxygen on the reactants side of the equation and carbon dioxide and water on the products side. Then balance the equation for carbon, then hydrogen and finally oxygen.

Solve The molecular formula for 2-methylpropane follows the general formula for alkanes. 2-methylpropane has four carbons so its molecular formula is C_4H_{10}. So, the unbalanced equation is

$$C_4H_{10}(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

Balancing for carbon and hydrogen yields

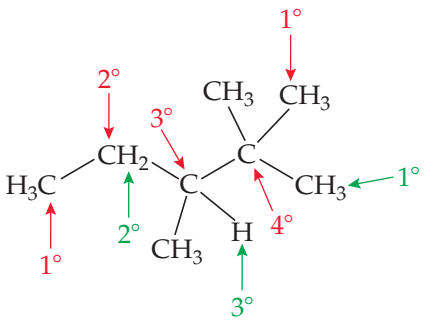
$$C_4H_{10}(g) + O_2(g) \rightarrow 4\,CO_2(g) + 5\,H_2O(l)$$

Now, balancing for oxygen using the total of oxygen present on the product side yields the balanced equation

$$2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(l)$$

Practice Exercise
Write the equation for the complete combustion of 2,3-dimethylbutane.

Figure 24.17 illustrates this classification by identifying the different carbon atoms of 2,2,3-trimethylpentane. This method of classification is useful, as we see in the following chapters, for determining the reactivity of a range of different functional groups.



▲ **Figure 24.17 Classification of carbon and hydrogen atom types.** The classification of a selected set of hydrogen (green) and carbon (red) atoms is shown for 2,2,3-trimethylpentane.

Free-Radical Reactions and Electron Movement

The majority of alkane reactions occur through the formation of **free radicals**, either by the scission of a C—C bond or by hydrogen abstraction. Free radicals gain their reactivity from having an unpaired electron. Both C—C bond scission and hydrogen abstraction are examples of a **homolytic bond cleavage** because one electron contained with the two-electron σ-bond is transferred to each atom, yielding two free radicals.

At this point, we will use one form of free-radical chemistry to emphasize the point that a single covalent bond contains two electrons and that reactions occur by making and breaking such bonds.

The most common of all the free-radical reactions of alkanes is **halogenation**. This term simply means the incorporation of halogen (that is, F, Cl, Br, I), although chlorine and bromine atoms are the easiest and hence the most common to incorporate. This type of free-radical halogenation is generally called a **substitution reaction** because the reaction proceeds by abstracting a hydrogen atom and replacing or *substituting* it with a halogen. The chlorination of methane, for example, to yield the mono-, di-, tri- and tetra-chlorinated products (and HCl) occurs only in the presence of light (photolysis), with radiation in the range 200–500 nm most common. The reaction produces all permutations of substitution, as shown in Equation 24.5. The ratio of the four products formed is dictated by the amount of chlorine gas present, the photolysis time and the wavelength of light.

$$CH_4 + Cl_2 \xrightarrow{\text{dark}} \text{no reaction} \qquad [24.4]$$

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 \qquad [24.5]$$

Electron movement in organic chemistry is a useful way of rationalising the conversion of starting materials to products. We call this the *mechanism* of a reaction. Remember that there are two electrons in any single covalent bond and how these electrons move gives rise to either a carbocation, carbanion or free radical, which are less stable (and hence more reactive) than the covalent bond from which they are formed. In Chapter 26, we will investigate a shorthand way of illustrating electron movement that simplifies the fundamental approach we are about to take to explain the free-radical halogenation of methane.

Here, we will begin our study of mechanisms and the three steps to a radical chain reaction:

1. **Initiation**
2. **Propagation**
3. **Termination**

using Equation 24.5 as an example. We will employ Lewis structures to demonstrate the electron movement.

1. ***Initiation step:*** This step produces the first radicals. In this example, the absorption of light by Cl_2 causes the homolytic cleavage of the Cl—Cl bond, leading to the formation of two chlorine radicals:

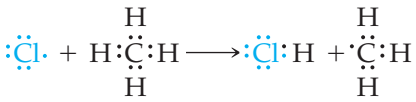


[24.6]

   The generation of chlorine or bromine radicals can also be initiated by heat.

2. ***Propagation steps:*** As these newly formed radicals collide with other molecules (which are not radicals), they generate or *propagate* new radicals. In the example, a newly formed chlorine radical (chlorine atom) can remove a hydrogen atom from a methane molecule. This step produces a stable product molecule, HCl, and an unstable methyl radical that is highly reactive because its carbon has only seven valence electrons.

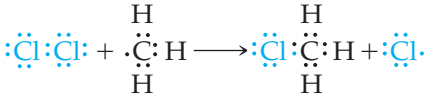
Step 1



[24.7]

When a molecule of Cl_2 encounters the methyl radical, one chlorine atom is transferred to the carbon to form a stable molecule of chloromethane. The second chlorine atom, now formed, can react with a new molecule of methane as in step 1.

Step 2

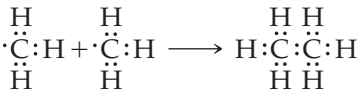


[24.8]

The reaction of the methyl radical with chlorine (step 2) yields another chlorine radical which can propagate causing the *chain reaction*. Since each step produces a molecule of product and a newly formed radical, one radical gives rise to many product molecules. This means that only a small number of radicals need be generated during the initiation to allow the chain reaction to proceed.

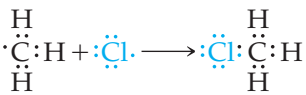
Once the amount of CH_3Cl begins to build up in the mixture, it too can have a hydrogen atom abstracted by a chlorine radical, leading to the formation of CH_2Cl_2. Chloroform ($CHCl_3$) and CCl_4 are formed by the same process.

3. ***Termination steps:*** These occur when two radicals combine to form an unreactive product. For example:



[24.9]

or

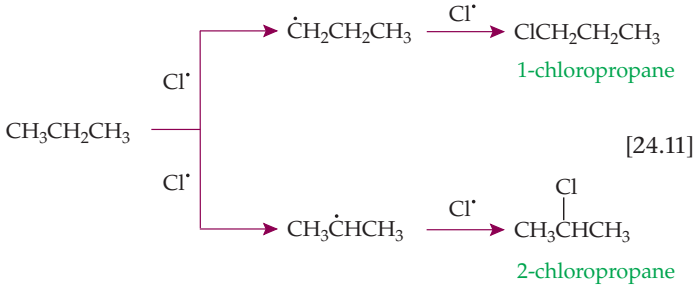


[24.10]

Termination steps such as those displayed in Equation 24.9 complicate the reaction by extending the carbon chain. Products such as those in Equations 24.9 and 24.10, which also contain C—H bonds, are also prone to further radical generation and

A CLOSER LOOK Reactivity by Carbon Classification

When propane is mono-halogenated two products are likely since both primary and secondary hydrogens exist (Equation 24.11).



[24.11]

The direction of the reaction—that is, via abstraction of the primary or secondary hydrogen atom—depends on two factors: the C—H bond dissociation energy and the relative stability of the two radical intermediates formed (Section 8.8). The two factors are interrelated. There is a trend that suggests the more stable the radical, the lower the energy needed to cause C—H bond homolysis. There is approximately 15 kJ/mol difference in C—H bond dissociation energies between primary C—H bonds and secondary C—H bonds, with the latter being easier to cleave. However, the size of the energy difference between homolysis of a primary and secondary C—H bond cannot fully account for the approximate 1 : 1 product ratio.

There is also a valence bond argument that supports the bond dissociation energy arguments. Alkyl free radicals have a potentially filled *p* orbital and are stabilized by **electron-donating groups** such as alkyl groups. As a consequence, the order of alkyl radical stability is:

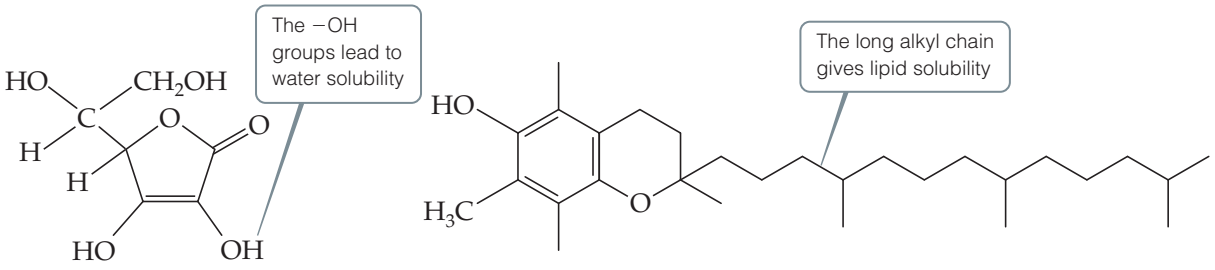
Methyl radical < ***Primary radical*** < ***Secondary radical*** < ***Tertiary radical***
(least stable) (most stable)

At this point, it appears there is little difference between the two pathways leading to the monochlorinated products if the product ratio is 1 : 1. Actually, there is a significant difference as it is statistically *three times* more likely to abstract a primary hydrogen (there are six of these in propane) as it is to abstract a secondary hydrogen (there are two of these in propane). So, in fact, there is a large discrimination for the formation of 2-chloropropane. Typically, the ratio of selectivity for monochlorination is of the order 1° : 2° : 3° = 1 : 4 : 5.

Bromine also reacts with alkanes via a free-radical mechanism and bromination is a more selective process. The ratio of **regioselectivity** for bromination is of the order 1° : 2° : 3° = 1 : 100 : 1500.

substitution steps. The generation of a single radical can lead to the formation of many product molecules before the chain is terminated.

Free-radical chain reactions are also found in biological systems, in which harmful radicals such as ·OH attack functional and structural molecules within cells, leading to dysfunction or cell death. Natural **antioxidants** such as vitamin C (ascorbic acid) and vitamin E (α-tocopherol) react readily with free radicals, terminating their propagation.



Vitamin C
(*water soluble*)

Vitamin E
(*lipid soluble*)

Sample Integrative Exercise

Putting concepts together

Combustion analysis of a hydrocarbon determined it contained 82.8% carbon and 17.2% hydrogen by mass. **(a)** What is the empirical formula of this compound? **(b)** Explain why your empirical formula cannot also be the molecular formula of this hydrocarbon. **(c)** If the molar mass of the compound is 58.1 g/mol, draw the structural formula of all possible constitutional isomers and give their names. **(d)** Does an equilibrium exist between the constitutional isomers at room temperature?

SOLUTION

Analyze In this problem we determine the formula of a compound and examine the relationship between its isomers.

Plan First determine the empirical formula of the compound then examine the bonding arrangement of the atoms involved to see if the empirical formula and molecular formula could be the same. Next determine the molecular formula and name all possible structures with this formula. Finally consider whether the constitutional isomers may be easily interconverted at room temperature.

Solve

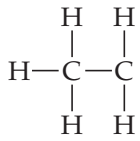
(a) A 100 g sample of the hydrocarbon will contain 82.8 g of carbon and 17.2 g of hydrogen. This represents

$$\frac{82.8\text{ g}}{12.01\text{ g/mol}} = 6.89\text{ mol carbon}$$

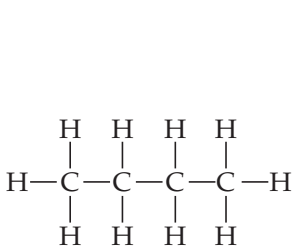
$$\frac{17.2\text{ g}}{1.008\text{ g/mol}} = 17.1\text{ mol hydrogen}$$

The mole ratio of C : H is 6.89 : 17.1 = 1 : 2.48 or 2 : 5
The empirical formula of the hydrocarbon is therefore C_2H_5.

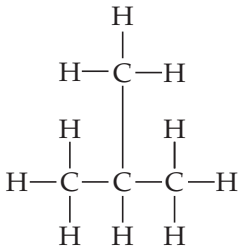
(b) In a stable bonding arrangement hydrogen forms one bond and carbon forms four bonds. The odd number of hydrogen atoms mean that it is not possible to construct a compound in which all atoms have a stable bonding arrangement; one carbon has just three bonds.



(c) An empirical formula of C_2H_5 would have a molar mass of 29.06 g/mol; the actual molar mass is double this and so the molecular formula is C_4H_{10}. The structural isomers with this formula are:



butane



2-methylpropane

(d) To convert one constitutional isomer to another involves the breaking of chemical bonds. This requires quite a lot of energy and does not spontaneously occur at room temperature. So no equilibrium exists between the two isomers at room temperature.

Self-Assessment Exercises

24.34 How many primary, secondary and tertiary hydrogens are there in 2-methylbutane?

(a) 3 × 1° H; 2 × 2° H; 1 × 3° H
(b) 9 × 1° H; 2 × 2° H; 1 × 3° H
(c) 1 × 1° H; 2 × 2° H; 9 × 3° H

24.35 Name, in order of occurrence, the three steps in a radical polymerization.

(a) Initiation, propagation, termination
(b) Initiation, termination, propagation
(c) Propagation, initiation, termination
(d) Termination, propagation, initiation

Exercises

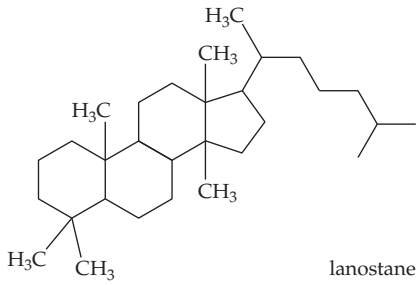
24.36 **(a)** Write a balanced equation for the complete combustion of propane. **(b)** Use table 8.3 and your answer to part (a) to estimate ΔH for this reaction.

24.37 An unknown aliphatic alkane, A, yields 4.800 g CO_2 and 2.475 g H_2O when fully combusted. Suggest a plausible molecular formula for A that is less than or equal to C_6H_{14}.

24.38 Propose structures for compounds with formulas less than C_6H_{14} containing:

(a) two tertiary carbons
(b) three primary carbons
(c) a quaternary carbon
(d) only two methyl groups.

24.39 The structure of lanostane, a biogenic precursor of steroids, is shown here. Classify each carbon atom as primary, secondary, tertiary, or quaternary.



lanostane

24.40 Draw Lewis structures for the following radicals:

(a) methyl radical
(b) chlorine atom
(c) isopropyl radical.

24.41 **(a)** What ratio of cyclohexane to chlorine would you suggest in order to achieve a monochlorination? **(b)** The free-radical chlorination of cyclohexane is much cleaner and occurs in far greater yield than that of hexane under the same conditions. Account for this difference.

Answers to Self-Assessment Exercises

24.34 (b) **24.35** (a)

Chapter Summary and Key Terms

INTRODUCTION AND SECTION 24.1 **Organic chemistry** is the study of compounds that contain carbon. We have encountered many aspects of organic chemistry in earlier chapters. Carbon forms four bonds in its stable compounds.

SECTION 24.2 The simplest class of organic molecules consists of **hydrocarbons**, which contain only carbon and hydrogen. Alkanes are hydrocarbons that contain only single bonds. Alkanes have names that end in *-ane*, such as methane and ethane. **Alkanes** are **aliphatic**, forming straight-chain, branched-chain and cyclic arrangements.

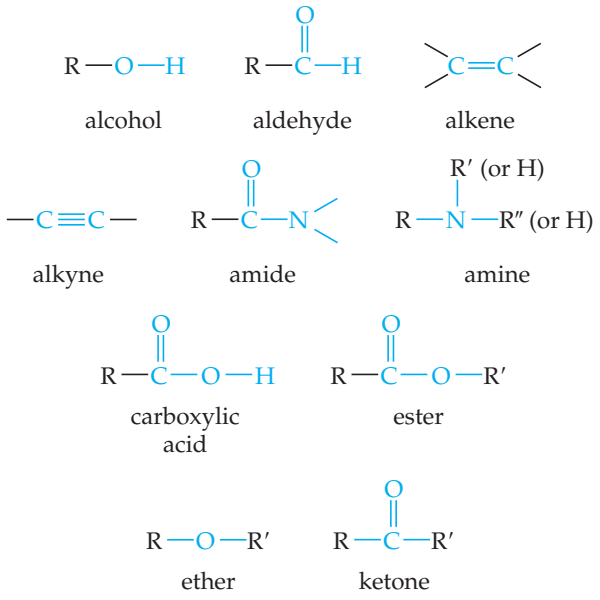
Alkanes are used primarily as fuels. Their properties, such as melting and boiling point, change in a regular fashion as the length of the chain increases. These properties are known as a **homologous series**.

SECTION 24.3 **Hybridization** is used as a model to rationalize the bonding geometry of a saturated carbon atom (109.5°). The rotation about C—C single bonds gives rise to different **conformations**, ranging from **staggered** to **eclipsed** forms. The staggered forms dominate due to the added **steric** interactions involved in the eclipsed forms of a molecule. We can use **Newman projections** to describe the different conformers easily. **Structural** or **constitutional isomers** have the same molecular formula but a different connectivity of atoms.

SECTION 24.4 The **nomenclature** used for hydrocarbons is based on the longest continuous chain of carbon atoms in the structure and contains a prefix, parent and suffix. The locations of **alkyl groups**, which branch off the chain, are specified by numbering along the carbon chain.

SECTION 24.5 Alkanes with ring structures are called **cycloalkanes**. Five- and six-membered rings are most common. Cyclohexane has two conformations, **chair** and **boat** forms. The chair form is more stable as it reduces unfavourable steric interactions and has two types of hydrogen positions, **axial** and **equatorial**. When a substituent is added to the ring, it typically adopts an equatorial position to minimize **1,3-diaxial interactions**.

SECTION 24.6 The chemistry of organic compounds is dominated by the nature of their **functional groups**. The functional groups we have considered are:



R, R' and R" represent hydrocarbon groups—for example, methyl (CH_3) or ethyl (CH_2CH_3). **Alcohols**, which contain —OH, the alcohol functional group, are represented as R—OH. Organic molecules need the reactivity imparted by **heteroatoms** in order to demonstrate their usefulness. Of the types of heteroatoms available, oxygen plays a major role.

SECTION 24.7 Alkanes and cycloalkanes are relatively unreactive. They do, however, undergo **combustion** in air (**oxidation**), and their main use is as sources of heat energy (exothermic reaction). Recognition of carbon and hydrogen atoms as primary, secondary or tertiary is important for determining the product distribution in organic reactions. **Free-radical** reactions are typically initiated by heat or light which leads to **homolytic bond cleavage** of halogens, leading to **halogenation**. The three phases of a free-radical reaction are **initiation**, **propagation** and **termination**. The preference of substitution is 3° H > 2° H > 1° H and is assisted by the presence of **electron-donating groups** around the carbon-centerd radical. The preference for one product over its isomer is called **regioselectivity**. **Antioxidants** such as vitamins E and C eliminate free-radicals within the human body.

Key Skills

- Draw alkane structures based on their names and name alkanes based on their structures. (Sections 24.2 and 24.3)
- Understand trends in the alkane homologous series. (Section 24.2)
- Be able to describe the concept of sp^3 hybridization and σ-bonds. (Section 24.3)
- Be able to name systematically alkanes from structures and draw structures from systematic names. (Section 24.4)
- Be able to draw cycloalkanes containing 3–8 carbon atoms. (Section 24.5)
- Understand the difference between equatorial and axial positions in cyclohexane. (Section 24.5)
- Know the structure of the functional groups: alkene, alkyne, alcohol, ether, aldehyde, ketone, carboxylic acid, amine, amide. (Section 24.6)
- Be able to identify primary, secondary and tertiary carbon atoms. (Section 24.6)
- Be able to demonstrate the making and breaking of σ-bonds in a free-radical reaction. (Section 24.7)

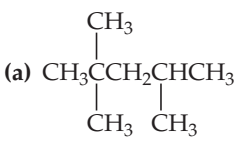
Key Equations

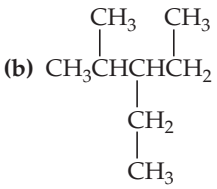
- General formula for alkanes C_nH_{2n+2} [24.1]
- General formula for cycloalkanes C_nH_{2n} [24.2]

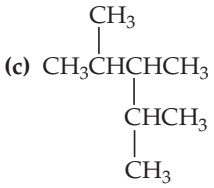
Exercises

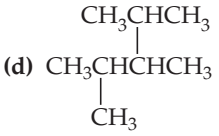
Visualizing concepts

24.42 All the structures that follow have the same molecular formula, C_8H_{18}. Which structures are of the same molecule? [Section 24.2]

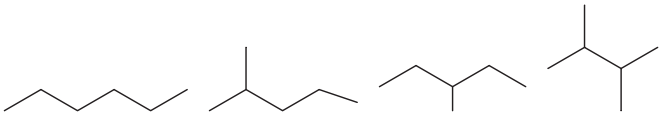




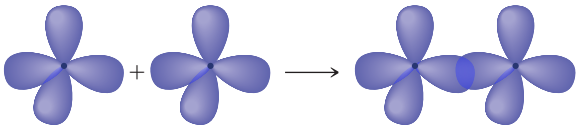




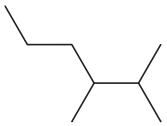
24.43 Which constitutional isomer is missing? [Section 24.3]



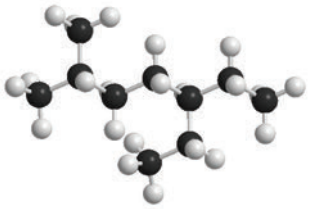
24.44 Define the following bond. [Section 24.3]



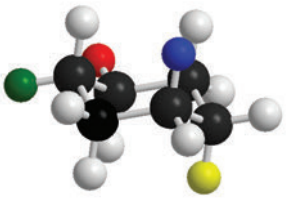
24.45 The structure of an alkane is drawn here as a line drawing representation. Is 2-propyl-3-methylbutane a suitable systematic name for this compound? Provide a better name using the guidelines in Section 24.4.



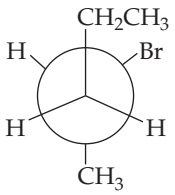
24.46 Draw the structural formula for the following molecular model. [Section 24.3]



24.47 A selection of hydrogen atoms on the chair conformation of cyclohexane are colored red, green, blue and yellow. Identify the position of each colored ball (that is, axial or equatorial). What happens to these positions if an interconversion occurs to produce the other possible chair conformation. [Section 24.5]



24.48 Convert the following Newman projection into a standard structural formula. [Section 24.3]



24.49 **(a)** Write the propagation steps leading to the formation of dichloromethane from chloromethane.

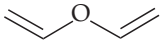
$$CH_3Cl + Cl^{\bullet} \rightarrow CH_2Cl_2$$

(b) Explain why free-radical halogenations usually give rise to mixtures of products. **(c)** Comment on the stoichiometry of chloromethane and chlorine needed to form carbon tetrachloride as the major product. [Section 24.7]

$$CH_3Cl + Cl^{\bullet} \rightarrow CCl_4$$

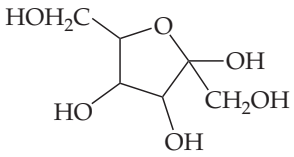
24.50 Identify each of the functional groups in the following molecules. [Section 24.6]

(a)



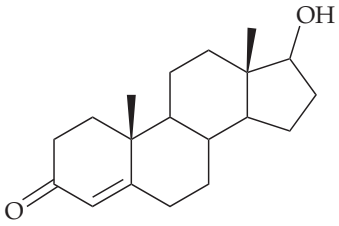
an anaesthetic

(b)



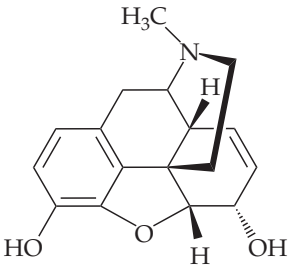
fructose

(c)



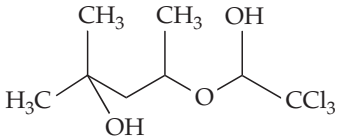
testosterone
(a male sex hormone)

(d)



morphine
(an alkaloid extracted
from poppies)

(e)



Chlorhexadol
(a depressant)

General Characteristics of Organic Molecules (Section 24.1)

24.51 Are carbon monoxide or ammonia considered organic molecules? Why or why not?

24.52 Urea has been identified as an organic molecule. What features make it so?

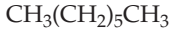
24.53 **(a)** What are the approximate bond angles about carbon in an alkane? **(b)** What are the characteristic hybrid orbitals employed by carbon in an alkane?

An Introduction to Hydrocarbons (Section 24.2)

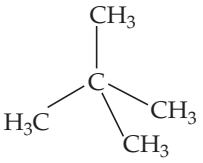
24.54 Give the molecular formula of a hydrocarbon containing six carbon atoms that is **(a)** an alkane, **(b)** aromatic.

24.55 What structural features help us identify a compound as **(a)** an alkane, **(b)** a cycloalkane, **(c)** a saturated hydrocarbon?

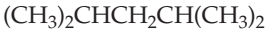
24.56 Rank the following compounds in order of increasing boiling points and explain your choice of order.



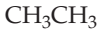
heptane



2,2-dimethylpropane
(neopentane)



2,4-dimethylpentane



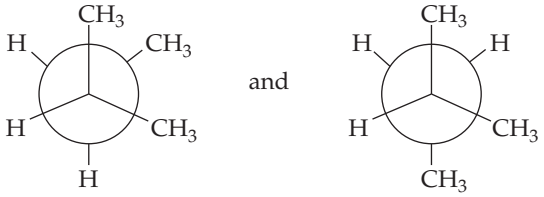
ethane

Structure of Alkanes (Section 24.3)

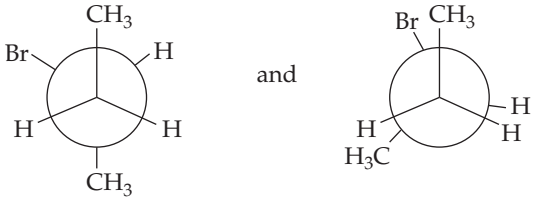
24.57 Draw a valence-bond description for ethane. Include the hybridization for each carbon atom.

24.58 Which conformer in each pair of Newman projections is lower in energy?

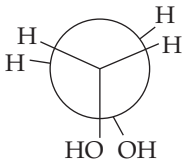
(a)



(b)

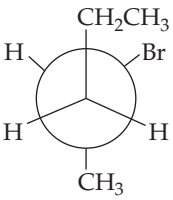


24.59 Ethylene glycol ($HOCH_2CH_2OH$) prefers to exist almost entirely in the following eclipsed form in the vapor phase. Give an explanation for this.

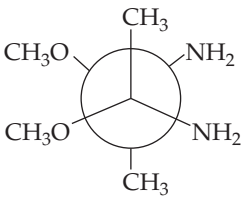


24.60 Convert the following Newman projections into their standard structural formula.

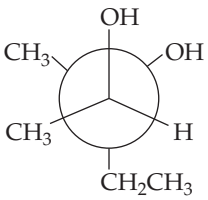
(a)



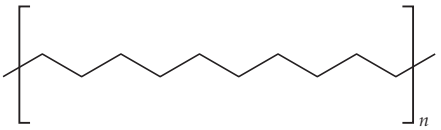
(b)



(c)



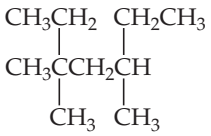
24.61 Polyethylene is a polymer used in many plastic applications, such as food wrap and soft-drink bottles. A general structure for polyethylene is shown here. Would such a polymer be more soluble in an organic solvent such as hexane or in water? Why?



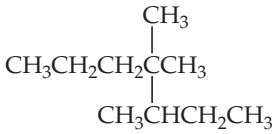
Alkane Nomenclature (Section 24.4)

24.62 Draw the structural formula or give the systematic name, as appropriate, for the following:

(a)



(b)



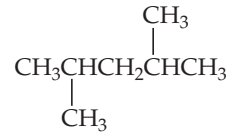
(c) 2,5-dimethylnonane

(d) 3-ethyl-4,4-dimethylheptane

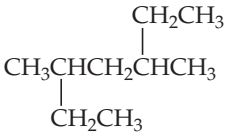
(e) 1-ethyl-4-methylcyclohexane

24.63 Give IUPAC names for the following alkanes:

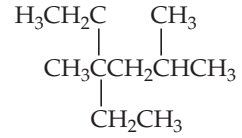
(a)



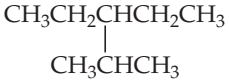
(b)



(c)



(d)



24.64 Draw 3-ethyl-2,3-dimethylbutane. What would be the correct systematic name for this compound?

24.65 Butane and 2-methylpropane are both non-polar molecules and have the same molecular formula, yet butane has the higher boiling point (−0.5 °C compared with −11.7 °C). Explain.

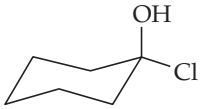
Cycloalkanes (Section 24.5)

24.66 The molar heat of combustion of gaseous cyclopropane is $-2089\ kJ\ mol^{-1}$; that for gaseous cyclopentane is $-3317\ kJ\ mol^{-1}$. Calculate the heat of combustion per CH_2 group in the two cases, and account for the difference.

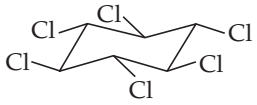
24.67 Draw both possible cyclic structural isomers of C_4H_8. Systematically name each compound.

24.68 Label each CH_3, OH or Cl group in the following compounds as axial or equatorial.

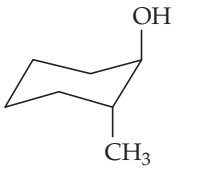
(a)



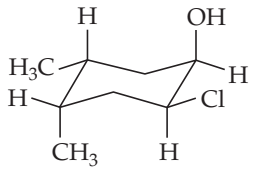
(b)



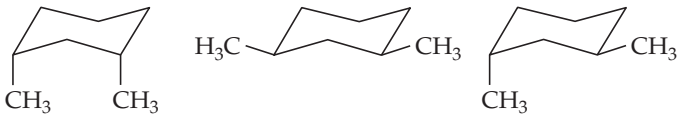
(c)



(d)



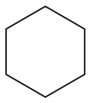
24.69 Place the following dimethylcycloalkanes in order of relative stability.



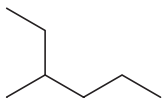
24.70 Why is geometric isomerism possible for cycloalkanes but not for alkanes?

24.71 Draw a cyclic, straight-chain or branched-chain constitutional isomer for each of the following:

(a)



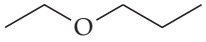
(b)



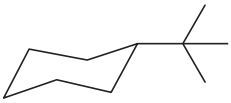
(c)



(d)

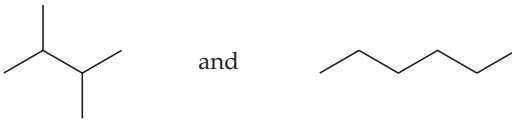


(e)



24.72 Which of the following pairs are constitutional isomers?

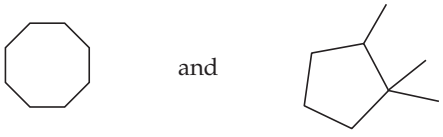
(a)



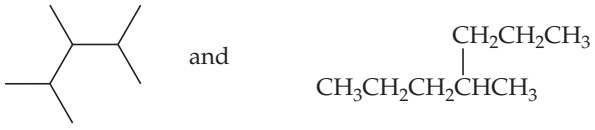
(b)



(c)



(d)

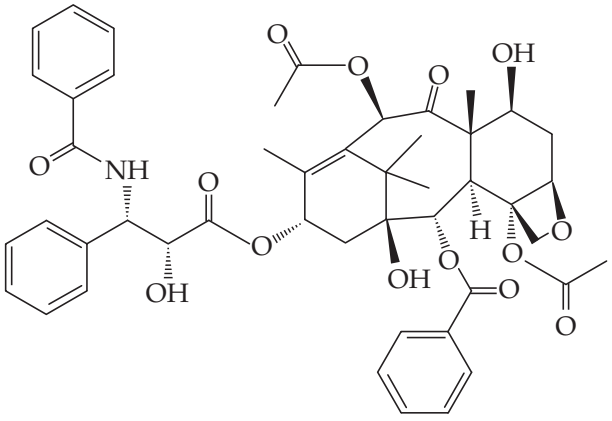


Functional Groups (Section 24.6)

24.73 **(a)** What is a functional group? **(b)** Why are functional groups important?

24.74 List three functional groups that are important in biology (there are more than three).

24.75 Taxol is a clinically important anticancer compound isolated from the bark of *Taxus*, the Pacific yew tree. Identify the following functional groups and the number of each present in the structure of Taxol: **(a)** alcohol; **(b)** ether; **(c)** amine; **(d)** amide; **(e)** carboxylic ester; **(f)** alkene; **(g)** ketone.



Reactions of Alkanes (Section 24.7)

24.76 **(a)** What is the difference between a substitution reaction and an oxidation reaction? **(b)** Using condensed structural formulas, write the balanced equation for the free-radical substitution reaction of 2,2,4-trimethylpentane with Br_2 in the presence of light. Explain, using this reaction as an example, what is meant by a regioselective reaction. **(c)** Write a balanced chemical equation for the complete combustion of 2,2-dimethylpropane.

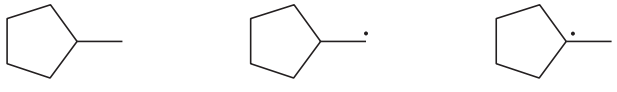
24.77 When cyclopropane is treated with HI, 1-iodopropane is formed. A similar type of reaction does not occur with cyclopentane or cyclohexane. What physical aspect of cyclopropane might account for its reactivity?

24.78 **(a)** How much oxygen is required for the complete combustion of 70 g of cyclohexane? **(b)** How much carbon dioxide is produced in this reaction?

24.79 **(a)** Write the propagation steps leading to the formation of dichloromethane, CH_2Cl_2, from methane. **(b)** Describe how termination of this chain reaction is possible.

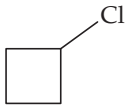
24.80 Rank each radical in order of its relative stability.

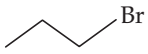
(a)

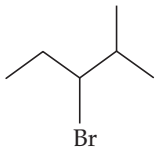


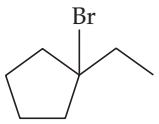
(b) $(CH_3)_2\dot{C}CH_2CH_3$ $(CH_3)_2CHCH_2\dot{C}H_2$ $\dot{C}H_3$

24.81 Which of the following alkyl halides can be prepared in good yield by radical halogenation?

(a) 

(b) 

(c) 

(d) 

24.82 Draw all monobromo derivatives of 3-methylhexane. Which one of these configurational isomers would be produced in highest yield by the reaction of bromine with 3-methylhexane?

Additional Exercises

24.83 Draw the condensed structural formulas for two different molecules with the formula C_3H_4O.

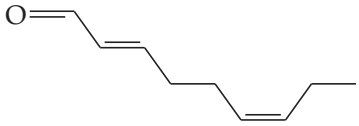
24.84 How many structural isomers are there for a five-member straight carbon chain with one double bond? For a six-member straight carbon chain with two double bonds?

24.85 Draw the condensed structural formulas for the *cis* and *trans* isomers of 2-pentene. Can cyclopentene exhibit *cis–trans* isomerism? Explain.

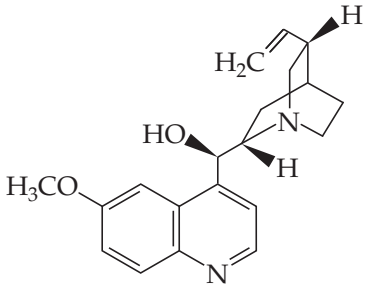
24.86 If a molecule is an "ene one", what functional groups must it have?

24.87 Write the structural formulas for as many alcohols as you can think of that have empirical formula C_3H_6O.

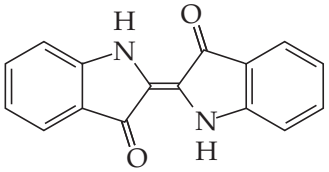
24.88 Identify each of the functional groups in these molecules:

(a) 

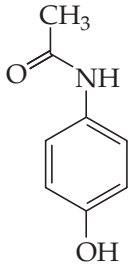
(Responsible for the odor of cucumbers)

(b) 

(Quinine—an antimalarial drug)

(c) 

(Indigo—a blue dye)

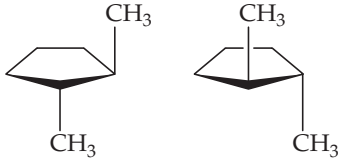
(d) 

(Acetaminophen—aka Paracetamol)

24.89 Write a condensed structural formula for each of the following: **(a)** an acid with the formula $C_4H_8O_2$, **(b)** a cyclic ketone with the formula C_5H_8O, **(c)** a dihydroxy compound with the formula $C_3H_8O_2$, **(d)** a cyclic ester with the formula $C_5H_8O_2$.

Integrative Exercises

24.90 **(a)** What type of isomeric relationship exists between pentane and 2-methylbutane? **(b)** What is the relationship between the two shown here? **(c)** Name this compound. **(d)** Identify the most likely point(s) for bromination in each molecule.



24.91 **(a)** Draw a relative energy profile similar to that shown in Figure 24.16 to illustrate the stability of the different conformers produced by rotation about one C—C single bond in propane. **(b)** What is the product of the complete combustion of propane? **(c)** How much energy is released upon the complete combustion of 44 dm^3 of propane? **(d)** Propane is converted into 2-bromopropane by a first-order process. The rate constant is $5.4 \times 102\ h^{-1}$. If the initial concentration of propane is 0.150 M, what will its concentration be after 24.0 h?

24.92 An unknown substance is found to contain only carbon and hydrogen. It is a liquid that boils at 49 °C at 1 bar pressure. Upon analysis it is found to contain 85.7% carbon and 14.3% hydrogen by mass. At 100 °C and 735 torr, the vapor of this unknown has a density of 2.21 g dm^{-3}. When it is dissolved in hexane solution and bromine water is added, no reaction occurs. What is the identity of the unknown compound?

24.93 Methane is a greenhouse gas that is present at a concentration of 1.8 ppm and has a half-life in the atmosphere of approximately 10 years. **(a)** What is the partial pressure of methane assuming the total pressure is 102 kPa? **(b)** If no new methane was added to the atmosphere, how long would it take for the concentration to drop to a pre-industrial level of 0.5 ppm assuming first-order kinetics?

Design an Experiment

The precise mixture of alkanes contained in a crude oil sample depends on the origin of the oil. A small amount of oil has washed up on the shore close to a major shipping lane and, as a member of the local environmental protection agency, you want to determine the origin of the oil and, hence, the tanker it came from. How would you collect samples of the oil to ensure they were representative of the spill? What physical property of alkanes enables you to separate them? How would you quantify the amount of the different alkanes present? How might you identify the alkanes present?

25

STEREOCHEMISTRY OF ORGANIC COMPOUNDS

WHAT'S AHEAD

25.1 Stereochemistry in Organic Chemistry

25.2 *Cis–Trans* Isomerism in Cycloalkanes

25.3 Chirality in Organic Compounds

25.4 Measuring Optical Activity

25.5 Absolute Stereochemistry

25.6 Molecules with More than One Stereocenter

25.1 | Stereochemistry in Organic Chemistry



Stereochemistry is about the three-dimensional shape of a molecule. This may sometimes be of crucial importance in determining the physical properties of a compound. Recall that coordination compounds that exhibit stereochemistry give rise to different properties such as color. Stereochemistry may also play a role in the chemical reactions of a compound. This is most clearly seen when an organic molecule interacts with a complex biological molecule such as an enzyme.

For example, the compound limonene is responsible for the distinct smells of both oranges and lemons. Limonene is a colorless liquid hydrocarbon containing 10 carbon atoms, yet it can adopt two different shapes. These shapes are mirror images of one another—rather like a right hand and a left hand—and this subtle difference in shape results in a different interaction with the smell receptors in our noses. One mirror image form smells of lemons and the other of oranges.

When you finish this section, you should be able to:

- Understand the relationship between different classes of isomers

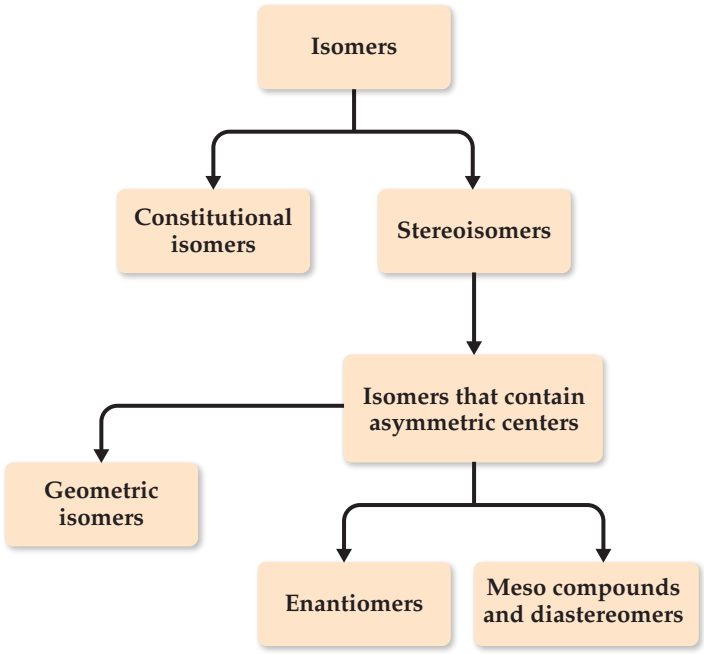
We have already discussed the dimensionality of simple organic molecules and seen that structure is responsible for a compound's physical properties, such as melting point, boiling point and density. As we see in this chapter, and again in Chapter 31, the three-dimensional structure of a molecule is also important for its chemical properties, especially in a biological environment.

The term *isomers* is used to describe molecules with the same molecular formula but some difference in structure **Figure 25.1** illustrates the relationship between the different classes of isomers. Constitutional isomers have a different bonding arrangement; for example, a straight-chain and a branched-chain alkane both of the formula C_6H_{14}.

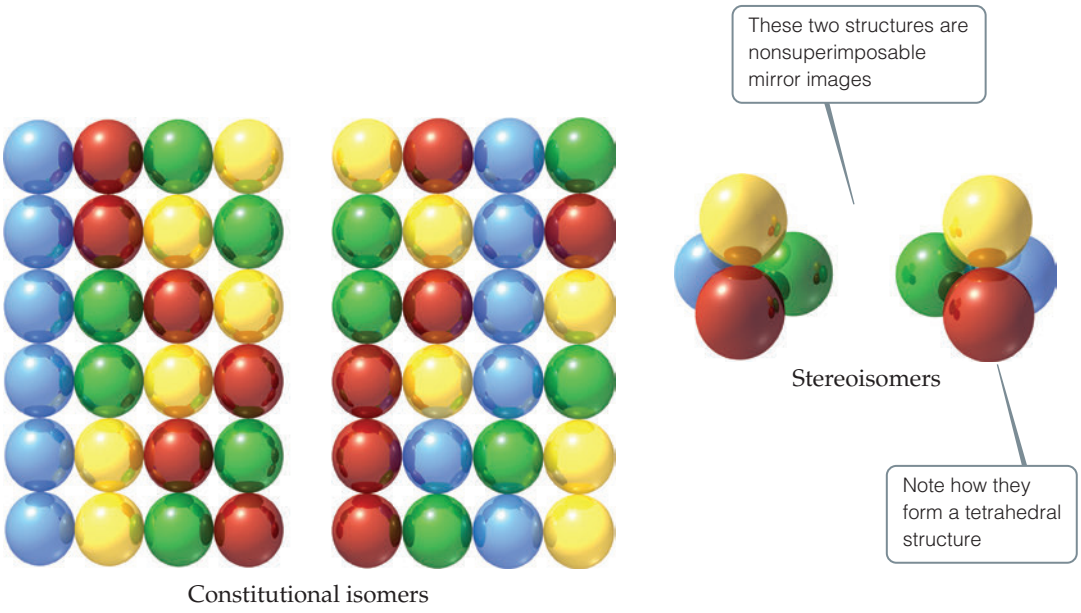
Stereoisomers have the same molecular formula and the same connectivity of atoms, but may be quite different in their physical and chemical properties. Stereoisomers can exist in several forms. Of these forms, there are three distinct classes: **geometric isomers**, **enantiomers**, and **diastereomers** (also called diastereoisomers). Stereoisomers cannot be interconverted without the breaking and remaking of a covalent bond.

We can begin our understanding of stereochemistry by considering simple representations of atoms, such as four colored balls—blue, green, red, and yellow. When the balls are laid in a row, there are 12 possible permutations, taking into account the ability to read from right to left or left to right (**Figure 25.2**). The relationship between any or all permutations can be described as *constitutional isomers*. In essence, the balls act as building blocks, in the same way as we described atoms or groups of atoms in Table 24.8. You can

Go Figure Can propane demonstrate constitutional isomerism?



▲ **Figure 25.1 There are several different forms of isomerism.** Although constitutional, geometric and diastereomers vary in their physical properties, enantiomers vary only when in a chiral environment.



▲ **Figure 25.2 Understanding isomerism.** Orientation of colored balls can be used as imagery to describe constitutional isomerism and stereoisomerism.

see from this example how easy it is to build up a library of compounds with the same molecular formula.

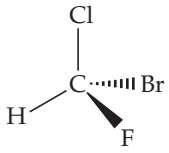
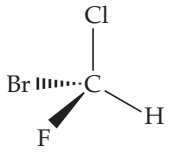
What happens when we change from a pseudo one-dimensional shape of the four balls, as occurs in a row, to one that is three-dimensional, such as a pyramid? The answer is a simplification in the number of permutations to just two. Notice that there is no way of superimposing the two pyramidal structures in Figure 25.2 onto one another—they are different. The two structures represented are, in fact, mirror images of each other. In chemical terms, they are stereoisomers and, more specifically, *enantiomers*.

Self-Assessment Exercise

25.1 Which of the pairs of structures represent stereoisomers?

(a) $CH_3CH_2CH_2CH_3$ and $CH_3CH_2CH_2CH_2CH_3$

(b) $CH_3CHCH_2CH_3$ (with CH_3 branch) and $CH_3CH_2CHCH_3$ (with CH_3 branch)

(c)  and 

(d) CH_3OCH_3 and CH_3CH_2OH

Answers to Self-Assessment Exercise

25.1 (c)

25.2 | *Cis–Trans* Isomerism in Cycloalkanes



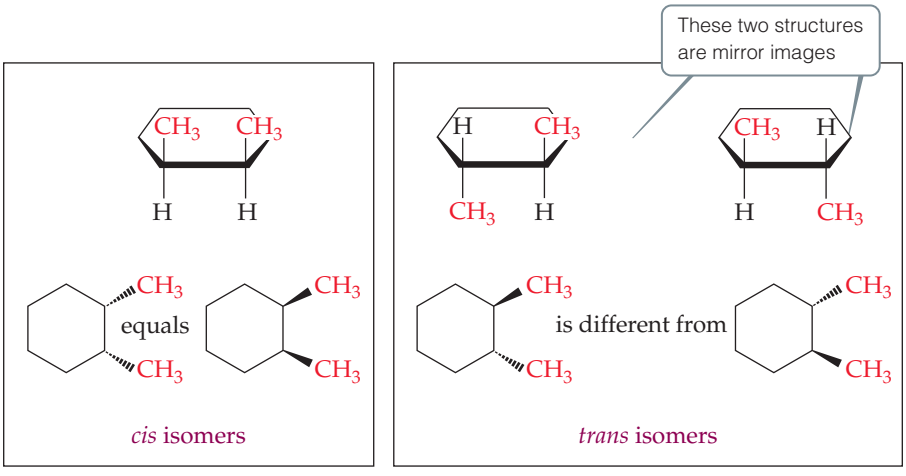
Inositol is a type of sugar that has a ring of six carbon atoms, each bearing an —OH group. It is important in the synthesis of neurotransmitter molecules and has been sold as a health supplement to improve brain function. There are eight geometries with different relative positions of the alcohol groups, only one of which is active in the body. In this section, we will look at the isomers possible in a cyclic compound with just two substituents.

When you finish this section, you should be able to:

- Identify the geometric isomers of a disubstituted cyclic compound

The three isomers of 1,2-dimethylcyclohexane shown in **Figure 25.3** differ in the relative locations of their methyl groups. These three compounds are *stereoisomers*. That is, they are compounds that have the same molecular formula and the same connectivity between atoms but differ in the spatial arrangement of these groups. Thus, the ***cis*** isomer of 1,2-dimethylcyclohexane has the two methyl groups orientated on the same side of the plane of the ring, whereas the ***trans*** isomers have the methyl groups orientated on opposite sides.

The three-dimensional orientation of groups within a structural formula or line drawing can be described using bold and dashed wedges, as shown in Figure 25.3. The notation employs the two-dimensional plane of the paper to draw a three-dimensional object. A bold wedge (▬) indicates that this bond extends towards you out of the plane of the



▶ **Figure 25.3 Geometric isomerism in disubstituted cycloalkanes.** *Cis* and *trans* isomerism is a feature of cycloalkanes. The easiest way to remember which isomer is which is to remember that *trans* (as in transpacific or transport) means "across".

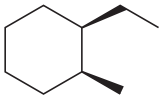
paper. A dashed wedge (·····) indicates that this bond is directed into the paper. This symbolism will become important in Section 25.3, where we investigate three-dimensional structure in more detail.

Despite the ability of C—C bonds to rotate under normal conditions, their ability to do so in a cycloalkane is greatly restricted by ring strain. Hence, the three stereoisomers shown in Figure 25.3 cannot be interconverted without breaking and remaking C—C bonds.

Sample Exercise 25.1

Naming *cis* and *trans* Isomers

Write the systematic name for the following cycloalkane:



SOLUTION

Analyze We are given the structure of a cycloalkane bearing two substituents and asked to name it, taking into account stereochemistry.

Plan Understand the type of cycloalkane, the names of the substituents and their relative orientation to each other using the wedged nature of the bonds.

Solve The cycloalkane has six carbons associated with the ring structure, so the full name is derived from cyclohexane. The two substituent groups are an ethyl group at position 1 and a methyl group at position 2 based on nomenclature rules.

The name for this alkane would be 1-ethyl-2-methylcyclohexane. However, this name tells us nothing about the relative orientations of the alkyl substituents. These two groups are *cis* to one another because the symbolism used in the line drawing has both substituents extending out of the page in the same direction. Hence, a full systematic name would be cis-1-ethyl-2-methylcyclohexane.

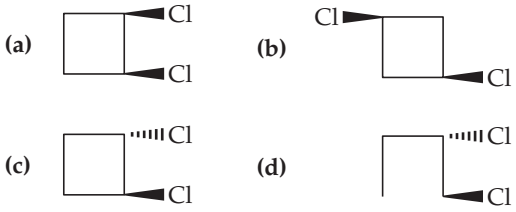
Practice Exercise

Write the systematic name for the following cycloalkane:



Self-Assessment Exercises

25.2 Which structure represents *cis*-1,2-dichlorocyclobutane?



25.3 Give the correct name, including the stereochemical descriptor, for:



(a) 1,4-dimethylcyclohexane

(b) *cis*-1,4-dimethylcyclohexane

(c) *trans*-1,4-dimethylcyclohexane

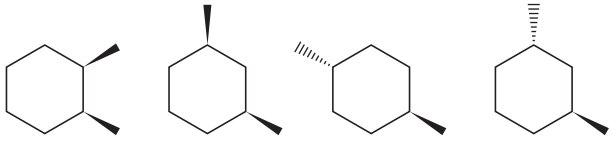
Exercises

25.4 Write the systematic name for the following cycloalkane:



25.5 Draw the structure of *cis*-1,2-dimethylcycloheptane.

25.6 Which pair of structures represent geometric isomers?



Answers to Self-Assessment Exercises

25.2 (a) 25.3 (c)

25.3 | Chirality in Organic Compounds

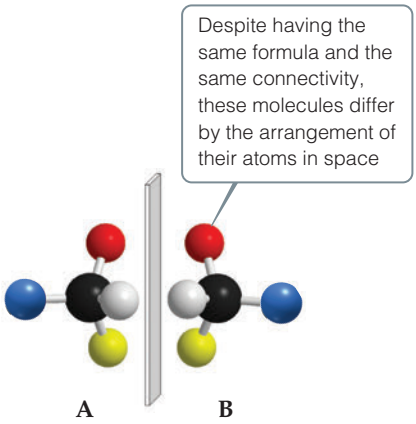


In 1875, a book by Charles Darwin was published titled *On the Movements and Habits of Climbing Plants*. One observation Darwin made was that some species of vines always twisted up a stake in a clockwise direction, while other species adopted an anti-clockwise direction. The two different spirals are mirror images of one another. There are many instances in nature of this sort of symmetry and a preference to adopt one form over the other. Our hands are an example of a mirror-image pair in which the two elements are not superimposable on one another. The very specific interactions this may lead to are shown by pulling on a pair of gloves and finding it is impossible to wear the glove that is not matched to the correct hand. Certain molecules possess non-superimposable mirror images and are called *optical isomers*.

When you finish this section, you should be able to:

- Identify the stereogenic center in a chiral molecule
- Draw the mirror-image structures of a chiral molecule

Let us begin our discussion of **optical isomers** in organic chemistry by looking at Figure 25.4. Molecule **A** consists of a tetrahedral carbon atom with four different groups attached, represented by the white, blue, red, and yellow balls. Is **A** identical to its mirror image, **B**? This question is best explored by making three-dimensional models and trying to overlay them; alternatively, try to imagine rotating **A** by 180° and placing it on top of **B**. What happens? The blue, black and white balls align, but the red and yellow are reversed. In fact, any way you try to overlay these two molecules, the result is the same—three of the balls are superimposable but the other two are not.



▲ **Figure 25.4 Mirror images.** These two molecules are non-superimposable mirror images. Being able to move molecules around mentally in three-dimensional space to prove two molecules are non-superimposable is extremely difficult and will require practice before it is mastered.

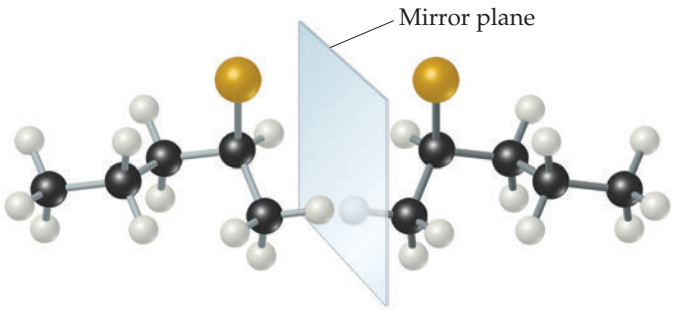
Molecules possessing non-superimposable mirror images, such as **A** and **B**, are termed **chiral** (Greek *cheir*, "hand"; pronounced *ky-ral*)—that is, they show handedness. In fact, *all molecules containing a single carbon atom bearing four different groups are chiral*. The fact that molecules **A** and **B** cannot be overlaid demonstrates that they are *different substances*. The relationship between two molecules that are non-superimposable mirror images is described by the term **enantiomer**. Hence, molecules **A** and **B** are enantiomers. For example, Figure 25.5 shows the two enantiomers of 2-bromopentane.

All enantiomers have a **chiral center** (also known as a **stereogenic center** or simply a **stereocenter**)—an atom (usually carbon) to which four different groups are attached.

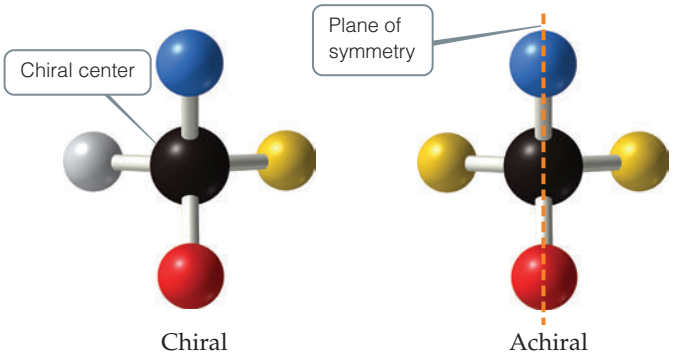
Molecules that have superimposable mirror images are **achiral**, meaning *not chiral*. Achiral molecules can usually be identified because they possess a plane of symmetry (Figure 25.6).

We can make the following general rules at this point:

1. *Stereocenters within any compound can be recognized because they have four different groups bonded to them.*
2. *The presence of one or more stereocenters always results in stereoisomers.*



◀ **Figure 25.5 The two enantiomeric forms of 2-bromopentane.** The mirror-image isomers are not superimposable with each other.

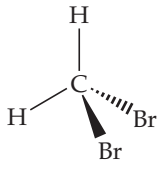


◀ **Figure 25.6 Chiral and achiral.** A molecule that contains one chiral center (stereocenter) is chiral (left). If a plane of symmetry exists, as in the molecule on the right, that molecule is said to be achiral.

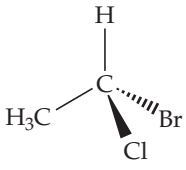
Sample Exercise 25.2

Predicting Chirality

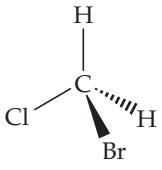
Determine which of the following structures is chiral:



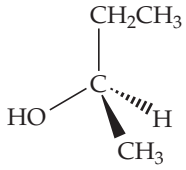
I



II



III



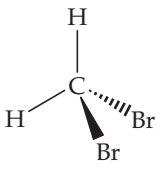
IV

SOLUTION

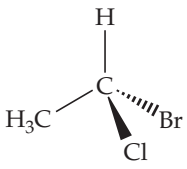
Analyze We are given four structures containing wedged bonds and are asked to determine which are chiral.

Plan Identify any planes of symmetry among the structures to determine achiral molecules. If there is no plane of symmetry, identify the stereogenic center to determine chirality.

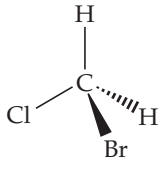
Solve Two compounds are chiral: II and IV. Compounds I and III have at least one plane of symmetry—in fact, compound I has two planes of symmetry. Note that methyl and ethyl groups are classed as different groups, as are the halogens, chlorine, and bromine. Remember, the alternative (and sometimes easier) way to determine whether a molecule is chiral or not is to check each carbon atom to see whether it is a stereocenter.



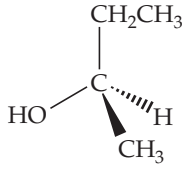
I
achiral



II
chiral



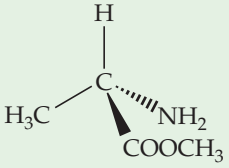
III
achiral

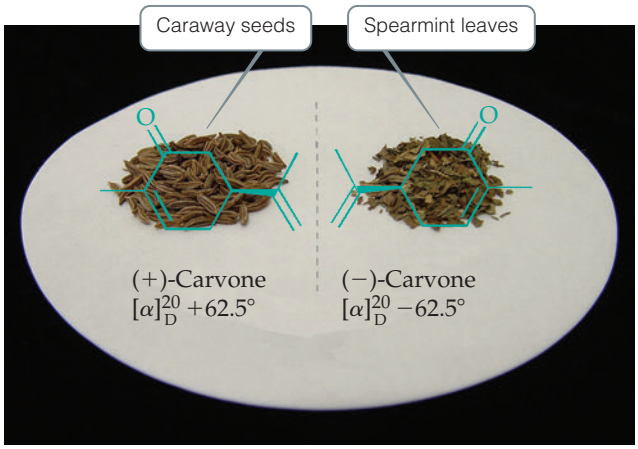


IV
chiral

Practice Exercise

Identify the chiral center in the following molecule and label it with an asterisk. Draw the molecule's mirror image.





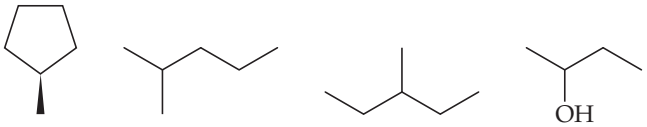
▶ **Figure 25.7 Enantiomers of carvone.** Caraway seeds smell very different from spearmint leaves or oil. The difference is a result of how each molecule interacts with the chiral receptors in the nose.

Most of the physical and chemical properties of enantiomers are identical because each enantiomer contains the same functional groups and the same non-bonding interactions. Enantiomers, such as the two forms of 2-bromopentane shown in Figure 25.5, have identical physical properties, such as melting and boiling points, and identical chemical properties when they react with achiral reagents. The properties of two enantiomers *differ only if they are in a chiral environment*. An easy way of demonstrating the differences between enantiomers in a chiral environment is to purchase caraway seeds and spearmint leaves from your local supermarket. Each product contains a different enantiomer of carvone (**Figure 25.7**). Now smell them and note the stark difference.

The difference in their smell is a result of the chirality of the receptors contained within your nose. Each enantiomer fits into the receptor's binding site in a similar way to how our right or left hands would fit into a left-hand glove. For one enantiomer, the fit is perfect, leading to a maximum interaction between the molecule and receptor. The other enantiomer fits awkwardly, leading to less than perfect binding and a different response, perhaps a different smell or taste.

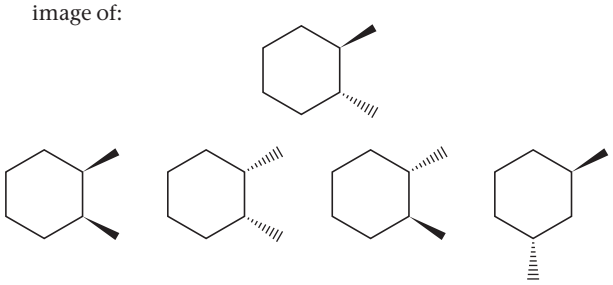
Self-Assessment Exercises

25.7 Which structure represents a chiral molecule—contains a stereocenter?



(a) (b) (c) (d)

25.8 Identify the structure that is a non-superimposable mirror image of:

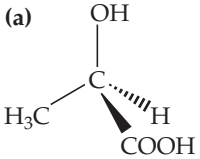


(a) (b) (c) (d)

Exercises

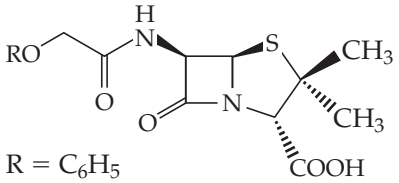
25.9 Locate the chiral carbon atoms, if any, in each of the following natural products:

(a)



lactic acid

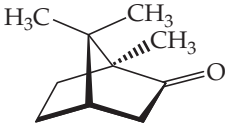
(b)



R = C_6H_5

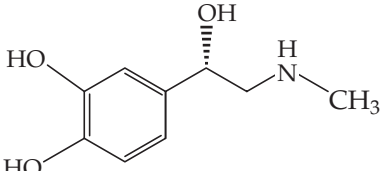
penicillin V

(c)



camphor

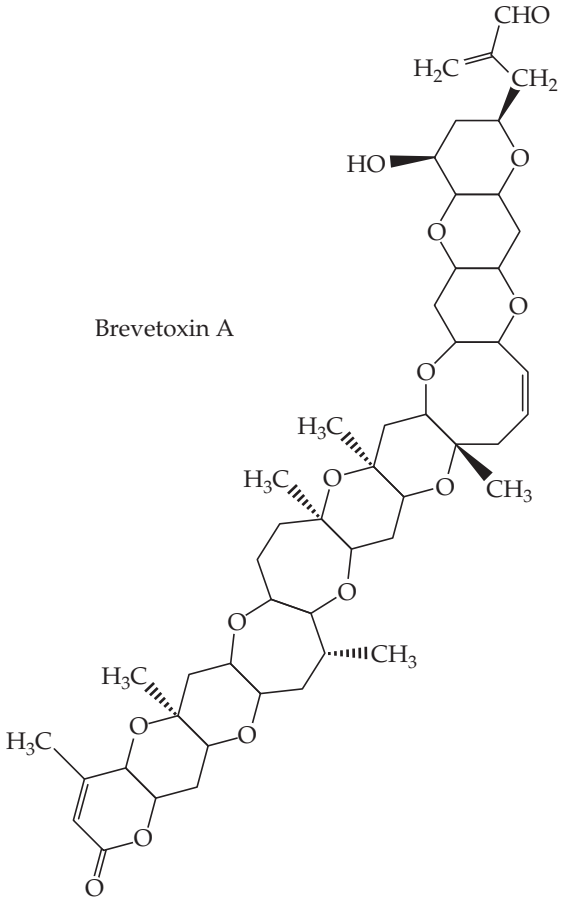
(d)



epinephrine

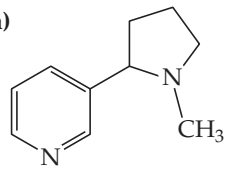
26.10 Brevetoxin A, a cyclic polyether made up of 11 rings, is a potent neurotoxin. It is named from the *brevis* family of algae from which it was extracted. Locate all the stereocenters in Brevetoxin A.

Brevetoxin A



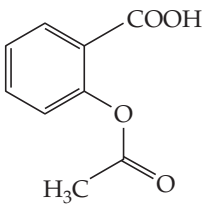
26.11 Which of the following molecules are chiral?

(a)



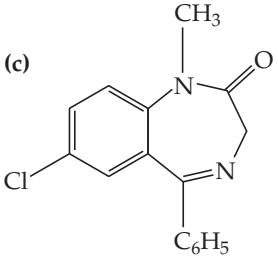
nicotine

(b)



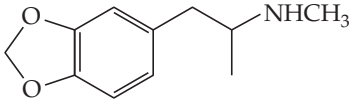
aspirin

(c)



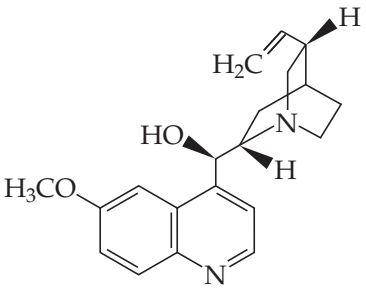
valium

(d)



ecstasy

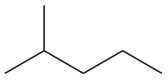
26.12 Quinine is a well-know antimalarial drug. How many chiral centers exist in quinine?



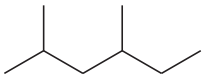
(quinine—an antimalarial drug)

26.13 Which of the following molecules contain stereogenic centers?

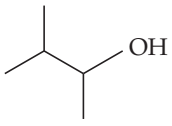
(a)



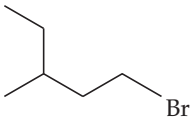
(b)



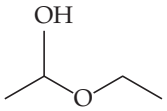
(c)



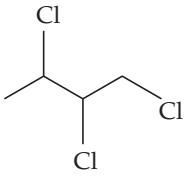
(d)



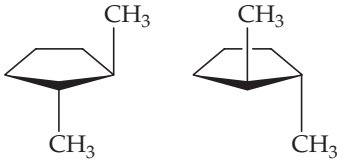
(e)



(f)



26.14 **(a)** What type of isomeric relationship exists between pentane and 2-methylbutane? **(b)** What is the relationship between these two *trans*-structures?



Answers to Self-Assessment Exercises

25.7 (d) **25.8** (c)

25.4 Measuring Optical Activity

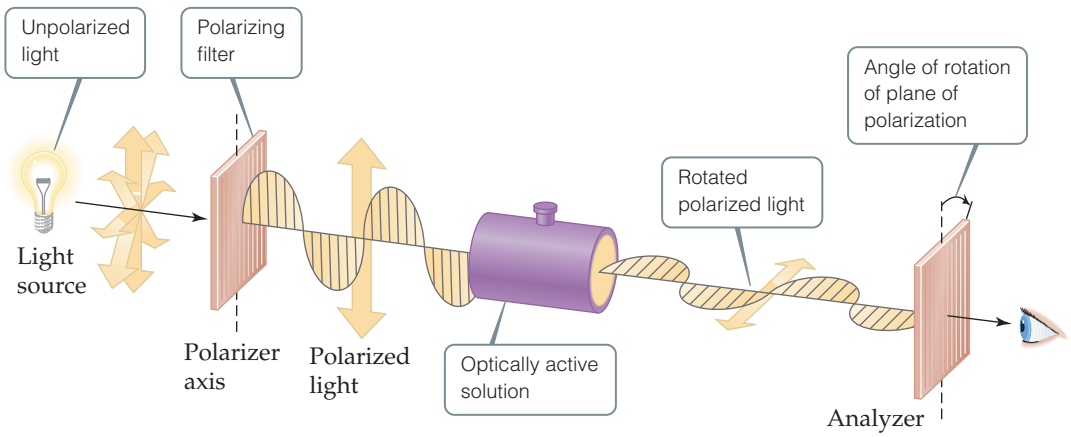


Louis Pasteur (1822–1895) was a French chemist and biologist. He was responsible for some of the most important concepts and applications of modern science, including the discovery of the science of microbiology, the process of pasteurization, and molecular asymmetry. In 1848, Pasteur noticed that a saturated solution of sodium ammonium tartrate crystallized to form crystals that were mirror images of one another. He separated "right-handed" crystals from "left-handed" crystals using a microscope and a pair of tweezers. Dissolving the two crystalline forms in water and subjecting them to plane-polarized light, Pasteur was able to demonstrate that the optical activity of the mirror image crystals was opposite to one another. White wines contain a relatively high concentration of tartaric acid and crystals of calcium tartrate may sometimes be seen on corks of wine after long cellaring.

In this section, we will learn about the optical properties of chiral compounds and, by the end, you will:

- Understand the relationship between non-superimposable mirror images and rotation of plane polarized light.

Chiral molecules are said to be optically active because of their effect on plane-polarized light. If light is polarized—for example, by passage through a polarizing filter—the light in only one particular plane is allowed to pass through, as shown in **Figure 25.8**. If the



▲ **Figure 25.8 Optical activity.** Effect of an optically active solution on the plane of polarization of plane-polarized light. The unpolarized light is passed through a polarizer. The resultant polarized light then passes through a solution containing a dextrorotatory optical isomer. As a result, the plane of polarization of the light is rotated to the right relative to an observer looking towards the light source and so the optically active compound is dextrorotatory.

plane-polarized light is passed through a solution containing one enantiomer, this plane is rotated through an angle a, measured in degrees, to the right (clockwise, or +) or to the left (anticlockwise, or −) as viewed by an observer. The isomer that rotates plane-polarized light to the right is **dextrorotatory** (Latin *dexter*, "right"); it is labelled the (+)-isomer. Its enantiomer rotates plane-polarized light to the left and is called **levorotatory** (Latin *laevus*, "left"); it is labelled the (−)-isomer.

Figure 25.7 provides information on the results of the plane-polarized light experiment for the enantiomers of carvone. Notice that one enantiomer rotates light in a positive direction while the other rotates light in a negative direction. The term $[\alpha]_D$ is known as the **specific rotation** (Equation 25.1) and takes into account the concentration of the sample c (g cm^{-3}) and the path length l of the sample (dm, 1 dm = 0.1 m) confined within a solution cell, as well as the observed rotation α (degrees). The specific rotation is usually expressed in degrees, even though the units formally should be ° cm^3 dm^{-1} g^{-1}.

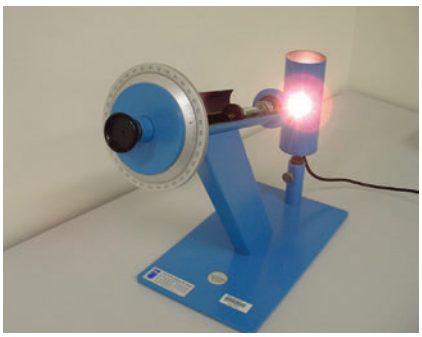
$$[\alpha]_D^{20} = \frac{\alpha}{c \times l} \qquad [25.1]$$

The subscript D refers to the source of monochromatic radiation used for the measurement (typically the sodium-D line, λ = 589 nm). The superscript 20 above the D refers to the temperature (in degrees Celsius) of the measurement, as optical activity is temperature dependent. Note that the magnitudes of the specific rotation for (+)- and (−)-carvone are identical—only the sign changes. An example of the instrument used to perform this optical experiment, called a **polarimeter**, as well as the type of solution cell used, is shown in Figure 25.9.

Optical rotation is a useful way of determining whether a compound is **enantiomerically pure**—that is, contains a single enantiomer. Failure to obtain the same specific rotation for a compound prepared in the laboratory as that reported in the literature most often happens because some of the other enantiomer is present. Often, no rotation can be observed for a substance whose molecules contain a chiral center. This usually means a 50 : 50 mixture of the two enantiomers has formed under the reaction conditions. A mixture with an equal amount of both enantiomers is called a **racemic mixture**, or *racemate*. A racemic mixture of enantiomers does not rotate plane-polarized light because the two enantiomeric forms rotate the light to equal extents in opposite directions, cancelling out any optical effect. Since a racemic mixture contains equal amounts of the (+) and (−) enantiomer it is often designated (±) or (*dl*).

Table 25.1 lists the specific rotation for several well-known organic compounds. Note that *specific rotation is an experimental quantity* and neither the magnitude nor the sign is easily predicted from the structure. An example of the difficulties in prediction is shown in the acid hydrolysis of sucrose, a compound that contains nine stereogenic centers. Here we need not concentrate so much on the complex sugar structures as on the sign and magnitudes of the specific rotation of starting materials and products.

Sucrose, $[\alpha]_D^{25}$ = +65°, is hydrolysed (broken up by the addition of water) under acidic conditions to give glucose, $[\alpha]_D^{25}$ = +53°, and fructose, $[\alpha]_D^{25}$ = −89.5° (Figure 25.10). The 1 : 1 mixture of glucose and fructose that is obtained upon the hydrolysis of sucrose is called *invert sugar* because the specific rotation of the mixture is dominated by the negative rotation of fructose. Since the total specific rotation is effectively the sum of individual specific



(a)

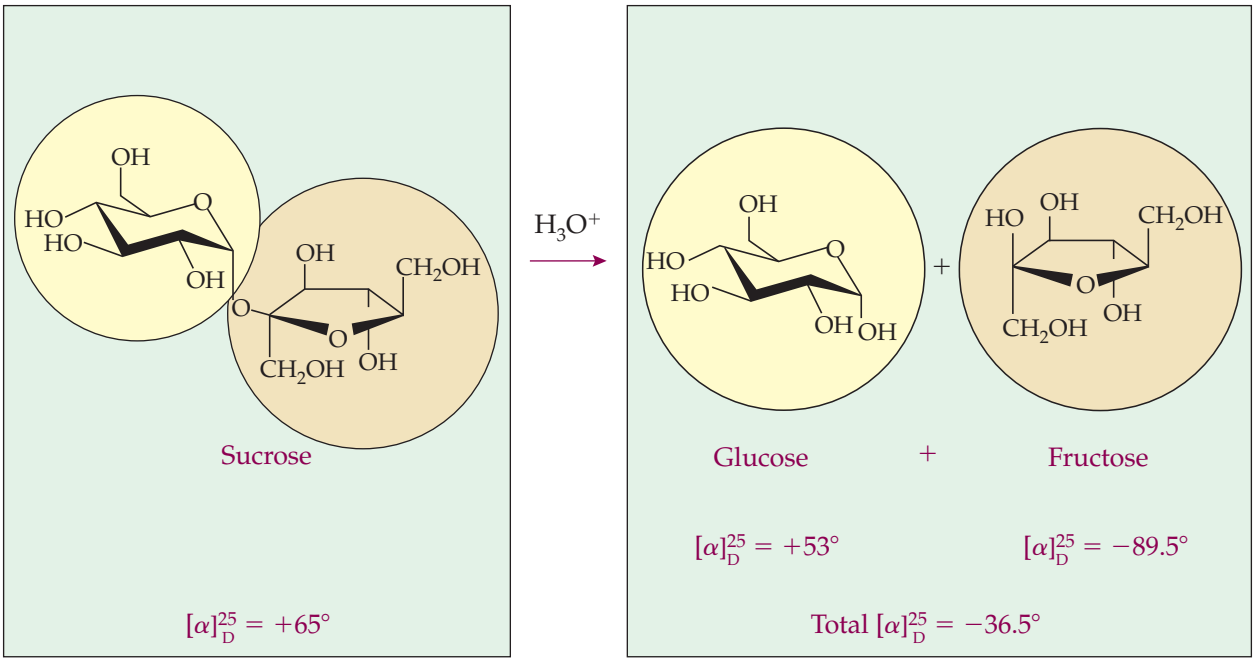


(b)

▲ **Figure 25.9 A polarimeter and solution cell.** A polarimeter (a) is used to measure the rotation of plane-polarized light as it passes through a sample contained within a 1 dm cell (b).

TABLE 25.1 Specific rotations, $[\alpha]_D$, of some common organic compounds

Compound	$[\alpha]_D$ (°)	Compound	$[\alpha]_D$ (°)
Cholesterol	−39	*d*-Camphor	+44
Penicillin-V	+233	*l*-lactic acid	−4
Sucrose	+66.5	Quinine	−178
Morphine	−132	*d*-Tartaric acid	+12
Strychnine	−139	Maltose	+141
Fructose	−92	Glucose	+53



▲ **Figure 25.10 Forming invert sugar.** The complete hydrolysis of sucrose gives glucose and fructose as products. Complete hydrolysis of sucrose yields a specific rotation of −36.5°. Fructose is the sweetest common sugar, being about twice as sweet as sucrose; consequently, invert sugar is sweeter than sucrose. The enzyme *invertase*, which bees use in making honey, accomplishes the same chemical result as the acid-catalysed hydrolysis of sucrose.

rotations, hydrolysis changes the optical properties of the solution from rotating light clockwise (+) to anticlockwise (−), despite very little molecular difference between the two sides of the equation. Hence, specific rotation is extremely sensitive to molecular structure.

Sample Exercise 25.3

Specific Rotation

The specific rotation of (−)-carvone is −62.5°, measured at 20 °C. Calculate the observed rotation at 20 °C for a solution prepared by dissolving 1000 mg of (−)-carvone in 30 cm^3 of ethanol and placing it in a solution cell 10 cm long.

SOLUTION

Analyze We are given the specific rotation, temperature, concentration and path length and asked to determine the observed rotation.

Plan These variables are all related by Equation 25.1, where $[\alpha]_D = -62.5$, $l = 10\text{ cm} = 1\text{ dm}$, $c = 1/30\text{ g cm}^{-3}$. We can solve for α.

Solve Substituting into Equation 25.1 yields

$$-62.5 = \frac{30\alpha}{1 \times 1}$$

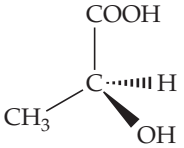
$$\alpha = -2.1°$$

Practice Exercise

The observed rotation of a solution of camphor prepared by dissolving 1.6 g in 20 cm^3 of hexane was +2.4°. Determine the specific rotation of this sample, which was contained in a 1 dm-long cell, and use Table 25.1 to conclude whether the sample is that of a single enantiomer.

Self-Assessment Exercise

25.15 Lactic acid is a chiral molecule with the structure:



One enantiomer has a specific rotation of +2.6°. What is the specific rotation of the other (mirror image) enantiomer?

(a) 0.0°.

(b) −2.6°.

(c) +2.6°.

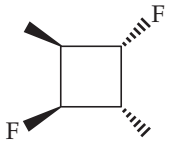
(d) It is impossible to tell from the data given

Exercises

25.16 Is it possible to determine the sign and magnitude of the optical rotation from the structure of the molecule?

25.17 Does 3-chloro-3-methylhexane have optical isomers? Why or why not?

25.18 Is the following compound optically active?



25.19 An 8 g sample of sucrose, $[\alpha]_D = +65°$, was dissolved in 25 cm^3 of water and placed in a solution cell of 5 cm length. What was the observed rotation? Is sucrose levorotatory or dextrorotatory?

25.20 The specific rotation, $[\alpha]_D$, of a pure compound obtained from plant material was found to be $-20°$. Explain the symbolism used to describe specific rotation and comment on what the result means.

Answers to Self-Assessment Exercise

25.15 (b)

25.5 | Absolute Stereochemistry



Using Priority Rules to Find a Stereocenter's Absolute Configuration

The "Hammerhead ribozyme" shown in the picture carries out a simple reaction but at a very specific site in RNA. This is a complex molecule, but even a molecule with one stereocenter, in a biological system, may show reactions of one enantiomer that are very different from its pair. While we can measure optical activity for the enantiomers, we need a system to describe the actual shape of each mirror image. The British chemists Robert Cahn (1899–1981) and Christopher Ingold (1893–1970), together with Vladimir Prelog (1906–1998), a Yugoslav chemist based in Switzerland, proposed a set of rules in 1956 to bring some order to the complex world of organic stereochemistry. Prelog was awarded the Nobel Prize in Chemistry in 1975 (jointly with Australian-born Sir John Cornforth) for his work on stereochemistry and complex naturally occurring chemical products.

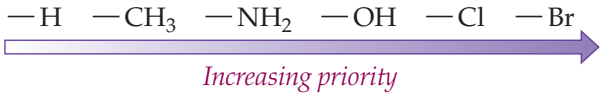
By the end of this section, you will be able to:

- Assign the configuration to a stereocenter using the nomenclature *R* or *S*.

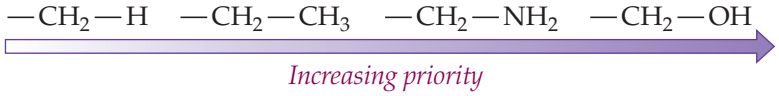
Although the (+)- and (−)-notation yields important experimental information about a compound, it tells us nothing about the **absolute configuration** (that is, the exact three-dimensional structure) of the molecule. To remove any ambiguity when describing the absolute configuration at a stereocenter, the **Cahn–Ingold–Prelog *R,S* notation** has been employed. The Cahn–Ingold–Prelog notation uses **sequence priority rules** to determine a stereocenter's absolute configuration.

We can use the following steps to determine the absolute configuration of a stereocenter:

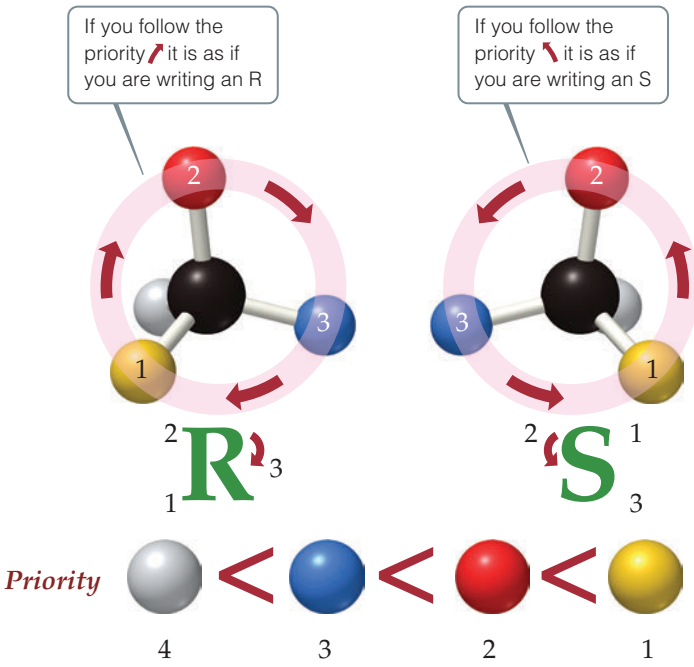
1. Locate the stereocenter.
2. Assign a priority to each substituent from 1 (highest) to 4 (lowest) based on the *atomic number* of the four atoms directly attached to the stereocenter. The higher the atomic number, the higher the priority. A representative set of groups in increasing priority order is



   If two atoms are identical in terms of priority, you need to move out along the respective chains until a difference in priority is encountered. Continue to reapply rule 2 to determine priority or until the end of the group is reached. If no difference is found, the molecule has symmetry and is therefore achiral. Examples of increasing priority fragments are



3. Orient the molecule so that the group with the lowest priority (often hydrogen) is directed away from you, that is, it is connected to the stereocenter by a dashed wedge (·····).



4. Read the three groups orientated towards you in order from highest (1) to lowest (3) priority.
5. If the numbers increase from 1–3 in a clockwise manner, the configuration is *R* (from the Latin *rectus*, "straight, correct, right"). If the numbers increase in an anticlockwise manner, the configuration is *S* (from the Latin *sinister*, "left").
6. If the compound containing the stereocenter is *R*, then its enantiomer is *S*, and *vice versa*.

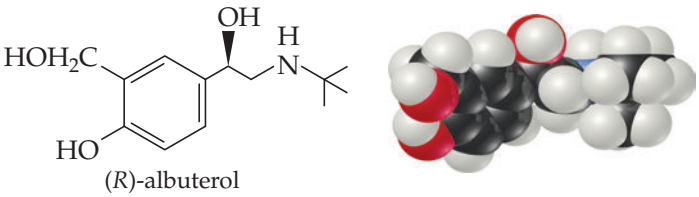
CHEMISTRY AND LIFE Chiral Drugs

Many drugs of importance in medicine are chiral substances. When a drug is prepared, sold and administered as a racemic mixture, it often turns out that only one of the enantiomers has beneficial results. The other enantiomer is either inert or nearly so, or may even have a harmful effect. For the last reason, a great deal of attention has been given in recent years to methods for synthesising the desired enantiomer of chiral drugs. Chemical research directed at understanding how to control the stereochemistry of a reaction has led to new synthetic methods that make it not only possible, but relatively cost-effective, to produce chiral molecules in *enantiomerically pure* form. Worldwide sales of single-enantiomer drugs amounts to over $225 billion annually.

Albuterol is a good example of the different physiological behaviour of enantiomers. The drug (*R*)-albuterol (Figure 25.11) is an effective bronchodilator used to relieve the symptoms of asthma. Its enantiomer, (*S*)-albuterol, is not only ineffective as a bronchodilator but actually counters the effects of (*R*)-albuterol.

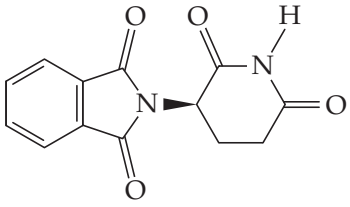
The non-steroidal analgesic ibuprofen (marketed under the trade names Advil™ and Nurofen™) is a chiral molecule usually sold as a racemic mixture. The more active enantiomer, (*S*)-ibuprofen (Figure 25.12), relieves pain and reduces inflammation, whereas the weakly active *R* enantiomer, which isn't as easily utilized, is actually converted by enzymes within the body to the active S form.

In the 1950s and 1960s the drug thalidomide was administered to pregnant women as an anti-emetic to combat morning sickness. It was found to be teratogenic, being responsible for severe deformities in over 12 000 foeteuses worldwide. The case against thalidomide has two sides, however. First, rigorous testing of all chiral drug candidates has now been made mandatory for both enantiomers after the thalidomide experience. The *R* enantiomer of thalidomide was active in preventing morning sickness during pregnancy, whereas the *S* enantiomer was responsible for the terrible side-effects in humans. Unfortunately, racemization of (*R*)-thalidomide (to form the *S* enantiomer) occurs easily within the body, so even the useful *R* enantiomer has no therapeutic use for pregnant women. Thalidomide has also been approved by the US Food and Drug Administration for the treatment of leprosy. Trials are also under way for epilepsy and HIV.



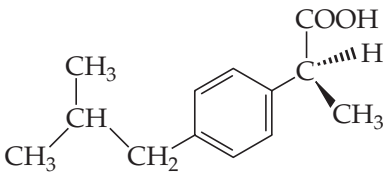
(*R*)-albuterol

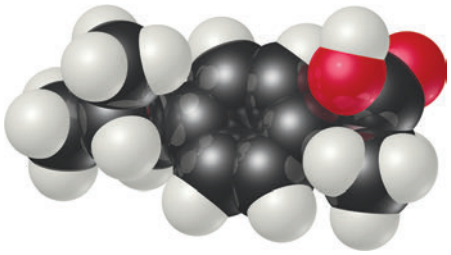
▲ **Figure 25.11 (*R*)-Albuterol.** This compound acts as a bronchodilator in patients with asthma. In contrast, (*S*)-albuterol counters this effect.



(*R*)-thalidomide

Go Figure Locate the chiral center in Ibuprofen. What evidence immediately drew you to that choice?



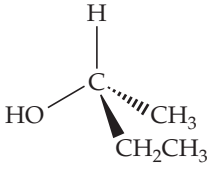


▲ **Figure 25.12 (*S*)-Ibuprofen.** For relieving pain and reducing inflammation, the ability of this enantiomer far outweighs that of the *R* enantiomer.

Sample Exercise 25.4

R and *S* Notation

Assign the absolute configuration as *R* or *S* to the following compound:



SOLUTION

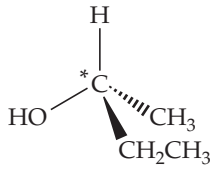
Analyze We are asked to identify this molecule as *R* or *S*.

Plan Follow the sequence priority rules after identifying the stereocenter.

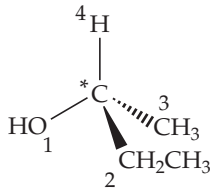
Continued

Solve

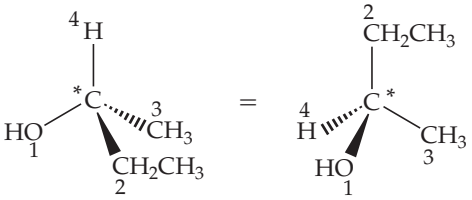
Step 1



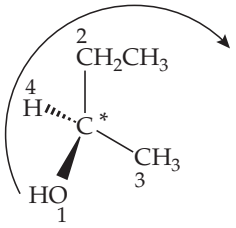
Step 2



Step 3



Step 4



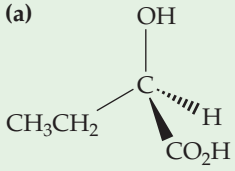
Step 5 *R* configuration

Name (*R*)-2-butanol

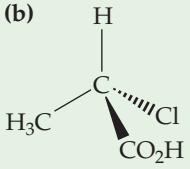
Practice Exercise

Assign the absolute configuration as *R* or *S* to the following:

(a)

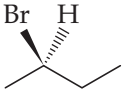


(b)



Self-Assessment Exercise

25.21 Give the full systematic name of the following molecule:

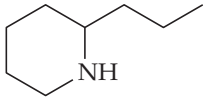


(a) (*R*)-2-bromobutane

(b) (*S*)-2-bromobutane

Exercises

25.22 Coniine is the active natural ingredient in the poison hemlock. Locate the stereocenter in this structure and assign priorities to each of the substituents.



coniine

25.23 Draw the structure for 2-bromo-2-chloro-3-methyl-pentane, and indicate any stereogenic centers in the molecule.

25.24 Assign priorities to the following sets of substituents:

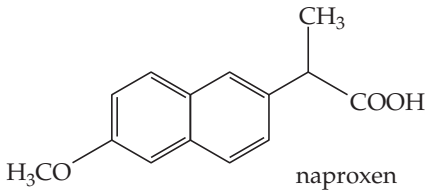
(a) $-Br$, $-CH_2CH_3$, $-CH_3$, $-OH$

(b) $-COOH$, $-CH(CH_3)_2$, $-H$, $-OCH_3$

(c) $-CH_2CH_2CH_2COOH$, $-NH_2$, $-COOH$, $-H$

(d) $-COOH$, $-COOCH_3$, $-CH_2OH$, $-OH$

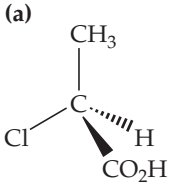
25.25 The *S* enantiomer of naproxen is a potent antiinflammatory agent whereas the *R* enantiomer is a harmful liver toxin. Draw the *S* enantiomer of naproxen and its mirror image.



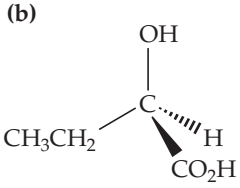
naproxen

25.26 Assign an *R*,*S* configuration to each stereocenter.

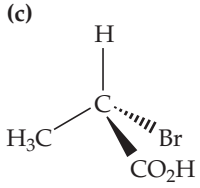
(a)



(b)



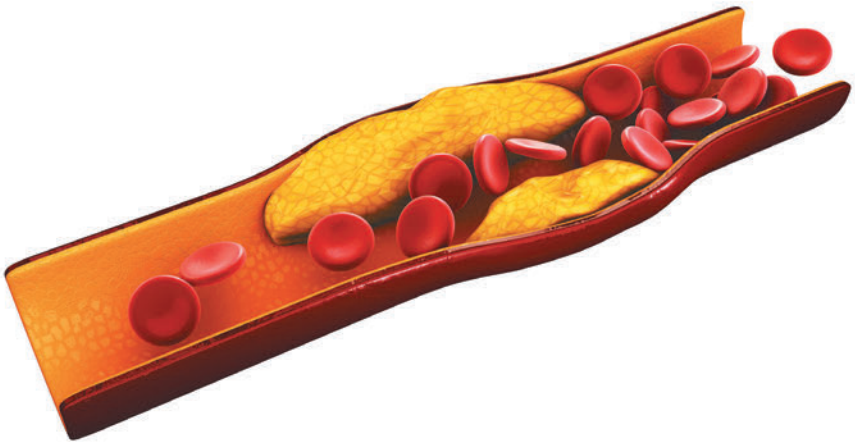
(c)



Answers to Self-Assessment Exercise

25.21 (a)

25.6 Molecules with More than One Stereocenter



A diet rich in saturated fat can result in an excess of cholesterol in the body. When this surplus is deposited on the walls of arteries, it can restrict the flow of blood to vital organs such as the heart or brain and lead to heart attack or stroke. Cholesterol is a chiral molecule with eight stereocenters and a possible 256 different stereoisomers. Remarkably, only one of these isomers is produced naturally.

In this section, we examine molecules containing two stereocenters, and by the end, you will:

- Recognize the relationship between different isomers of the same molecule
- Appreciate one method by which enantiomers may be separated

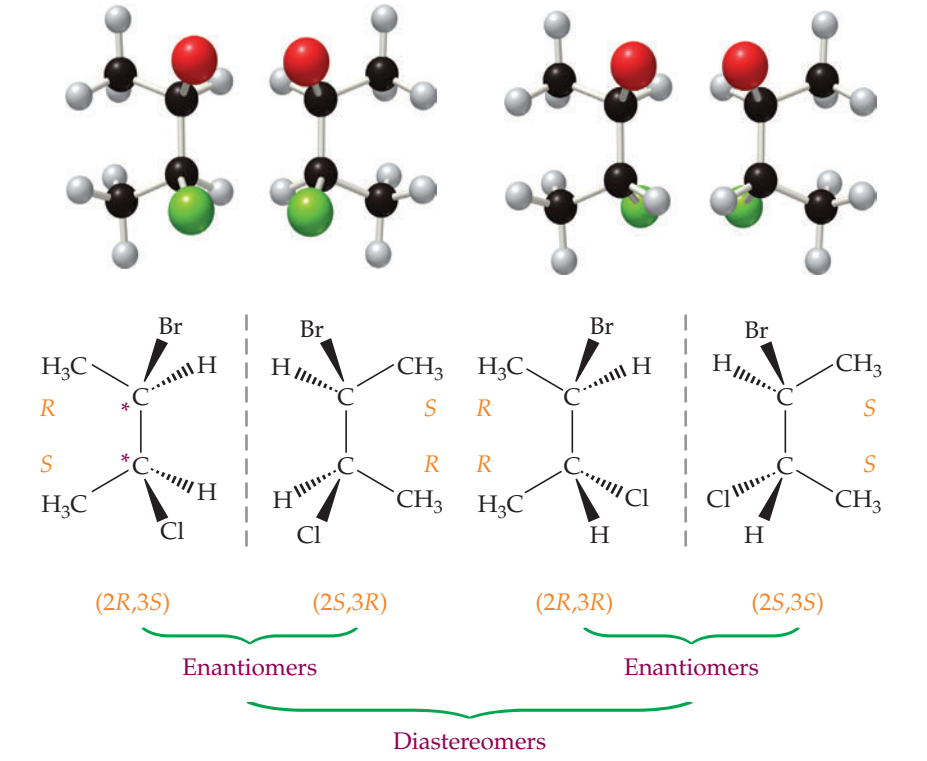
A chiral molecule with one stereocenter can exist as one of two enantiomers, *R* or *S*. Generally, for a molecule with *n* stereocenters, the maximum number of stereoisomers possible is given by Equation 25.2

$$\text{Number of stereoisomers} = 2^n \qquad [25.2]$$

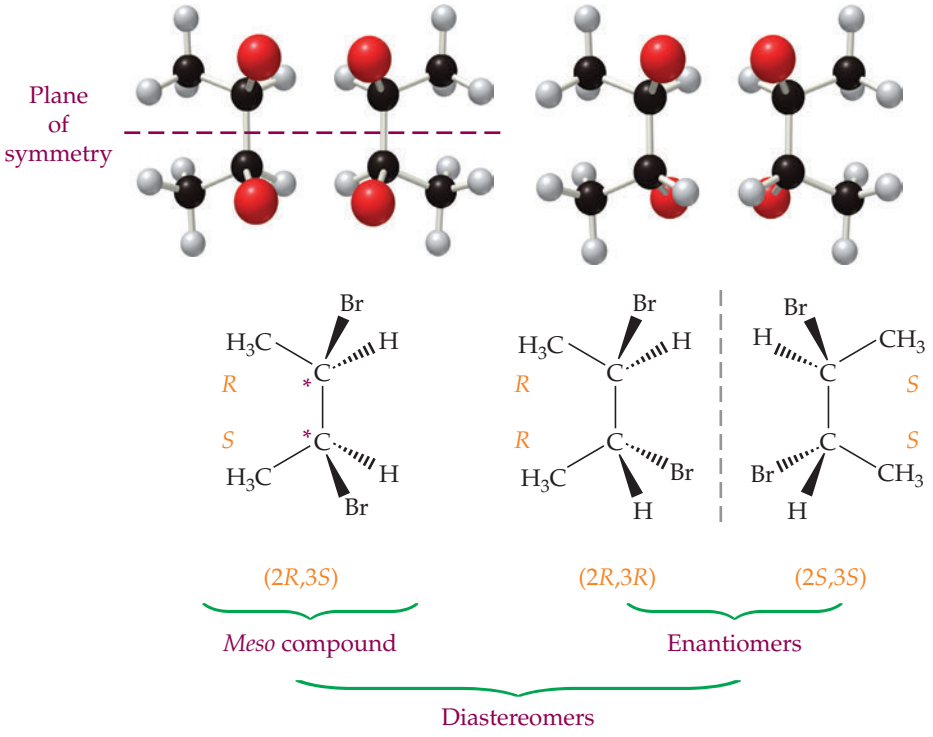
Let us consider a molecule with two stereocenters—that is, a molecule that can exist as a maximum of four stereoisomers. All the possible stereoisomeric permutations for the compound 2-bromo-3-chlorobutane are shown in **Figure 25.13**. This compound contains two stereocenters (labelled with an asterisk) and so can exist in (2*R*,3*S*), (2*S*,3*R*), (2*R*,3*R*), (2*S*,3*S*) forms. This notation is used to describe the stereochemistry at each stereocenter: the number represents the position of the chiral carbon atom on the longest chain and the *R*,*S* notation is used to describe the absolute stereochemistry at that position.

Each of the chiral molecules in Figure 25.13 is related to the other three. Notice that two pairs of enantiomers exist. Thus, one pair of enantiomers is labelled (*R*,*R*) and (*S*,*S*), while the other pair will be labelled (*R*,*S*) and (*S*,*R*). The two pairs of enantiomers are also related (for example, compare (*R*,*S*) and (*R*,*R*)). They are neither non-superimposable nor mirror images and are called **diastereomers**. Diastereomers, by definition, are any set of stereoisomers that are not enantiomers. *Whereas enantiomers have identical physical and chemical properties in an achiral environment, diastereomers always have different chemical and physical properties*.

Let's now consider 2,3-dibromobutane as an example (**Figure 25.14**). This compound has two stereocenters. However, a plane of symmetry exists through the C—C single bond between the two stereocenters in the (*R*,*S*) form, making it identical to the (*S*,*R*) form. The two forms are now superimposable and so are not enantiomers. From our earlier definition, a molecule possessing a plane of symmetry is not chiral. An achiral compound possessing two or more stereocenters is known as a ***meso* compound**.



▶ **Figure 25.13 Enantiomers and diastereomers.** Compounds with two stereocenters have a maximum of four stereoisomers. These stereoisomers have a relationship to each other. The name describing the relationship differs if the two molecules in question are non-superimposable mirror images (enantiomers) or not (diastereomers).



▶ **Figure 25.14 *Meso* compounds.** Despite possessing two stereocenters, 2,3-dibromobutane has only three stereoisomers. The *meso* form is achiral because it contains a plane of symmetry.

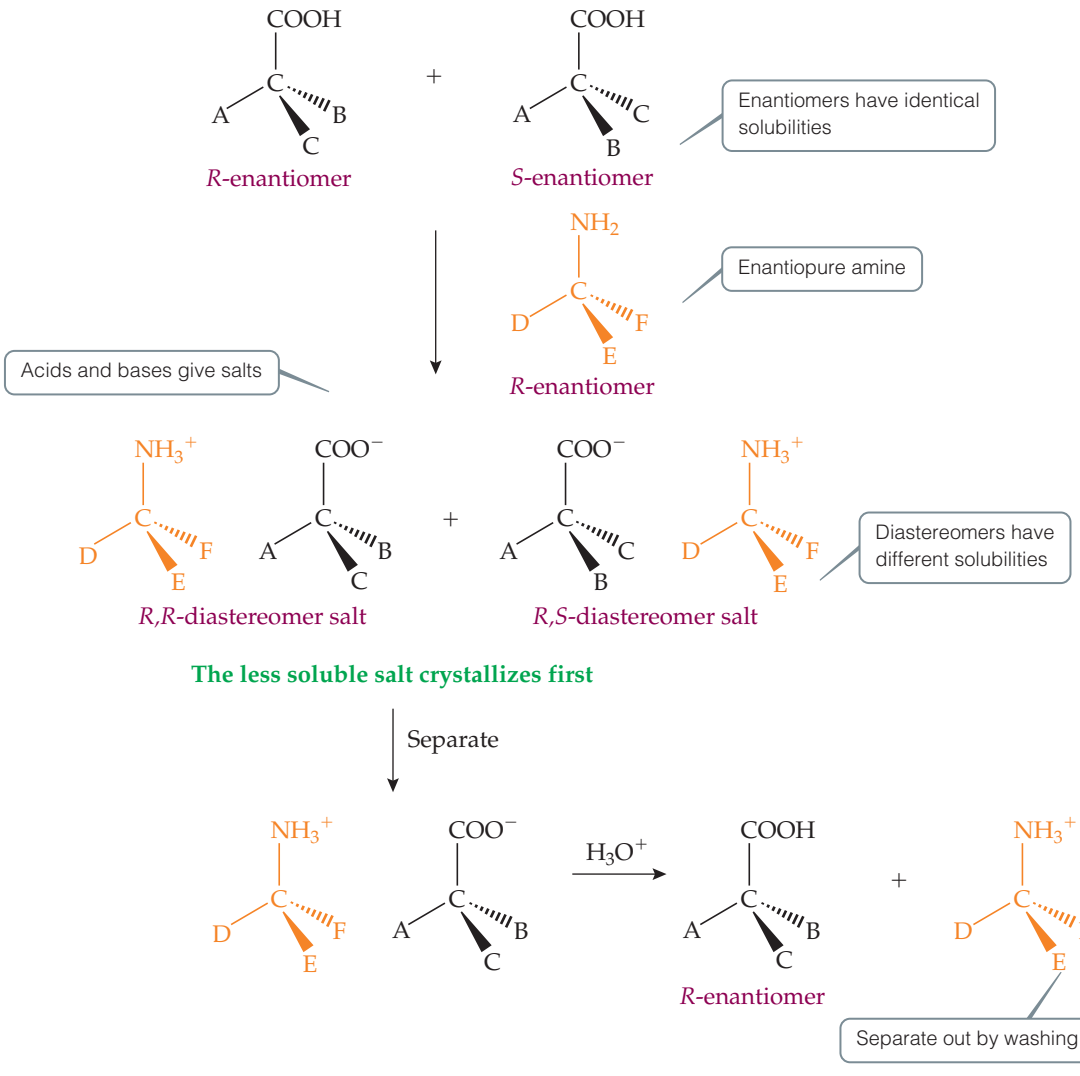
Resolution: Separating Enantiomers

Separating a racemic mixture into two enantiomers with high optical purity is extremely difficult to do without the aid of a chiral auxiliary. Pasteur was indeed fortunate that the racemic tartaric salts crystallized in such a way as to contain a single enantiomer within one crystalline form. More often than not, the two enantiomers co-crystallize to form crystals that are indistinguishable from each other. Even with the aid of chiral separating agents, this process of separating enantiomers (called **resolution**) is extremely

expensive and time-consuming. We can, however, use the different chemical and physical properties of diastereomers to perform a clever experiment to resolve two enantiomers. The trick is to convert the enantiomers into diastereomers in order to separate them.

The resolution process is explained schematically in **Figure 25.15**. Whenever possible, the chemical reactions involved in the formation of diastereomers and their conversion into separate enantiomers are acid–base reactions. The reason for this is simple: organic salts crystallize well in almost any solvent (including water) and the acid–base chemistry employed is uncomplicated. For example, a racemic mixture of a chiral carboxylic acid is reacted with a single enantiomer of an amine such as (*R*)-α-methylbenzylamine (RAMBA). The two salts that form are diastereomeric because they each contain two chiral centers, yet are not mirror images. Separation of one diastereomeric salt from the other is typically achieved by crystallization methods. In order to maximize enantiomeric purity, the crystallization is repeated several times. The pure enantiomer is subsequently liberated by treatment with aqueous acid.

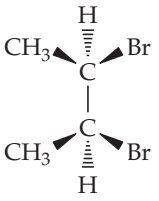
The method described in Figure 25.15 is also widely used for the resolution of chiral amines, using an *enantiopure* carboxylic acid such as the naturally occurring carboxylic acid, (*S*)-malic acid. Other methods, depending on the functionality present within the *racemate*, have also been developed. One of the more interesting methods involves an enzymatic resolution. Since biological systems such as enzymes are highly specific for a particular enantiomer, they can be conveniently used to perform simple derivatizations to a single enantiomer in a racemic mix. Derivatization (for example, hydrolysis of an ester functionality) changes both the physical and chemical properties, allowing for easy separation and hence resolution.



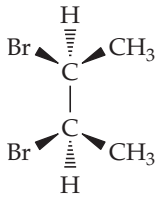
◀ **Figure 25.15**
Resolution. Enantiomers, especially those containing a carboxylic acid functionality, can be separated by converting them into diastereomeric salts. Typically, crystallization leads to the separation of one diastereomeric salt over the other. Conversion of the salt back to the carboxylic acid yields a purified enantiomer.

Self-Assessment Exercises

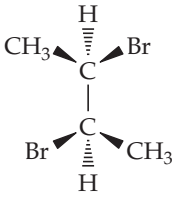
25.27 Consider the following structures of 2,3-dibromobutane:



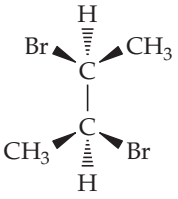
A



B



C



D

What is the relationship between the following pairs of structures?

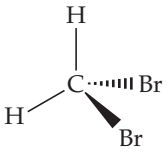
(a) **A** and **B** are enantiomers; **C** and **D** are enantiomers

(b) **A** and **B** are identical (the *meso* form); **C** and **D** are enantiomers

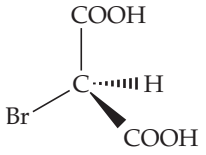
(c) **A** and **C** are diastereomers; **C** and **D** are identical (the *meso* form)

(d) **A** and **B** are identical (the *meso* form); **C** and **D** are diastereomers

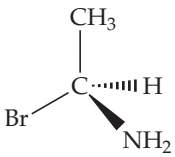
25.28 Which of the following molecules could be used to resolve a racemic mixture of a chiral amines?



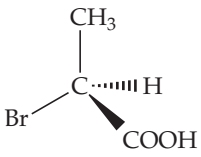
(a)



(b)



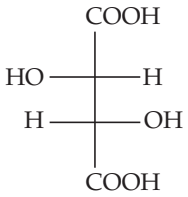
(c)



(d)

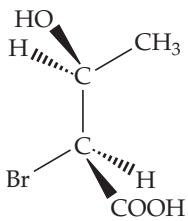
Exercises

25.29 Draw all possible stereoisomers of tartaric acid and comment on their relationship. Identify any *meso* compounds.

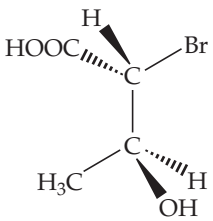


25.30 Assign *R* or *S* configurations to each stereocenter in the following molecules:

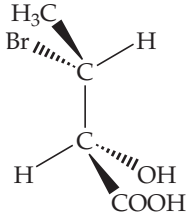
(a)



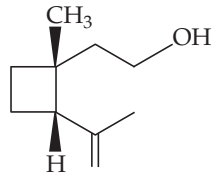
(b)



(c)

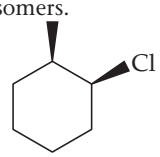


25.31 Grandisol is a pheromone of the male cotton boll weevil. What is the maximum number of stereoisomers that could exist for this molecule?

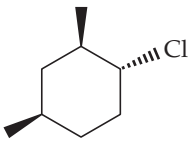


25.32 Indicate whether each of the following pairs of compounds are identical, enantiomers, diasteromers or constitutional isomers.

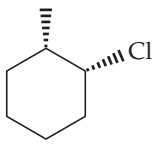
(a)



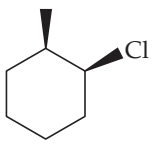
and



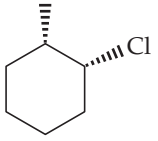
(b)



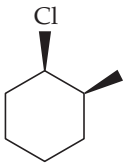
and



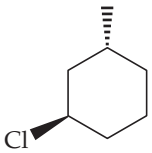
(c)



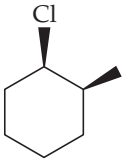
and



(d)



and



25.33 Revisit the stereoisomers shown in Figure 25.3 for 1,2-dimethylcyclohexane. Identify the stereocenters present as *R* or *S* and relate pairs of structures in terms of enantiomers and diastereomers.

25.34 Briefly explain how the resolution of a racemic carboxylic acid may be carried out.

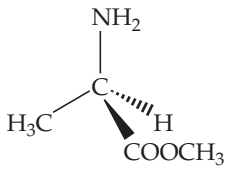
Answers to Self-Assessment Exercises

25.27 (b) 25.28 (d)

Sample Integrative Exercise

Putting Concepts Together

Alanine is one of the 20 most common naturally occurring amino acids. A methyl ester derivative ($RCOOCH_3$), prepared in the laboratory, had the following stereochemistry:



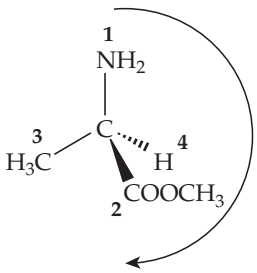
alanine methyl ester

(a) Identify the chiral center in alanine methyl ester. How many possible stereoisomers exist for alanine? **(b)** List the groups attached to this chiral center in *decreasing order* of sequence rule priority, then state whether the compound has the *R* or *S* configuration about this center. **(c)** Draw the other enantiomer of alanine methyl ester. **(d)** Describe how a pure sample of this compound may be obtained from a racemic mixture.

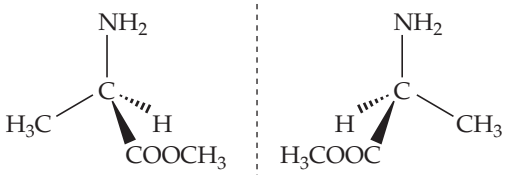
SOLUTION

(a) The central carbon atom in alanine methyl ester is the only chiral center since it has four different groups attached to it. Having only one stereocenter means that only two stereoisomers are possible.

(b) Using the sequence priority rules in Section 25.5, $NH_2 > COOCH_3 > CH_3 > H$. Since the lowest-priority group is already oriented back into the page, this compound has an *R* configuration.



(c)



(d) It is very difficult to separate enantiomers directly, and in quantity. Since this compound contains an amine functional group, the best way to achieve resolution would be to react it with a single enantiomer of a chiral carboxylic acid such as (*S*)-malic acid. This would form the *R,S* and *S,S* diastereomeric salts, which can be separated by fractional crystallization. Once isolated, addition of base would re-generate the amine, which could be separated by extraction from the water-soluble carboxylate salt and dried. Removing the solvent leaves the pure enantiomer.

(See also Exercise 25.40.)

Chapter Summary and Key Terms

SECTION 25.1 **Stereoisomers** are isomers with the same connectivity of atoms (bonding) but different arrangement of their atoms in space. The most common forms of stereoisomerism are **geometric isomers**, **enantiomers** and **diastereomers**.

SECTION 25.2 Two substituents on a cycloalkane can be ***cis*** or ***trans*** to each other. *Cis* and *trans* isomers are called geometric isomers. Geometric isomers differ from one another in their chemical and physical properties.

SECTION 25.3 **Optical isomers** are non-superimposable mirror images of one another. They are molecules that contain a **stereocenter**. Optical isomers, or enantiomers, are **chiral**, meaning that they have a specific "handedness" and their physical and chemical properties differ only in the presence of a chiral environment. Molecules that are superimposable are **achiral**, meaning not chiral.

SECTION 25.4 Optical isomers can be distinguished from each other by their interactions with **plane-polarized light**; solutions of one

enantiomer rotate the plane of polarization to the right (**dextrorotatory**, +) and solutions of its mirror image rotate the plane to the left (**levorotatory**, −) with the same magnitude. Chiral molecules, therefore, are **optically active**. A **polarimeter** is used to determine the **specific rotation** of a chiral sample. A compound that is **enantiomerically pure** contains a single enantiomer. A mixture with an equal amount of two enantiomers is called a **racemic mixture**, or *racemate*.

SECTION 25.5 The **absolute configuration** around a stereocenter can be described with the **Cahn–Ingold–Prelog *R,S* notation**. This notation uses a set of **sequence priority rules** to assign priority to each group around a stereocenter.

SECTION 25.6 Molecules with two or more chiral centers can form enantiomers and *diastereomers*. Diastereomers have different physical and chemical properties, a trait that can be used in the **resolution** of enantiomers from a *racemic mixture* to yield an enantiomerically pure compound. An achiral compound possessing two or more stereocenters is known as a ***meso* compound**.

Key Skills

- Be able to draw three-dimensional structures in two dimensions using bold and dashed wedges. (Sections 25.1 and 25.3)
- Understand the concept of chirality and be able to identify a chiral center. (Section 25.3)
- Use the Cahn–Ingold–Prelog rules to describe unambiguously the absolute configuration of a stereocenter. (Section 25.5)
- Calculate the number of potential stereoisomers based on the number of chiral centers. (Section 25.6)

Key Equations

- Specific rotation

$$[\alpha]_D^{20} = \frac{\alpha}{c \times l} \qquad [25.1]$$

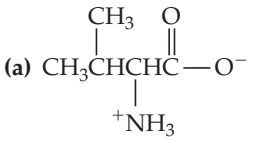
- Maximum number of stereoisomers for a compound with n stereocenters

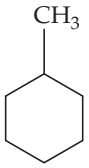
$$\text{No. of stereoisomers} = 2^n \qquad [25.2]$$

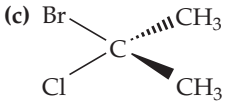
Exercises

Visualizing concepts

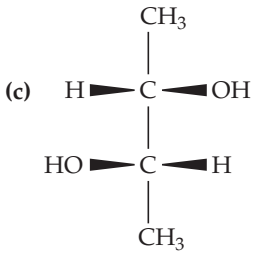
25.35 Which of the following compounds is capable of possessing isomerism? In each case where isomerism is possible, identify the type or types of isomerism.

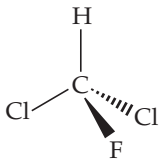
(a) 

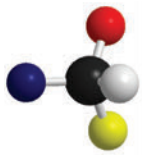
(b) 

(c) 

(d) $CH_3CH_2CH_2CH_3$

(c) 

(d) 

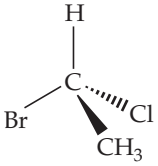
(e) 

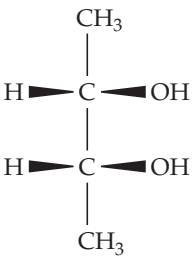
(f) 

Stereochemistry In Organic Chemistry (Section 25.1)

25.36 List some of the many items used in everyday life that are chiral.

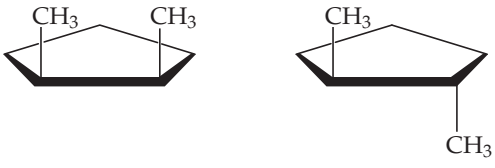
25.37 Which of the following have a non-superimposable mirror image?

(a) 

(b) 

Cis–Trans Isomerism in Cycloalkanes (Section 25.2)

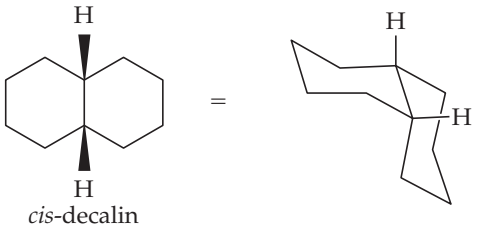
25.38 **(a)** Give the systematic or IUPAC name for each structure, assigning absolute stereochemistry to each center. Are any of these compounds achiral?



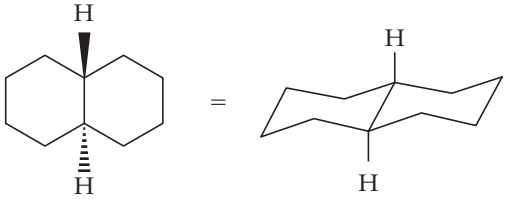
(b) Draw a *trans*-1,2-disubstituted cyclohexane in the chair conformation with your choice of alkyl substituent. What

do you notice about the position of the two substituents? Are both substituents axial, or equatorial, or is there one of each? Is this general? Explain. **(c)** Systematically name the structure you drew in part (b), taking into account absolute stereochemistry.

25.39 Decalin is a C_{10} compound composed of two fused six-membered rings. It is often used as a model to describe conformations in steroids, such as cholesterol. Two geometric isomers are possible, *cis*-decalin and *trans*-decalin. Which of these two isomers is the most stable? Explain your answer.



cis-decalin

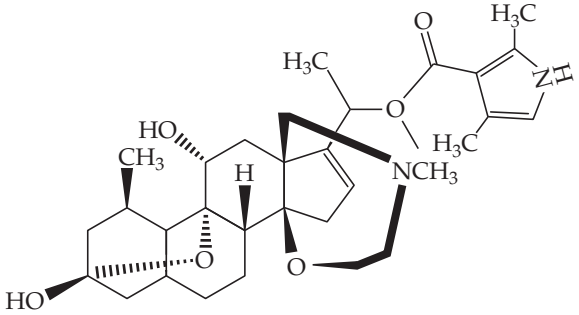


trans-decalin

Chirality in Organic Compounds (Section 25.3)

25.40 **(a)** What conditions are necessary for an organic molecule to be classed as optically active? **(b)** What is a *racemic mixture*, and why doesn't it rotate plane-polarized light?

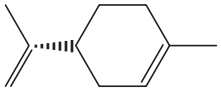
25.41 Batrachotoxin is one of the most potent toxins ever discovered. The poison is secreted from the skin of frogs and is used to coat the tip of blow darts. Only 200 μg is needed to kill a healthy adult. Locate all the stereocenters in batrachotoxin.



batrachotoxin

Measuring Optical Activity (Section 25.4)

25.42 You are very familiar with limonene. (+)-Limonene gives oranges and lemons their odour.



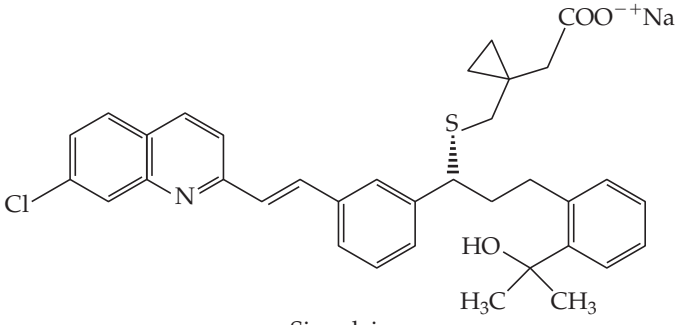
(+)-limonene

(a) Is it possible to tell the absolute configuration of (+)-limonene from its name? **(b)** Identify the chiral center in (+)-limonene. **(c)** Draw the mirror image of (+)-limonene. **(d)** Indicate the absolute stereochemistry of (+)-limonene.

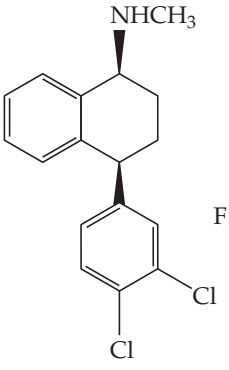
25.43 The specific rotation $[\alpha]_D$ of enantiomerically pure *d*-lactic acid is +4°. Calculate the observed rotation of a 5 cm^3 solution of lactic acid containing 6 g of *d*-lactic acid and 2 g of *l*-lactic acid in a standard 10 cm solution cell.

Absolute Stereochemistry (Section 25.5)

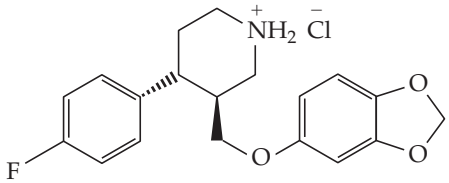
25.44 The fastest growing new treatment for asthma is the single-enantiomer drug Singulair (montelukast sodium) from Merck. Sales of the product in 2001 were worth $1.4 billion worldwide. Antidepressants such as GlaxoSmithKline's Paxil (paroxetine hydrochloride) and Pfizer's Zoloft (sertraline) had sales worth over $2 billion worldwide in 2005. Assign an *R,S* configuration to each stereocenter in each drug.



Singulair



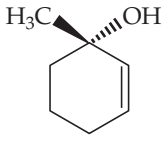
zoloft



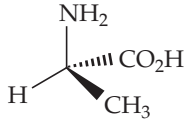
Paxil

25.45 Assign the configuration (*R* or *S*) to the stereogenic center(s) in the following compounds.

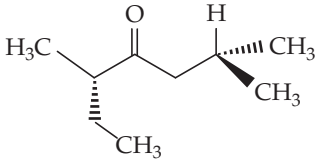
(a)



(b)



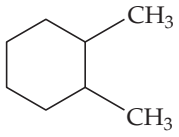
(c)



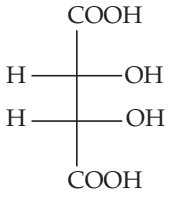
Molecules with More than One Stereocenter (Section 25.6)

25.46 Draw the *meso* form of each of the following molecules:

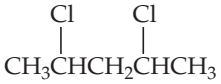
(a)



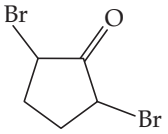
(b)



(c)



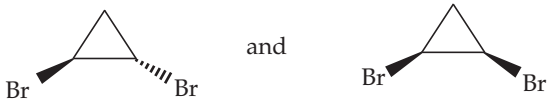
(d)



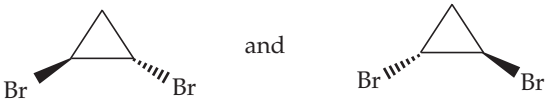
25.47 **(a)** Draw the structure of (2*R*,3*S*)-2-chloro-3-methyl pentane. **(b)** How many different 2,3-dichlorobutanes are there?

25.48 Indicate whether each of the following pairs of compounds are identical, enantiomers, diasteromers or constitutional isomers.

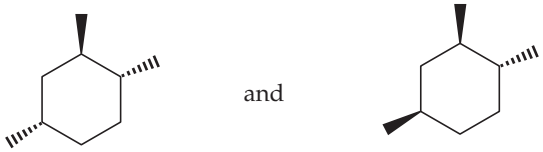
(a)



(b)



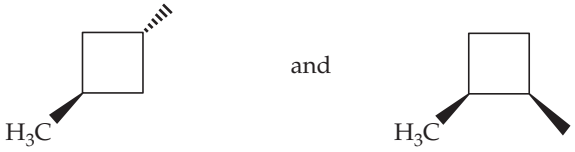
(c)



(d)

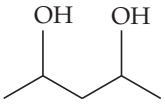


(e)

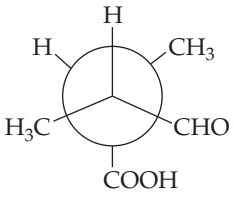


Additional Exercises

25.49 What stereoisomers exist for pentane-2,4-diol?

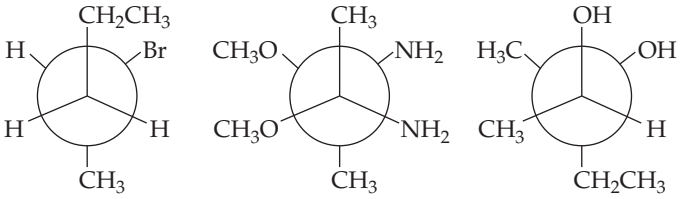


25.50 **(a)** Determine the stereochemistry at the two stereocenters within the Newman projection shown here. **(b)** Draw a Newman projection that is enantiomeric with the one shown here. **(c)** What relationship in specific rotation exists between these two structures?



25.51 Convert the following Newman projections into their standard structural formula, retaining stereochemistry.

(a) **(b)** **(c)**



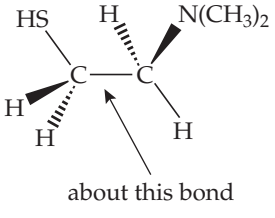
25.52 Draw the structure for 2-bromo-2-chloro-3-methylpentane, and indicate any stereogenic centers in the molecule.

25.53 Does 3-chloro-3-methylhexane have optical isomers? Why or why not?

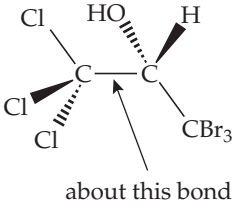
Integrative Exercises

25.54 Using Newman projections, draw the most stable staggered form of the following compounds:

(a)

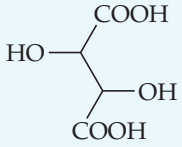


(b)



Design an Experiment

Tartaric acid occurs naturally in grapes and plays an important role in the wine industry. It also has other industrial uses such as a chelate ligand in the formation of complexes that, when enantiopure, are used in the chiral synthesis of many natural products and pharmaceuticals.



Tartaric Acid

The form of tartaric acid obtained from grapes has a configuration of (2*R*, 3*R*) and rotates plane polarized light in a (+) direction (see Table 25.1). The synthesis of tartaric acid in the lab typically produces a mixture of all possible stereoisomers. You are tasked with separating a sample of laboratory-made tartaric acid into the different isomers and identifying which is which. You have at your disposal a polarimeter and the enantiomerically pure amine, (+)-cinchonine, as well as standard laboratory glassware and reagents.

(a) How many stereocenters are there in tartaric acid? Draw out the isomers and assign the configuration at each stereocenter. **(b)** What is the expected direction of optical rotation of the isomers? **(c)** Outline the experimental procedure you would use to resolve the sample of tartaric acid. **(d)** How could you check whether the samples you obtain are pure? **(e)** Finally, how do you link your samples with the absolute configuration of the tartaric acid stereoisomers?

WHAT'S AHEAD

26.1 ▶ The Structure of Unsaturated Hydrocarbons

26.2 ▶ Isomerism and Nomenclature

26.3 ▶ Arrow Notation and Resonance Structures: Electron Counting

26.4 ▶ Electrophilic Addition Reactions

26.5 ▶ Alkanes from Alkenes: Catalytic Hydrogenation

26.6 ▶ Addition Polymerization

26

CHEMISTRY OF ALKENES AND ALKYNES

26.1 The Structure of Unsaturated Hydrocarbons



Unsaturated hydrocarbons contain a double or triple bond between two carbon atoms, and they differ greatly from alkanes in much of their chemistry. Understanding the molecular basis of this different reactivity allows us to predict what reactions may occur and enhances our ability to use basic chemicals to synthesize more complex substances. These, in turn, may be built into the modern materials that surround us and used, for example, in construction, medicine and technology.

When you finish this section, you should be able to:

- Recognize alkene and alkyne functional groups
- Understand the characteristics of a π-bond including the effect it has on the geometry of a molecule

Alkenes, also known as olefins, are unsaturated hydrocarbons that contain a carbon-carbon double bond. They have the general formula:

$$C_nH_{2n} \qquad [26.1]$$

The simplest alkene is $CH_2{=}CH_2$, called ethene (IUPAC name) or ethylene (common name). Ethene is a plant hormone that plays important roles in seed germination and fruit ripening. The carbon-carbon double bond makes ethene much more reactive than ethane.

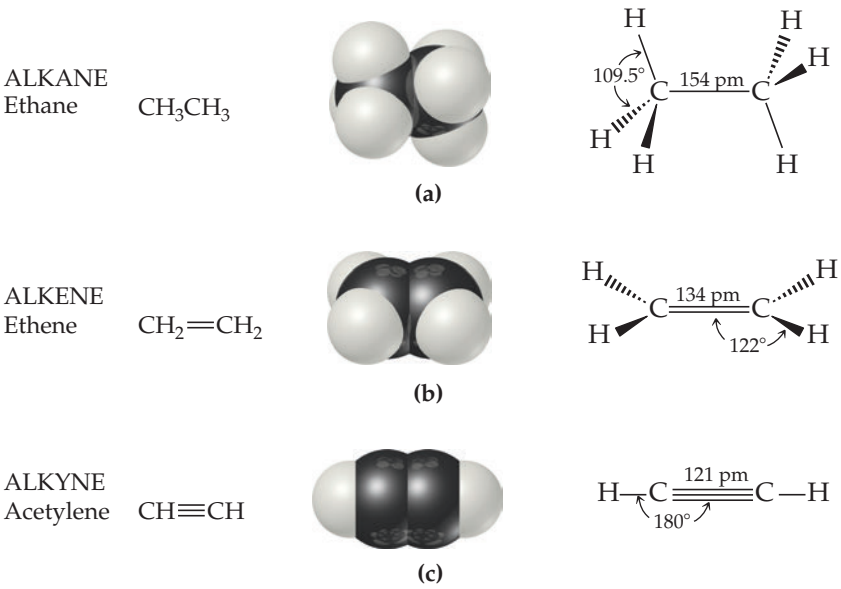
Alkynes are hydrocarbons that contain a carbon-carbon triple bond, as in acetylene (HC≡CH), whose systematic name is ethyne. When acetylene is burned in a stream of oxygen, as in an oxy-acetylene torch, the flame reaches about 3200 K. The oxy-acetylene torch is used widely in welding, which requires high temperatures. Acetylene, and alkynes in general, are highly reactive molecules. Because of their higher reactivity, they are not as widely distributed in nature as alkenes; alkynes are, however, important intermediates in many industrial processes. Alkynes have the general molecular formula

$$C_nH_{2n-2} \qquad [26.2]$$

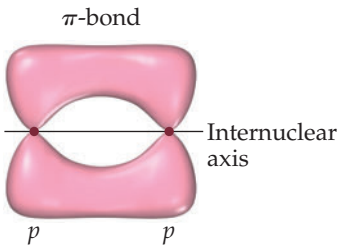
The π-bond

In the types of covalent bonds we have considered so far, the electron density is concentrated symmetrically about the line connecting the nuclei (the *internu clear axis*). In other words, the line joining the two nuclei passes through the middle of the electron overlap region. These bonds are all called **sigma (σ)-bonds**.

To describe the bonding in unsaturated hydrocarbons, we must consider a second kind of bond, one that results from the overlap between two *p* orbitals perpendicular to the internuclear axis (**Figure 26.2**). This "sideways" overlap of *p* orbitals produces a **pi (π)-bond**. A π-bond is a covalent bond in which the electron overlap regions lie above and below the internuclear axis. Unlike a σ-bond, in a π-bond there is no probability of finding an electron on the internuclear axis. Because the *p* orbitals in a π-bond overlap sideways rather than directly facing each other, the total overlap in a π-bond



▲ **Figure 26.1** **Three hydrocarbon types for a two-carbon system.**



▲ **Figure 26.2** **The π-bond.** When two *p* orbitals overlap in a sideways fashion, the result is a π-bond. Note that the two regions of overlap constitute a *single* π-bond.

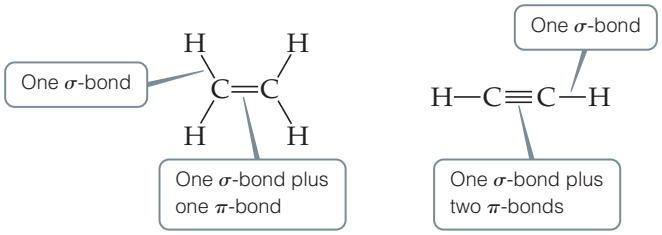
tends to be less than that in a σ-bond. As a consequence, π-bonds are generally weaker than σ-bonds.

We can summarize unsaturation in the following way:

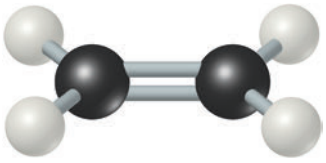
C—C single bonds are σ-bonds.

C=C double bonds consist of one σ-bond and one π-bond.

C≡C triple bonds consists of one σ-bond and two π-bonds.



Bonding in Alkenes



▲ **Figure 26.3 The molecular geometry of ethene.** Ethene, C_2H_4, has one carbon–carbon σ-bond and one π-bond.

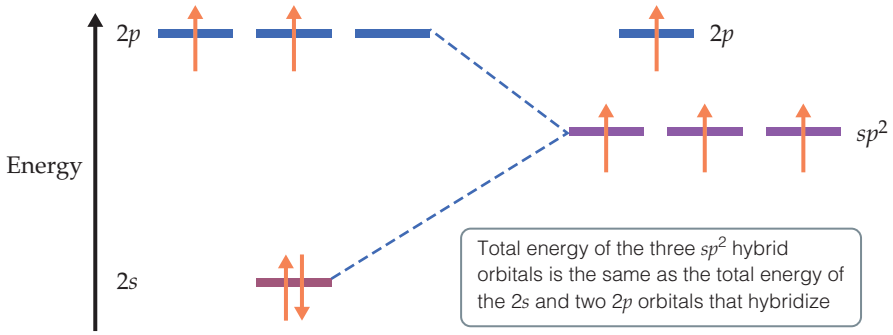
In order to rationalize the bonding and geometry of an alkene (**Figure 26.3**), let us consider ethene (C_2H_4). The bond angles about carbon in ethene are all approximately 120° (Figure 26.3), suggesting that each carbon atom uses sp^2 hybrid orbitals (Figure 9.18) to form σ-bonds with the other carbon and with two hydrogens. Because carbon has four valence electrons, after sp^2 hybridization carbon still has one electron remaining in the *unhybridized* 2*p* orbital (**Figure 26.4**).

The unhybridized 2*p* orbital is directed perpendicular to the plane that contains the three sp^2 hybrid orbitals. The hybrid orbitals separate within the same plane to give inter-orbital angles of 120°. This orbital pattern gives rise to a trigonal planar arrangement of σ-bonds.

Each sp^2 hybrid orbital on a carbon atom contains one electron. **Figure 26.5** shows how the four C—H σ-bonds are formed by overlap of sp^2 hybrid orbitals on C with the 1*s* orbitals on each H atom. We use eight electrons to form these four electron-pair bonds. The C—C σ-bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus 10 of the 12 valence electrons in C_2H_4 are used to form five σ-bonds.

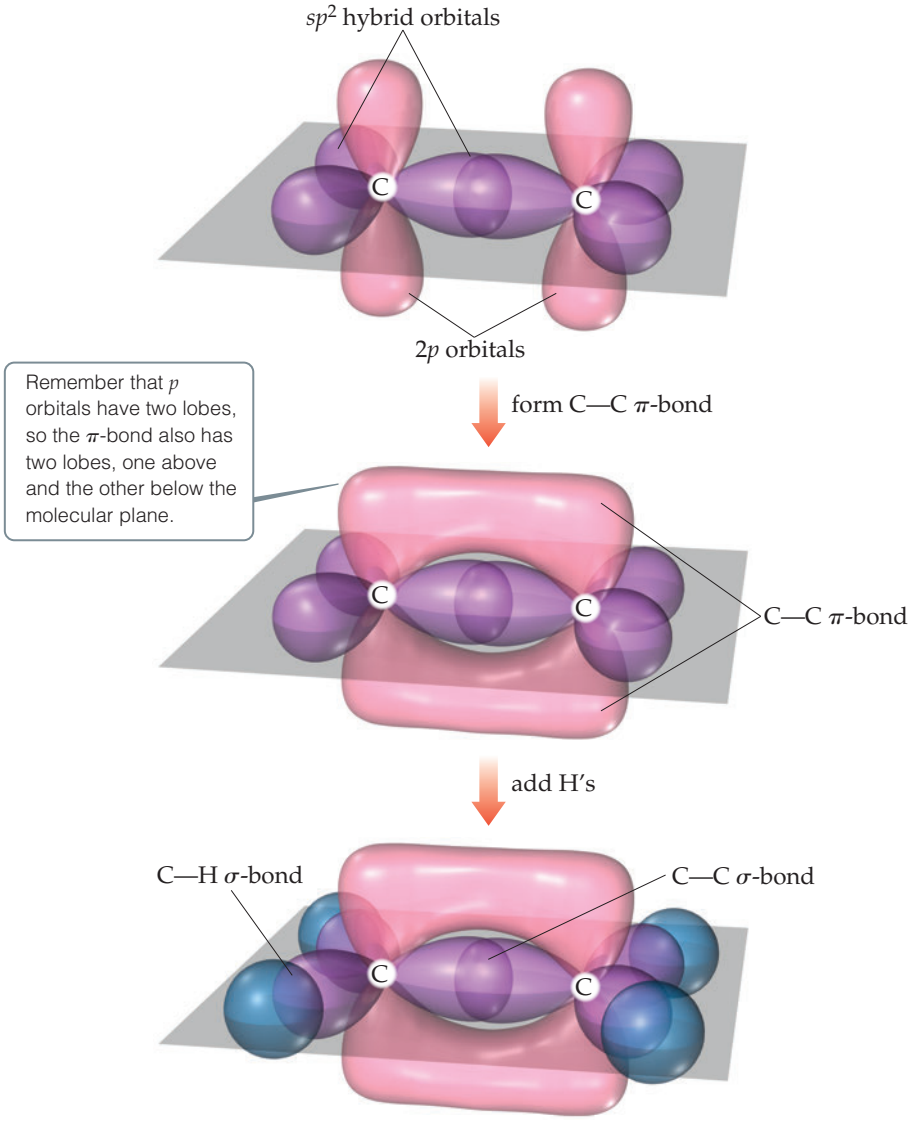
The remaining two valence electrons reside in the unhybridized 2*p* orbitals, one electron on each carbon atom. These two 2*p* orbitals can overlap with each other in a sideways fashion, as shown in Figure 26.2. The resultant electron density is concentrated above and below the C—C bond axis, forming a single π-bond. Thus the carbon-carbon double bond in ethene consists of one σ-bond and one π-bond. Note carefully that the unhybridized *p*-orbital overlap above and below the plane forms a single π-bond and not two π-bonds.

Although we cannot experimentally observe a π-bond directly (all we can observe are the positions of the atoms), the structure of ethene provides strong support for its presence. First, the carbon-carbon bond length in ethene (134 pm) is much shorter than in compounds with carbon-carbon single bonds (154 pm), consistent with the presence



◀ **Figure 26.4 Degeneracy of hybrid orbitals.** Mixing 2*s* and two 2*p* orbitals yields hybrid orbitals whose energies lie between those of the original atomic orbitals.

Go Figure Why is it important that the sp^2 hybrid orbitals of the two carbon atoms lie in the same plane?



▲ **Figure 26.5 Hybridization in ethene.** The σ-bonding framework is formed from sp^2 hybrid orbitals on the carbon atoms. The unhybridized 2p orbitals on the C atoms are used to make a π-bond.

of a stronger carbon-carbon double bond (Table 26.1). Second, all six atoms lie in the same plane, and stay in the same plane (Figures 26.3 and 26.5). If the π-bond were absent, there would be no reason for the two CH_2 fragments of ethene to lie in the same

TABLE 26.1 Carbon–carbon bond lengths, general molecular formulas and bond enthalpies for ethane, ethene and ethyne

Molecule	General formula of class	C—C bond length (pm)	Approximate bond enthalpy (kJ mol^{-1})
Ethane	$CH_3—CH_3$	154	350
Ethene	$CH_2=CH_2$	134	620
Ethyne	$CH\equiv CH$	121	840

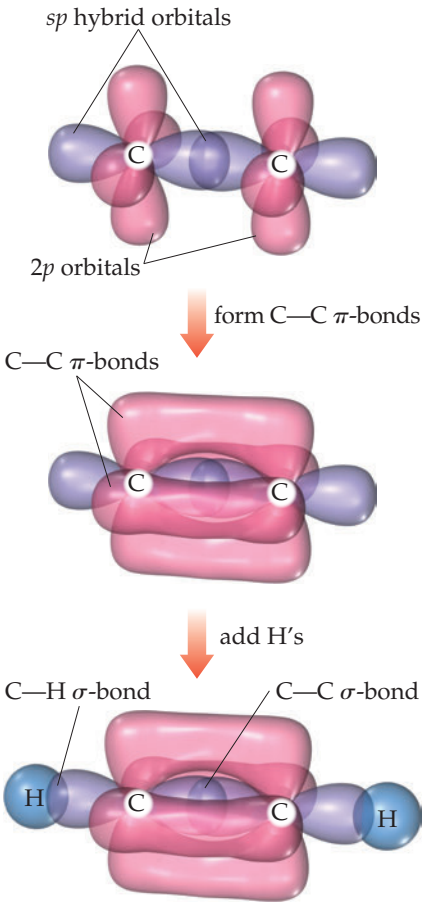
plane, as they could rotate with respect to each other in a similar way to alkanes. As a result, the introduction of one or more π-bonds introduces a degree of rigidity into molecules.

Note the difference in bond strength (bond enthalpy) between ethane and ethene in Table 26.1. The C—C double bond is not twice as strong (meaning twice as hard to break) as a single bond, nor is a triple bond three times as strong as a single bond. The fact that each π-bond is weaker than a σ-bond is part of the reason why alkenes and alkynes are far more reactive than alkanes.

Bonding in Alkynes

The bonding and geometry of carbon-carbon triple bonds can also be explained by hybridization. Ethyne (more commonly known as acetylene, C_2H_2), for example, is a linear molecule containing a triple bond: H—C≡C—H. The linear geometry about the triple bond suggests that each carbon atom uses *sp* hybrid orbitals to form σ-bonds with the other carbon and with one hydrogen. Each carbon atom thus has two remaining unhybridized 2*p* orbitals at right angles to each other and to the axis of the *sp* hybrid set (**Figure 26.6**). These *p* orbitals overlap to form a pair of π-bonds. Thus the triple bond in acetylene consists of one σ-bond and two π-bonds.

Go Figure Based on the models of bonding in ethene and acetylene, which molecule should have the higher carbon–carbon bond energy?

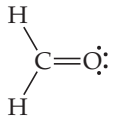


▲ **Figure 26.6 Formation of two π-bonds.** In acetylene, C_2H_2, the overlap of two sets of unhybridized carbon 2*p* orbitals leads to the formation of two π-bonds.

Sample Exercise 26.1

Describing σ-bonds and π-bonds in a molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlap of appropriate hybridized and unhybridized orbitals.

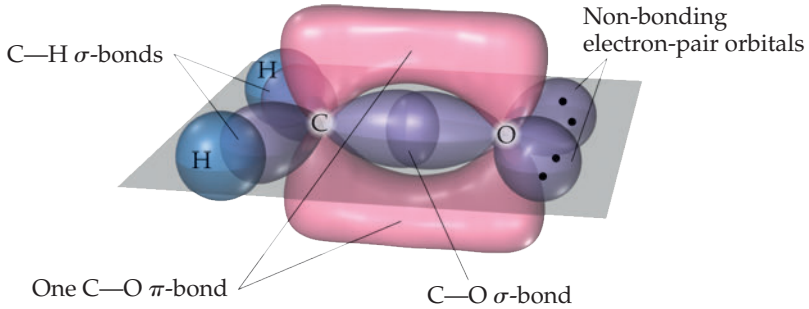
SOLUTION

Analyse We are given a structure containing several types of bonds and are asked to interpret these bonds in terms of hybrid orbitals.

Plan Single bonds are of the σ type, whereas double bonds consist of one σ-bond and one π-bond. The ways in which these bonds form can be deduced from the geometry of the molecule, which we predict using the VSEPR model.

Solve The C atom has three electron domains around it, which suggests a trigonal planar geometry with bond angles of about 120°. This geometry implies sp^2 hybrid orbitals on C. These hybrids are used to make the two C—H and one C—O σ-bonds to C. There remains an unhybridized $2p$ orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

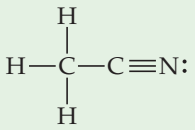
The O atom also has three electron domains around it, so we assume that it has sp^2 hybridization as well. One of these hybrids participates in the C—O σ-bond, while the other two hybrids hold the two non-bonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized $2p$ orbital that is perpendicular to the plane of the molecule. The unhybridized $2p$ orbitals on the C and O atoms overlap to form a C—O π-bond, as illustrated in Figure 26.7.



▲ **Figure 26.7 Formation of σ-bonds and π-bonds in formaldehyde, H_2CO.**

Practice Exercise

Consider the acetonitrile molecule:

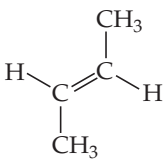


(a) Predict the bond angles around each carbon atom; **(b)** describe the hybridization at each of the carbon atoms; **(c)** determine the total number of σ-bonds and π-bonds in the molecule.

Sample Exercise 26.2

Determining hybridization

Locate the sp^3, sp^2 and sp hybridized carbon atoms in the following compounds.

(a) 

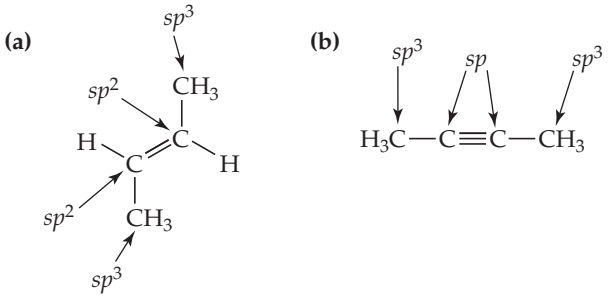
(b) $H_3C—C\equiv C—CH_3$

SOLUTION

Analyse We are given two compounds and are asked to relate the bonding types to a level of hybridization.

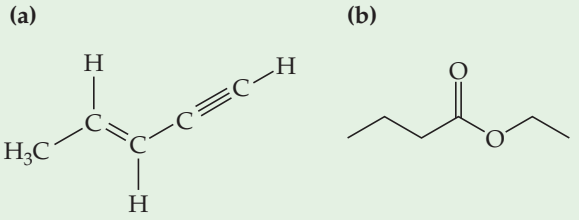
Plan This type of question is made easier by remembering that all carbons are sp^3 hybridized, except for those containing a double bond (in which case they are sp^2 hybridized) and those containing a triple bond (which are *sp* hybridized).

Solve Using these observations:



▶ Practice Exercise

Locate the sp^3, sp^2 and *sp* hybridized carbon atoms in the following compounds.



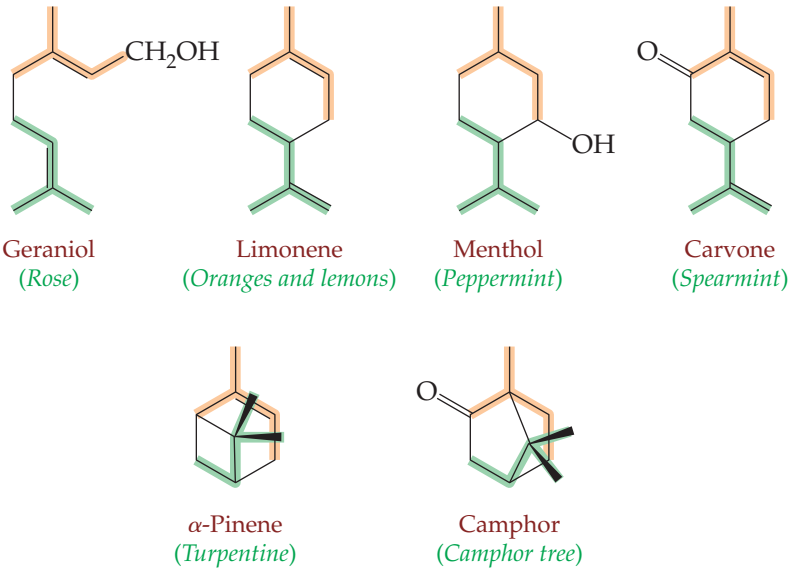
CHEMISTRY AND LIFE Terpenes and Isoprene

Terpenes are a class of naturally occurring compounds whose carbon skeleton can be divided into two or more isoprene units—a five-carbon unit whose systematic name is 2-methyl-1,3-butadiene (Figure 26.8). Terpenes are among the most widely distributed and utilized of all compound classes. Compounds such as camphor, menthol, pinene, geraniol, carvone and limonene are terpenes and each is divisible into two isoprene units.

Distant forest covered hills often appear to have a bluish haze, particularly on hot days. Isoprene is partly responsible for this. This haze is rich in isoprene, oxidized derivatives of isoprene, and other simple terpenes. The worldwide emission rate of these natural hydrocarbons by vegetation has been estimated to be 5×10^{11} kg / year. Eucalyptus trees are a particularly rich source of isoprene and are found covering the Blue Mountains, just west of Sydney, Australia (Figure 26.9).

Isoprene is a colourless liquid with a distinct aromatic odour. Large petroleum-based companies such as Shell Chemicals manufacture large quantities of it as a by-product of ethene production. The polymer polyisoprene is used in a wide variety of rubber applications including medical equipment, baby bottle teats/nipples, toys, shoe soles, tyres and the elastic films used inside golf balls. It is also used in adhesives and in paints and coatings.

As shown in the Chemistry and Life box in Section 26.3, several biologically important terpenes, such as vitamin A, play a large role in vision. The terpenes demonstrate effectively how nature uses simple building blocks such as isoprene to construct larger and more complex molecules with even more complex functions.



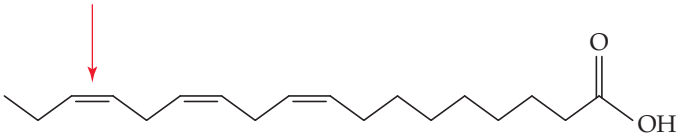
▲ **Figure 26.8 Well-known terpenes.** Geraniol, limonene, menthol, pinene and camphor are common terpenes. The positions of the isoprene units are highlighted. Note that the isoprene units are "linked" head-to-tail.



▲ **Figure 26.9 The Blue Mountains in Australia.** The blue haze is caused in part by isoprene emitted by the plants of the region.

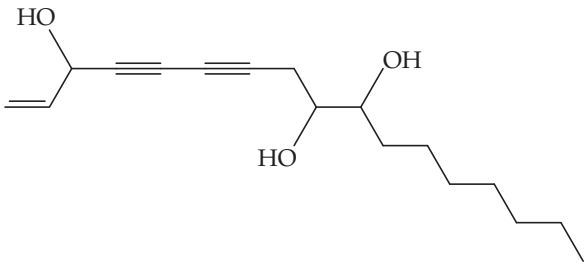
Self-Assessment Exercises

26.1 Many plant oils contain unsaturated fats, of which linolenic acid is an example of an omega-3 fatty acid.



Identify the functional group indicated by an arrow in linolenic acid? (**a**) alkane (**b**) alkene (**c**) alkyne (**d**) alcohol

26.2 Panaxytriol is a natural product found in ginseng. It has the following structure:



How many π-bonds are present in panaxytriol? (**a**) 1 (**b**) 2 (**c**) 3 (**d**) 5

Exercises

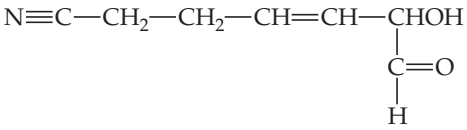
26.3 What structural features help us identify a compound as (**a**) an alkene, (**b**) an alkyne?

26.4 Give the molecular formula of a hydrocarbon containing five carbon atoms that is (**a**) an alkane, (**b**) an alkene, (**c**) an alkyne. Which are saturated and which are unsaturated hydrocarbons?

26.5 Give the molecular formula of a cyclic alkane, a cyclic alkene and a linear alkyne that in each case contains six carbon atoms. Which are saturated and which are unsaturated hydrocarbons?

26.6 What are the approximate bond angles (**a**) about carbon in an alkane, (**b**) about a C—C double bond in an alkene, (**c**) about a C—C triple bond in an alkyne?

26.7 Identify the carbon atom/s in the following structure that has/have each of the following hybridizations: (**a**) sp^3, (**b**) sp, (**c**) sp^2.



Answers to Self-Assessment Exercises

26.1 (b) **26.2** (d)

26.2 | Isomerism and Nomenclature



The π-bond of an alkene introduces a rigidity to the carbon–carbon chain at the double bond, which is not seen in an alkane. It is rather like the crosspiece of a five-barred gate lending strength to the structure. The consequence of this is that we may have two distinct

geometries resulting from a molecule of a single constitution. This is another example of the wonderful variety that arises from even simple molecules. The two different shapes of a double bond in the protein rhodopsin are central to the way we see and, in the area of polymers, we have a single monomer producing rubber with its elastic nature or gutta percha, which is a rigid material used as a filler in dental root canal therapy.

When you finish this section, you should be able to:

- Name simple alkene and alkyne molecules
- Recognize where geometric isomers arise and be able to assign a stereochemical descriptor to the name of the structure

Alkene nomenclature is based on the longest continuous chain of carbon atoms that *contains* the double bond. The name given to this longest chain is obtained from the name of the corresponding alkane (Table 24.3), by noting the position of unsaturation, and by changing the ending from *-ane* to *-ene*. Examples of an alkene and cycloalkene and their systematic names are shown in **Figure 26.10**. Note that the longest carbon chain in 2-ethyl-3-methylpent-1-ene is not the one that contains the double bond. This chain is ignored because the longest chain *containing the double bond* takes precedence in naming. Note too that the double bond is always given the lowest position number possible.

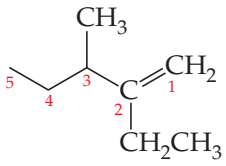
The general formula for a cycloalkene is

$$C_nH_{2n-2} \qquad [26.3]$$

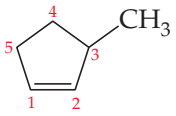
which is the same as that of an alkyne. Hence, cycloalkenes and alkynes with the same number of carbon atoms are constitutional isomers.

The location of the double bond along an alkene chain is indicated by a prefix number. The chain is always numbered from the end that brings us to the double bond sooner and hence gives the smallest-numbered prefix. In propene the only possible location for the double bond is between the first and second carbons; thus a prefix indicating its location is unnecessary. For butene (**Figure 26.11**) there are two possible positions for the double bond: either after the first carbon (but-1-ene) or after the second carbon (but-2-ene).

If a substance contains two or more double bonds, each one is located by a numerical prefix. The ending of the name is altered to identify the number of double bonds: diene (two), triene (three) and so forth. For example, $CH_2{=}CH{-}\ CH_2{-}CH{=}\ CH_2$ is named penta-1,4-diene.



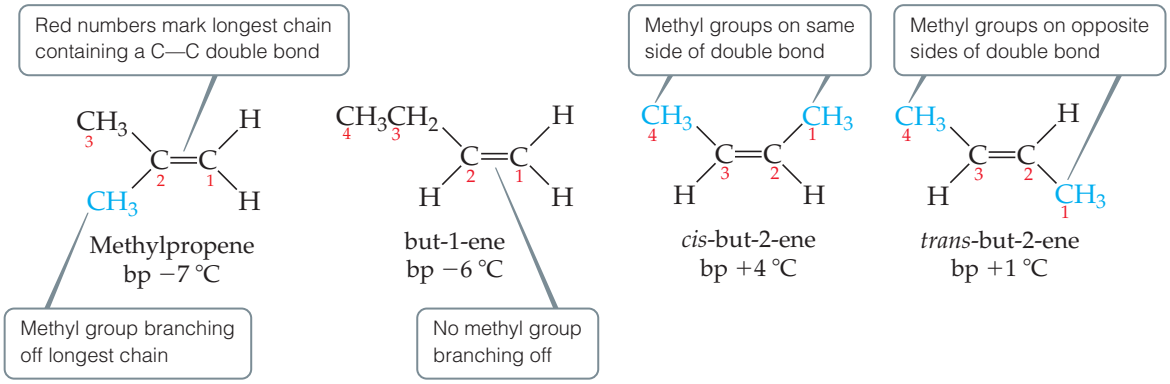
2-Ethyl-3-methylpent-1-ene



3-Methylcyclopentene

▶ **Figure 26.10 Nomenclature of alkenes.** Alkene nomenclature is derived from the longest carbon chain containing the double bond. The position of the double bond is always assigned the lowest position number possible. The position of the double bond in a cycloalkene is arbitrarily assigned as spanning positions 1 and 2.

Go Figure How many isomers are there for propene, C_3H_6?

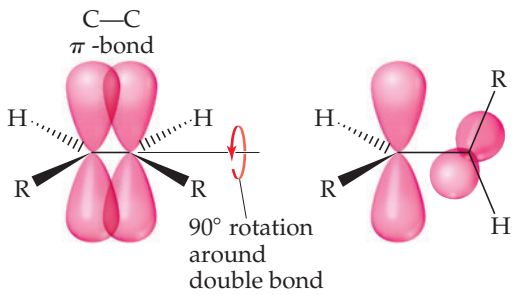


▲ **Figure 26.11 C_4H_8 structural isomers.** Full structural formulas names and boiling points of alkenes with the molecular formula C_4H_8.

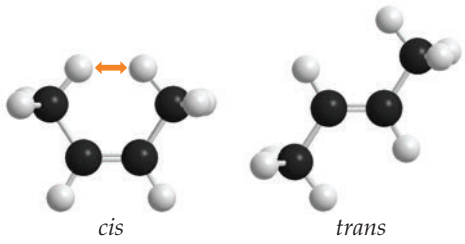
Isomerism in Alkenes—The *E*, *Z* System

Alkenes with two or more different substituents that lie on either side of the carbon-carbon double bond occur as geometrical isomers. For example, the two structures *cis*-but-2-ene and *trans*-but-2-ene (Figure 26.11) are geometric isomers. Their molecular formula and connectivity are the same; they differ only by the spatial arrangement of the two methyl groups. Geometric isomers, like diastereomers, possess distinct physical properties, such as boiling point, and often differ significantly in their chemical behaviour. This isomerism is a result of the restricted rotation about the carbon-carbon double bond, which in turn is caused by the *p*-orbital overlap required for formation of the π-bond (**Figure 26.12**). The carbon–carbon bond axis and the bonds to the hydrogen atoms and to the alkyl groups (designated R) are all in a plane. The *p* orbitals that overlap sideways to form the π-bond are perpendicular to the molecular plane. As Figure 26.12 shows, rotation around the carbon–carbon double bond requires the π-bond to be broken, a process that requires considerable energy (about 250 kJ/mol). Although rotation about a double bond doesn't occur easily, it is a key process in the chemistry of vision (see Chemistry and Life box later in Section 26.3).

Cis-alkenes tend to be less stable than *trans*-alkenes because of the extra steric interactions that occur when both alkyl substituents are on the same side of the double bond. **Figure 26.13** illustrates this point using the geometric isomers of but-2-ene.



▲ **Figure 26.12 Rotation about a carbon–carbon double bond.** In an alkene, the overlap of the *p* orbitals that form the π-bond is lost in the rotation. For this reason, rotation about carbon–carbon double bonds does not occur readily, usually requiring the absorption of energy.



▲ **Figure 26.13 Steric interactions in alkenes.** Alkenes such as *cis*-but-2-ene are less stable than their *trans* counterpart due to added steric interactions.

Sample Exercise 26.3

Drawing isomers

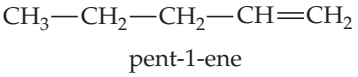
Draw all the structural and geometric isomers of pentene, C_5H_{10}, that have an unbranched hydrocarbon chain.

SOLUTION

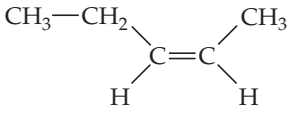
Analyse We are given the name of an alkene and asked to derive all possible isomer permutations.

Plan Because the compound is named pentene and not pentadiene or pentatriene, we know that the five-carbon chain contains only one carbon–carbon double bond. Thus we can begin by first placing the double bond in various locations along the chain, remembering that the chain can be numbered from either end. After finding the different distinct locations for the double bond, we can consider whether the molecule can have *cis* and *trans* isomers.

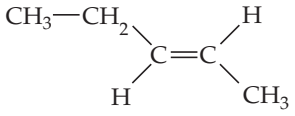
Solve There can be a double bond after either the first carbon (pent-1-ene) or second carbon (pent-2-ene). These are the only two possibilities because the chain can be numbered from either end. (Thus what we might erroneously call pent-4-ene is actually pent-1-ene, as seen by numbering the carbon chain from the other end.) Because the first C atom in pent-1-ene is bonded to two H atoms, there are no *cis*–*trans* isomers. However, there are *cis* and *trans* isomers for pent-2-ene. Thus the three isomers for pentene are



pent-1-ene



cis-pent-2-ene



trans-pent-2-ene

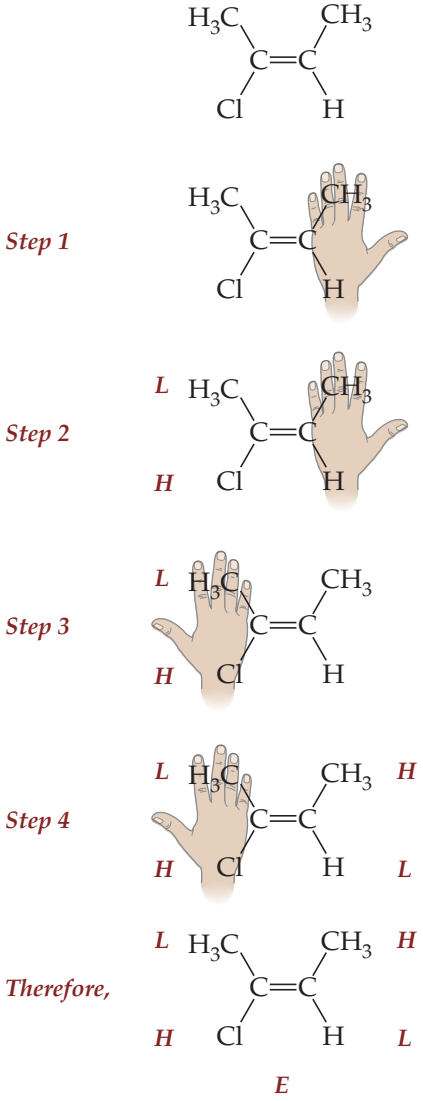
(You should convince yourself that *cis*- or *trans*-pent-3-ene is identical to *cis*- or *trans*-pent-2-ene, respectively.)

Practice Exercise

How many straight-chain isomers are there of hexene, C_6H_{12}?

Go Figure

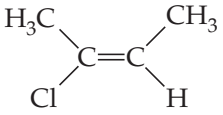
What stereoisomer would you get if you replaced Cl with H in this example? *E* or *Z*?



▲ **Figure 26.14 Assignment of *E* and *Z* isomers.** The hand acts to remove one side of the molecular structure from consideration.

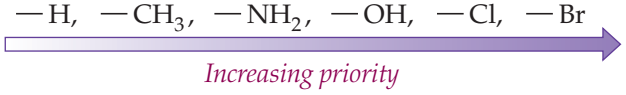
Although *cis* and *trans* nomenclature is useful to describe simple geometric isomers, it fails to describe more complex isomers accurately. To remove any ambiguity in naming geometric isomers, the IUPAC has established a set of priority rules similar to the Cahn–Ingold–Prelog priority rules used for determining stereochemistry.

The system for naming isomers is known as the ***E, Z* system**. An alkene is designated *E* (from German *entgegen*, meaning "opposite") or *Z* (from German *zusammen*, meaning "together") based on specific priority rules. The priority rules are listed and their application to the geometric isomer of 2-chloro but-2-ene is shown in **Figure 26.14**.

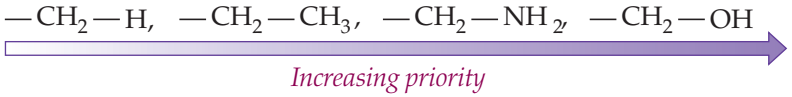


2-chloro-but-2-ene

1. Split the molecule through the C—C double bond into two parts and concentrate on setting the priority for one side at a time.
2. Assign a priority to each substituent using H for highest priority and L for lowest priority, based on the *atomic number* of the two atoms directly attached to the sp^2 carbon atom. The higher the atomic number, the higher the priority. A representative set of groups in increasing priority order is:



If two atoms are identical in terms of priority, you need to move out along the respective chains until you encounter a difference in priority. Reapply rule 2 to determine priority. If no difference is found, the two substituents must be identical and no *E*/*Z* isomerism is possible. An example of increasing priority fragments is:



3. Repeat step 2 for the other side of the C—C double bond.
4. If the two higher-priority groups are on the same side of the double bond, the alkene is the *Z* isomer. If they occur on opposite sides, as in the example shown in Figure 26.14, the alkene is the *E* isomer.

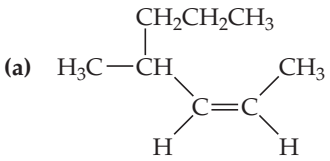
Alkynes

Alkynes are unsaturated hydrocarbons containing one or more C—C triple bonds. Alkynes are named by identifying the longest continuous chain in the molecule *containing the triple bond* and modifying the ending of the name, as listed in Table 24.3, from *-ane* to *-yne*, as shown in Sample Exercise 26.4. Alkynes are linear about the C—C triple bonds, so geometric isomerism is not possible about the triple bond. Alkynes are, however, constitutional isomers of cycloalkenes.

Sample Exercise 26.4

Naming unsaturated hydrocarbons

Name the following compounds:



Continued

SOLUTION

Analyse We are given the structural formulas for two compounds—the first an alkene and the second an alkyne—and asked to name them.

Plan In each case, the name is based on the number of carbon atoms in the longest continuous carbon chain that contains the multiple bond. In the case of (a), care must be taken to indicate whether *E, Z* isomerism is possible and, if so, which isomer is given.

Solve

(a) The longest continuous chain of carbons that contains the double bond is seven carbons in length. The parent compound is therefore heptene. Because the double bond begins at carbon 2 (numbering from the end closest to the double bond), the parent hydrocarbon chain is named hept-2-ene. A methyl group is located at carbon atom 4. Thus the compound is 4-methylhept-2-ene. The geometrical configuration at the double bond is *Z* (that is, the alkyl groups are bonded to the double bond on the same side). Thus the full name is *Z*-4-methylhept-2-ene.

(b) The longest continuous chain of carbon atoms containing the triple bond is six, so this compound is a derivative of hexyne. The triple bond comes after the first carbon (numbering from the right), making it a derivative of hex-1-yne. The branch from the hexyne chain contains three carbon atoms, making it a propyl group. Because it is located on the third carbon atom of the hexyne chain, the molecule is 3-propylhex-1-yne.

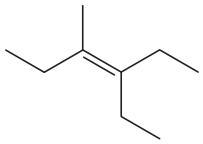
Practice Exercise

Draw the condensed structural formula for 4-methylpent-2-yne.

In Chapter 32, we will discuss the techniques used to determine the molecular structure of alkenes and alkynes—namely nuclear magnetic resonance spectroscopy, infrared spectroscopy and mass spectrometry.

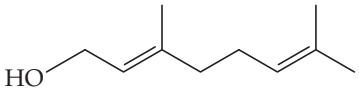
Self-Assessment Exercises

26.8 What is the correct name for this structure?



(**a**) 2,3-diethylpent-2-ene (**b**) 3-ethyl-4-methylhex-3-ene (**c**) 3,4-diethylpent-3-ene

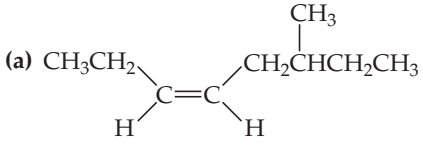
26.9 What is the correct descriptor (*E* or *Z*) for the double bonds in geraniol, a component in citronella oil.

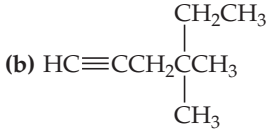


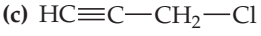
(**a**) both *E* (**b**) both *Z* (**c**) one *E* and one *Z* (**d**) only one double bond has stereochemistry and that is *E* (**e**) only one double bond has stereochemistry and that is *Z*

Exercises

26.10 Name the following compounds systematically:

(a) 

(b) 

(c) 

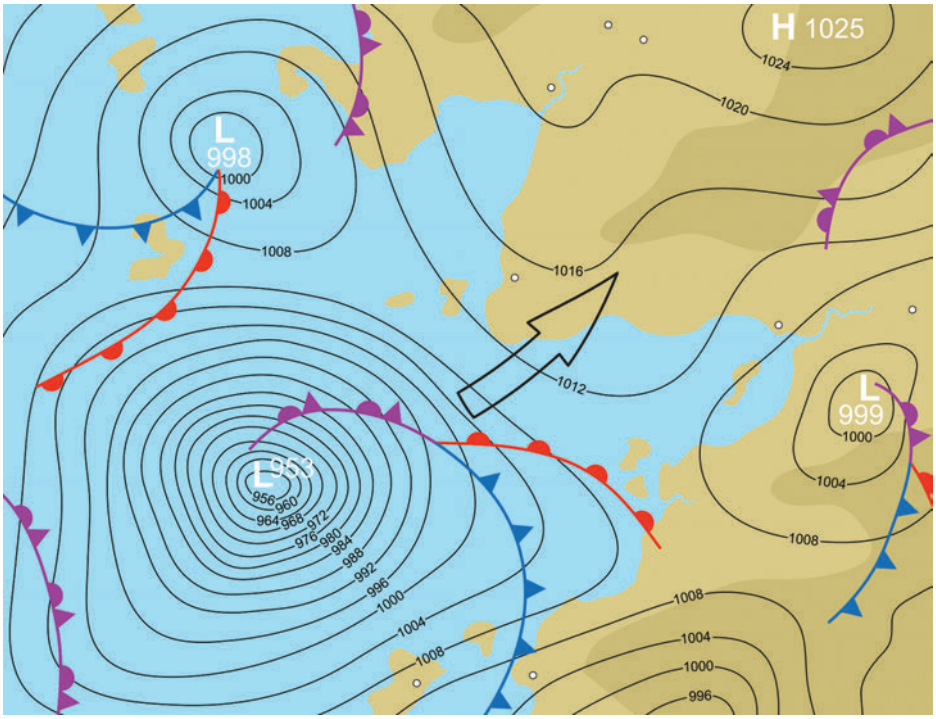
26.11 Why is geometric isomerism possible for alkenes, but not for aliphatic alkanes and alkynes?

26.12 Draw the condensed structural formulas for the *E* and *Z* isomers of pent-2-ene. Can cyclopentene exhibit *E, Z* isomerism? Explain.

Answers to Self-Assessment Exercises

26.8 (b) **26.9** (e)

26.3 Arrow Notation and Resonance Structures: Electron Counting



From the results of many experiments, we can learn the product we get from mixing two chemicals together. However, if we understand how the molecules interact to give this product, then our knowledge allows us to predict the outcome of reactions that have yet to be tried. Using a few basic rules, we can construct a likely *mechanism* for the reaction. While it is very difficult to see individual molecules reacting with one another (and even that through the use of highly advanced technology), the reaction mechanism can help us visualize what is going on at a molecular level. One tool we use to aid us with this is the drawing of "curved arrows". These arrows represent the movement of electrons either within a molecule or between two molecules and allow us to keep track of what is going on. Rather like predicting the weather, we use a combination of observations of past events with a model of how change occurs to predict outcomes.

When you finish this section, you should be able to:

- Draw curved arrows to show the electron movements in a resonance structure
- Extend the concept of curved arrows to a reaction between an electron donor and an electron acceptor

A "straight" arrow indicates the transformation of a reactant into a product in a chemical equation. Arrows can also be used to track the flow of electrons that is occurring. In this case a curved arrow is used so there is no confusion about which process we are showing. The curved arrows always start from where the electrons are coming from and end where the electrons are going to. Curved arrows are used for three common types of electron redistribution:

1. From a bond to an adjacent atom—this forms a lone pair on the receiving atom, or joins two molecules together.
2. From an atom to an adjacent bond—this uses a lone pair on the donor atom to form a π-bond.
3. From one bond to an adjacent bond—this redistributes the electrons although, overall, the same number of σ- and π-bonds is retained.

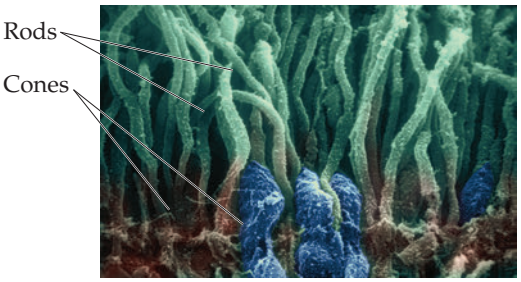
CHEMISTRY AND LIFE The Chemistry of Vision

Scientists have begun to understand the complex chemistry of vision. Vision begins when light is focused by the lens onto the retina, the layer of cells lining the interior of the eyeball. The retina contains *photoreceptor* cells known as rods and cones (**Figure 26.15**). The human retina contains about 3 million cones and 100 million rods. The rods are sensitive to dim light and are used in night vision. The cones are sensitive to colours. The tops of the rods and cones contain a substance called *rhodopsin*. Rhodopsin consists of a protein, called *opsin*, bonded to a reddish-purple pigment called *retinal*, which is similar in structure to β-carotene. Structural changes around a double bond in the retinal portion of the molecule trigger a series of chemical reactions that result in vision. Our recent discussions now allow us to appreciate another aspect of double bonds: the rigidity that they introduce into molecules.

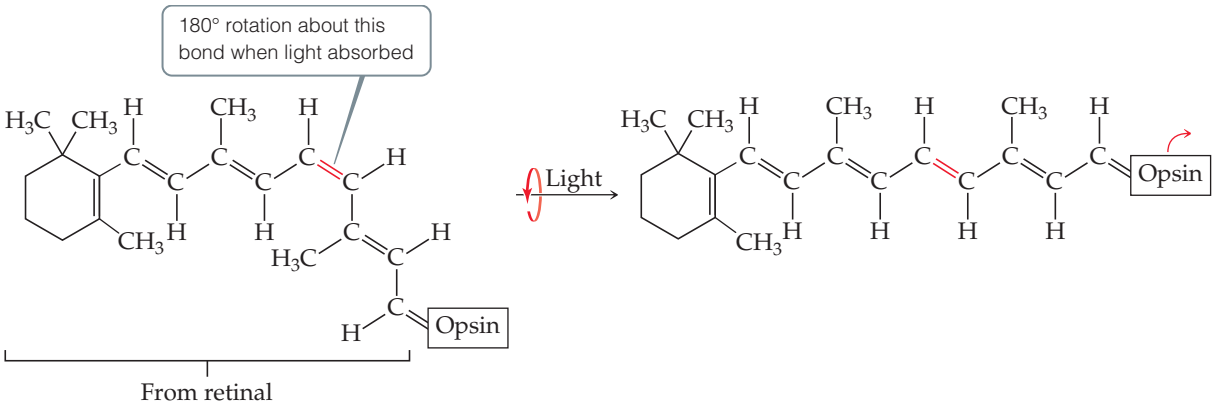
Imagine taking the $-CH_2$ group of the ethene molecule and rotating it relative to the other $-CH_2$ group, as shown in Figure 26.12. This rotation destroys the overlap of *p* orbitals, breaking the π-bond, a process that requires considerable energy. Thus the presence of a double bond restricts the rotation of the bonds in a molecule.

Our vision depends on this rigidity in retinal. In its normal form, retinal is held rigid by its double bonds, as shown on the left in **Figure 26.16**. Light entering the eye is absorbed by rhodopsin, and the energy is used to break the π-bond portion of the indicated double bond. The molecule then rotates around this bond, changing its geometry. The retinal then separates from the opsin, leading to conformational changes that trigger the reactions producing a nerve impulse. The brain interprets this impulse as the sensation of vision. It takes as few as five closely spaced molecules reacting in this fashion to produce the sensation of vision. Thus only five photons of light are necessary to stimulate the eye.

Enzymes in the retina revert the retinal to its original form and reattach it to the opsin. The slowness of this process helps to explain why intense bright light causes temporary blindness. The light causes all the retinal to separate from the opsin, leaving no further molecules to absorb light.



▲ **Figure 26.15 Inside the eye.** A colour-enhanced scanning electron micrograph of the rods (yellow) and cones (blue) in the retina of the human eye.

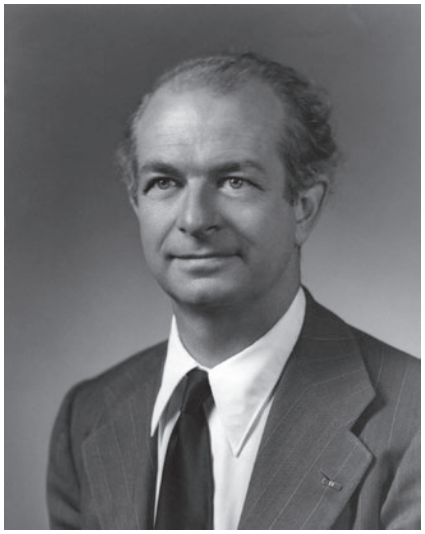


▲ **Figure 26.16 The chemical basis of vision.** When rhodopsin absorbs visible light, the π component of the double bond (shown in red) breaks, allowing rotation that produces a change in molecular geometry.

The use of curved arrows is a useful way to rationalize all your organic reactions or to demonstrate stability. Following this set of simple rules will help you master this technique. All structures generated using curved arrows must:

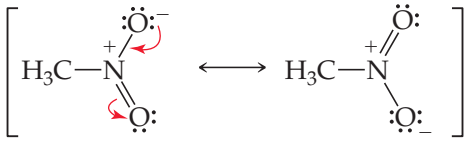
1. have the same number of valence electrons as the starting structure,
2. obey the rules of covalent bonding—for example, no more than four formal bonds to carbon,
3. differ only in the distribution of valence electrons,
4. have the same number of paired or unpaired electrons.

The concept of resonance was advanced in the 1930s by Linus Pauling (1901–1994) (**Figure 26.17**). He rationalized that many molecules and ions are best described by writing two or more Lewis structures, and that individual Lewis structures are *contributing structures*.



▲ **Figure 26.17 Linus Pauling,** a scientist of the highest calibre who won a Nobel Prize in 1954 for his contributions to chemistry. He was also very socially aware, using his scientific knowledge and his influence to combat nuclear testing in the 1950s and 1960s. For this effort, he was awarded the Nobel Peace Prize in 1962 and is still the only person in history to have won two unshared Nobel Prizes.

Let us consider the two contributing (resonance) structures of nitromethane using curved arrow notation to interconvert contributor A and contributor B:



Contributor A Contributor B

The curved arrows, shown in red, are placed on the first structure to show how the electrons move during the transformation into the second structure. In this case a lone pain on one oxygen atom becomes the new π-bond while the electron pair of the π-bond in contributor. A shifts to become a lone pair on the second oxygen atom. Note that the curved arrow indicates the movement of an electron *pair* and not of single electrons.

The two different contributing structures of nitromethane are linked by a double-headed (resonance) arrow as opposed to a set of equilibrium arrows ($\rightleftharpoons$) and are grouped together in square brackets since they both contribute to the same structure. This means that the actual molecule (or ion) is a hybrid of the various contributing structures. In other words the "real" structure of nitromethane is neither contributor A nor contributor B, but something in between—that is, a structure in which the negative charge is spread across both oxygens. We say that the negative charge is *delocalized* across the two N—O bonds. We can observe this delocalization experimentally by looking at the N—O bond lengths in *nitro* compounds. The two bond lengths are equal at 121 pm and lie between the size of a single N—O bond and a double N—O bond.

The presence, or absence, of contributing resonance structures plays a large part in the reactivity of molecules and ions. We will see a lot more of this, especially when discussing what constitutes a good leaving group and the reactivity of phenols.

A CLOSER LOOK Describing Charge

⊕ or +? Organic chemists tend to circle positive and negative signs on molecules to distinguish charge from bonds and plus signs. It also helps when describing electron redistribution. From here on, we will use this form of notation in our mechanistic considerations.

Sample Exercise 26.5

Resonance and curved arrows

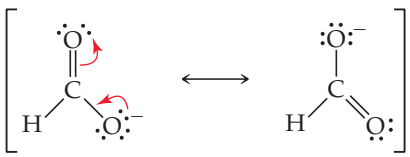
Draw two equivalent resonance structures for the formate ion, HCO_2^- using curved arrows to indicate movement of electrons.

SOLUTION

Analyse Draw the two contributing forms and note the differences.

Plan Redistribute valence electrons on the oxygen bearing the negative charge and within the double bond.

Solve



Practice Exercise

Which of the following molecules or ions will exhibit delocalized bonding: SO_3^{2-}, H_2CO, O_3, NH_4^+?

Arrow notation can also be used to rationalize a reaction's pathway or *mechanism*. A simple and general reaction may look like this:

$$Nu^-: + E^+ \longrightarrow Nu{-}E \qquad [26.4]$$

where "Nu" is not the fictional element "nubrium" but a nucleophile—that is, any molecule or ion with a lone pair of electrons available for reaction. We can use the arrow notation to describe pictorially how the lone pair on Nu is able to form a new covalent bond with an electrophile E (electro, meaning *negative*; phile, meaning *loving*), which is an electron-pair acceptor:

$$Nu^-: \curvearrowright E^+ \longrightarrow Nu{-}E \qquad [26.5]$$

An example of this type of reaction is



We will gain significant experience at using arrow notation in the next section and throughout the next five chapters as we discuss the reactivity of functional groups.

Self-Assessment Exercises

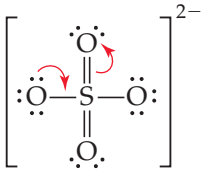
26.13 What does a curved arrow represent?

(**a**) The transformation of reactants into products

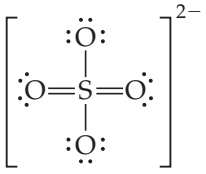
(**b**) The movement of a single electron

(**c**) The movement of a pair of electrons

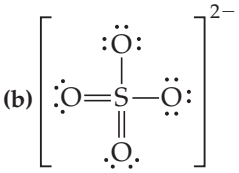
26.14 Which resonance structure results from the curved arrows shown in this contributor to the sulfate ion:



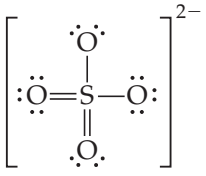
(a)



(b)



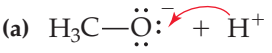
(c)



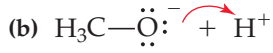
26.15 Which curved arrow correctly represents the following reaction:



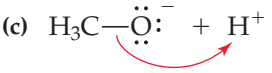
(a)



(b)



(c)



Exercises

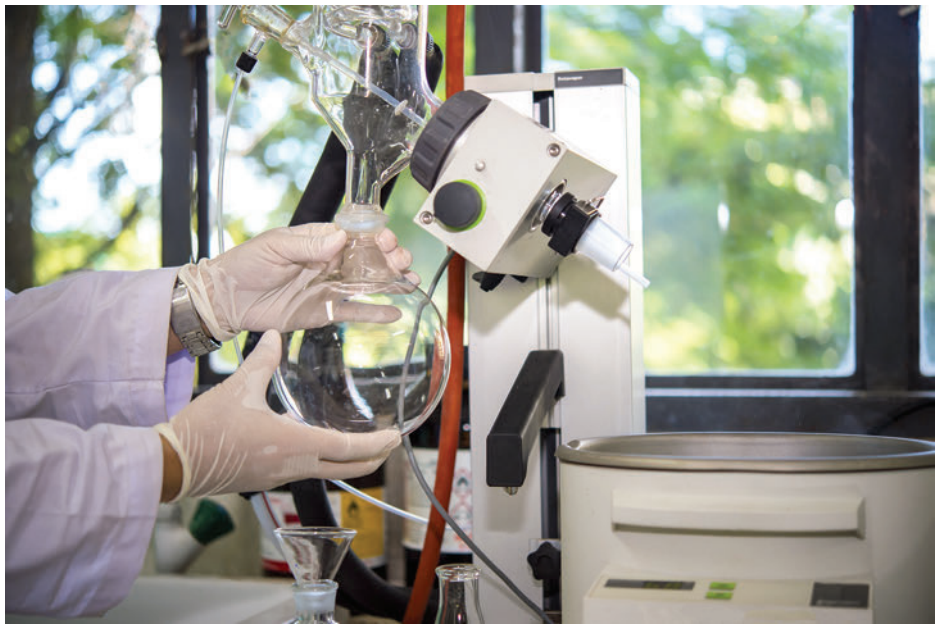
26.16 **(a)** Write a single Lewis structure for acetate, CH_3COO^-. **(b)** Are there other equivalent Lewis structures for the molecule? **(c)** Would you expect CH_3COO^- to exhibit delocalized π-bonding? **(d)** Draw the curved arrows that represent the electron movement linking the two resonance contributors of the acetate ion. Explain.

26.17 Draw the curved arrows representing the electron pair movement in the neutralization reaction of the acetate ion, CH_3COO^-, with H^+.

Answers to Self-Assessment Exercises

26.13 (c) **26.14** (b) **26.15** (a)

26.4 Electrophilic Addition Reactions



A synthetic organic research chemist is someone whose focus is to transform chemicals that are cheap and readily available into new molecules that have a specific purpose, for example as pharmaceuticals or a new type of glue or a material with a high strength to weight ratio. In this section, we see how the process may start as we look at reactions of unsaturated hydrocarbons. A few different combinations of chemicals can lead to a wide variety of products. While this may seem confusing at first, we find that the reactions all occur by the same basic mechanism so by visualizing what happens on a molecular level enables us to predict the outcome of all electrophilic addition reactions. There is a distinct pattern to what is occurring!

When you finish this section, you should be able to:

- Predict the outcome of any electrophilic addition reaction
- Understand the mechanism by which these reactions occur
- Use your knowledge of the reaction mechanism to rationalize the regioselective and stereoselective characteristics of the reaction

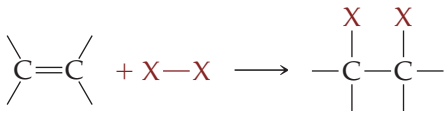
The presence of carbon–carbon double or triple bonds in a compound markedly increases its chemical reactivity. The most characteristic reactions of alkenes and alkynes are **addition reactions**, in which a reactant is added across the two carbon atoms that form the multiple bond. Three main types of addition reactions are typical of alkenes and alkynes, leading to increasing the degree of functionality within a hydrocarbon: **halogenation**, **hydrohalogenation** and **hydration**. These reactions involve the addition of X_2 (X = Cl, Br), HX (X = Cl, Br, I) and HOH (water), respectively. **Figure 26.18** shows a general representation of each reaction.

The reason why alkenes and alkynes are so reactive is twofold. In both cases, the unhybridized *p* orbitals that form the π-bonds are electron-rich, so would be expected to attract electron-deficient species. Also, we have seen that in carbon, π-bonds are weaker than σ-bonds, so would be expected to react to form σ-bonds wherever possible. Moreover, the shape of alkenes and alkynes make them easily accessible to reagents (**Figure 26.19**). The electron-rich nature of a multiple bond leads to enhanced reactivity with electrophiles. Hence, **electrophiles** are molecules that accept a pair of electrons in a chemical reaction. Reactions of alkenes and alkynes with electrophiles are called electrophilic addition reactions.

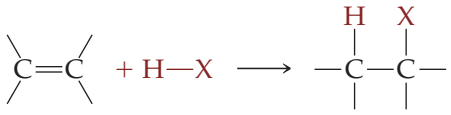
Addition Reactions Involving HX (X = Cl, Br, I)

Let's consider the addition reaction between HBr and but-2-ene as a representative of this reaction type. The reaction proceeds in two steps. In the first step, which is

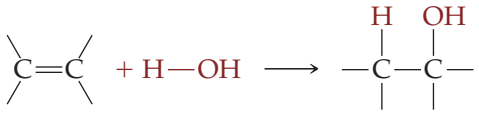
(a) Halogenation



(b) Hydrohalogenation

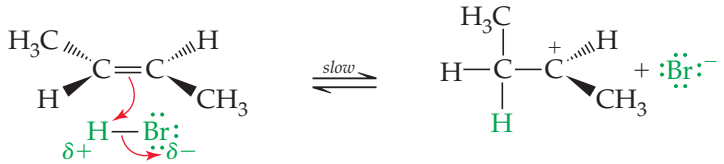


(c) Hydration



▲ **Figure 26.18 Addition reactions of alkenes and alkynes (X = halogen).** Halogenation, hydrohalogenation and hydration of an alkene are useful and efficient ways of preparing alkyl halides and alcohols. The addition reactions of alkynes follow those of the alkenes.

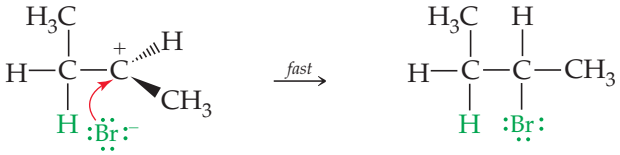
rate-determining, the electron-rich double bond attacks the hydrogen of HBr (the electrophile), which transfers a proton to one of the two alkene carbons and produces a bromide ion in the process:



[26.6]

The pair of electrons that formed the π-bond between the carbon atoms in the alkene are used to form the new C—H bond. As a result, one carbon has fewer valence electrons associated with it. This carbon is now electron-deficient, as indicated by the positive charge. Organic molecules bearing a positive charge on carbon are called **carbocations**. Carbocations are classified as *primary* (1°), *secondary* (2°) or *tertiary* (3°), depending on the number of carbon units bonded to the positively charged carbon. For example, the carbocation formed on the right-hand side in Equation 26.6 is secondary, as the carbon bearing the positive charge has two other carbons bonded directly to it.

The second step, involving the addition of Br^- to the carbocation, is faster:

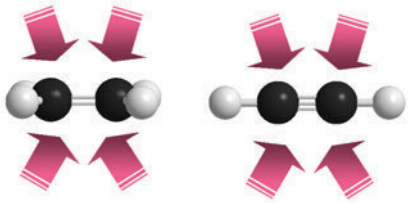


[26.7]

In this step the bromide ion donates a pair of electrons to the carbocation, forming the new C—Br bond. The bromide ion is behaving as a **nucleophile** (*nucleus-loving*). A nucleophile is a species that donates a pair of electrons in a chemical reaction. Nucleophiles are electron-rich species.

Since the first step in the reaction involves both the alkene and hydrogen halide, the rate law for the reaction is second order, first order in both the alkene and HBr:

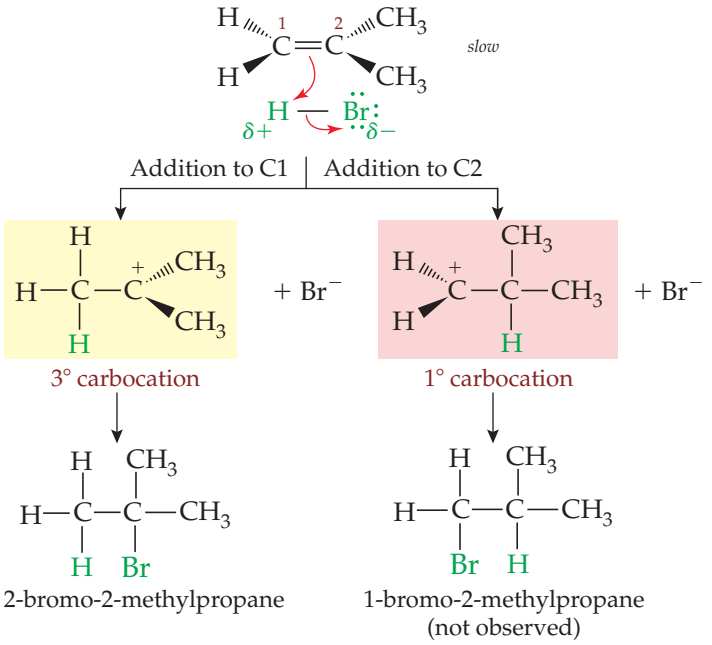
$$\text{Rate} = -\frac{\Delta[CH_3CH{=}CHCH_3]}{\Delta t} = k[CH_3CH{=}CHCH_3][HBr] \qquad [26.8]$$



▲ **Figure 26.19 The accessibility of alkenes and alkynes.** The trigonal planar and linear geometries of alkenes and alkynes makes the addition of halogens easier through the exposed faces, as indicated by the arrows. Alkynes have two additional regions of accessibility, one directed out of the page and the other into the page.

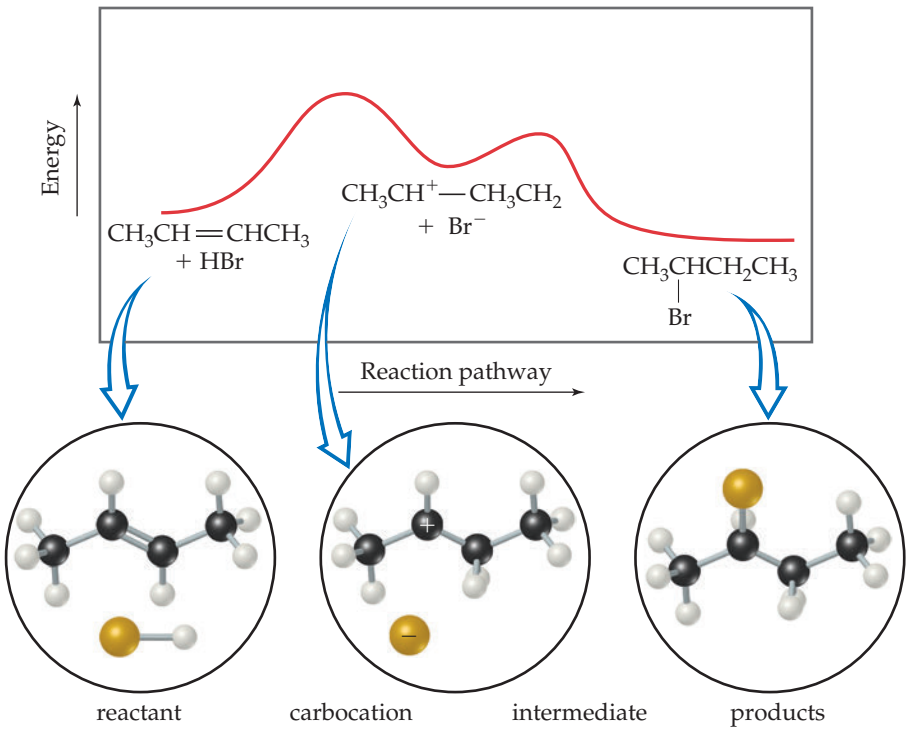
The energy profile for the reaction is shown in **Figure 26.20**. The first energy maximum represents the transition state in the first step of the mechanism. The second maximum represents the transition state for the second step. Notice that there is an energy minimum between the first and second steps of the reaction. This energy minimum corresponds to the intermediate carbocation.

Let us now consider the reaction of 2-methylpropene with HBr. This reaction is a *regioselective reaction* meaning that one product, 2-bromo-2-methylpropane, is formed predominantly. The first step of the addition leads to the possible formation of two intermediate carbocations:



[26.9]

Go Figure As shown, is this reaction endothermic or exothermic?



▲ **Figure 26.20** **Energy profile for addition of HBr to but-2-ene.**

From a large body of experiments, we know that 3° carbocations are more stable and require a lower activation barrier to formation than either 1° or 2° carbocations. Hence the product distribution can be rationalized based on which intermediate is formed in preference.

The relative stability of primary, secondary and tertiary carbocations is:

less stable 1° < 2° < 3° *most stable*

and is based on how easily the alkyl groups around the positive charge can spread the charge away. This is known as an *inductive effect*. The larger the area the positive charge is spread over, the more stable the carbocation. In the case of hydrocarbons, as the number of alkyl groups increases so too does the stability of the carbocation increase.

The first person to note the regioselectivity in hydrohalogenations (and hydrations) was Vladimir Markovnikov (1837–1904). The general rule for electrophilic additions to alkenes bears his name. **Markovnikov's rule** states:

In the addition of HX to an alkene, the hydrogen adds to the carbon atom of the double bond bearing the greater number of hydrogen atoms bonded directly to it.

This can also be written:

In the addition of HX to an alkene, the hydrogen adds to the least substituted carbon atom of the double bond.

This rule provides an easy way to predict the major product of an addition reaction involving HX.

Returning to Equation 26.9, C1 has two hydrogens directly attached whereas C2 has none (those on the methyl group hydrogens do not count because they are not directly attached to the sp^2 hybridized carbon of the double bond). The product predicted by using Markovnikov's rule is certainly the one predicted on the basis of carbocation stability.

Sample Exercise 26.6

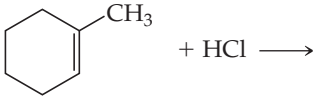
Addition of HX to alkenes

Name and draw the structural formula for the major product formed when 1-methylcyclohexene reacts with HCl. Justify your choice for the major product.

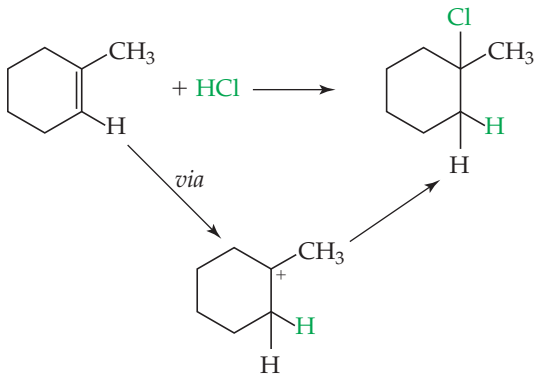
SOLUTION

Analyse We are asked for several things here, including knowing something about nomenclature and converting names into structures, as well as the reactivity of alkenes.

Plan Begin by drawing the structure of the reactants and identify the reaction as the addition of HCl to the double bond:



Solve Using Markovnikov's rule, the hydrogen atom of HX should add to the double bond on the side with the most number of hydrogens:

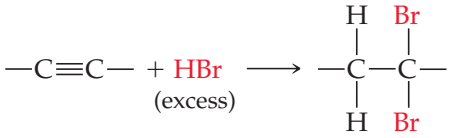


Hence our answer is *1-chloro-1-methylcyclohexane*. Our justification comes from the relative stabilities of the possible carbocation intermediates. Our chosen product forms a 3° carbocation intermediate over the alternative 2° carbocation intermediate because it is more stable due to enhanced inductive effects. To say "*because Markovnikov said so*" is not satisfactory.

Practice Exercise

Addition of HCl to an alkene forms 2-chloro-3-methylbutane. What is the alkene?

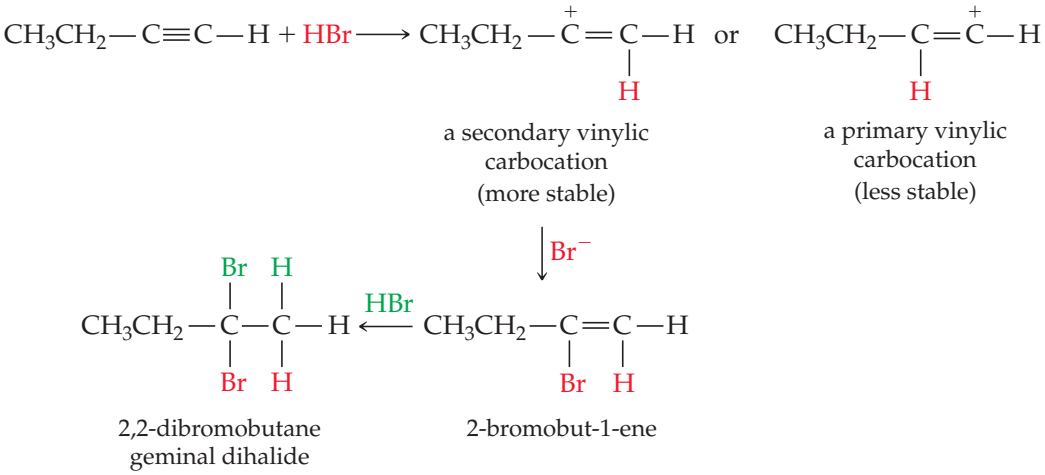
The addition of HX across an alkyne forms a *geminal* dihalide. The term *geminal* refers to two groups occupying the same carbon. Equation 26.10 demonstrates reactions of this class.



[26.10]

geminal dihalide

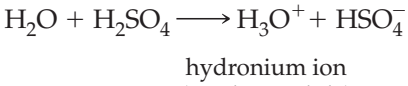
In the case of a terminal alkyne, for example but-1-yne, protonation occurs at the terminal carbon due to the formation of a stabilized secondary vinylic carbocation, which is relatively more stable than the alternative primary carbocation. Notice that the trend of carbocation stability is the same as that discussed for the addition of HBr to alkenes. Further reaction of this carbocation with the bromide nucleophile leads to 2-bromobut-1-ene as the sole product. Further addition of HBr to the alkene follows Markovnikov's rule, leading to the geminal dibromide 2,2-dibromobutane.



Addition Reactions Involving H_2O

The *hydration* of alkenes and alkynes is not as easy to accomplish as either the halogenation or hydrohalogenation of the same compounds. Hydration reactions need to be catalysed by a small amount of a strong acid, such as H_2SO_4. The reason is easily demonstrated mechanistically. Again, we can use but-2-ene as our alkene to illustrate this example.

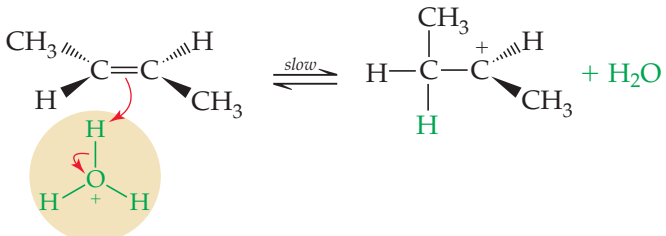
The addition of a few drops of sulfuric acid to a reaction mixture containing but-2-ene and water leads to the formation of the hydronium ion, as shown:



[26.11]

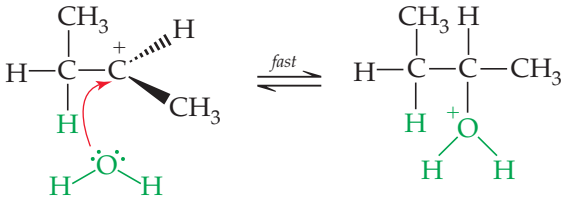
hydronium ion (an electrophile)

In terms of the addition of water, the hydronium species is the active electrophile. The reaction proceeds as shown in Equations 26.12 to 26.14. The first step involves the addition of a proton from the hydronium ion to one of the carbons that make up the double bond. This step is slow and rate-determining.



[26.12]

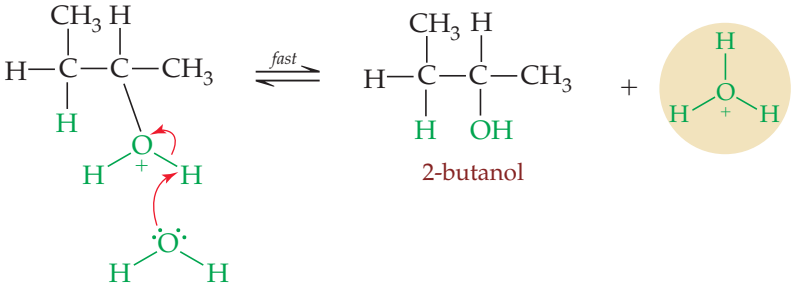
A molecule of water can then act as a nucleophile forming a C—O bond with the valence electrons of one of its two lone pairs. Note that a nucleophile need not be negatively charged; it just needs to be a species capable of donating a pair of electrons. In this case, an oxonium ion is formed.



oxonium ion

[26.13]

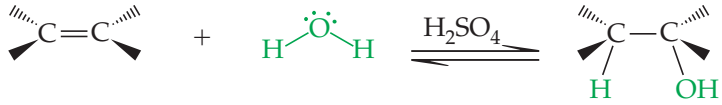
Loss of a proton from the oxonium ion yields the final alcohol product. The other product formed is a new hydronium ion. This ion is capable of reacting further with another alkene in the same way described in Equations 26.12 to 26.14. Theoretically, an amount of sulfuric acid large enough to initiate the formation of a single hydronium ion is enough to allow the reaction to proceed. In practice, more is required to make sure the reaction is completed in a timely manner.



2-butanol

[26.14]

You may have noticed in Equations 26.12 to 26.14 that equilibrium arrows are used to describe each step of the reaction mechanism. This is because the reverse reaction—that is, the *dehydration* of alcohols—is also catalysed by H_2SO_4. In fact, this reverse method is a very useful way of preparing alkenes.



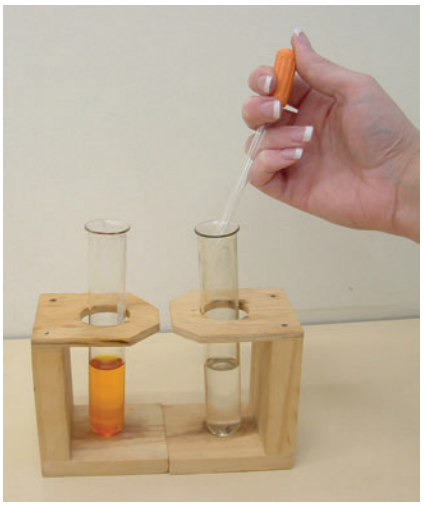
[26.15]

The direction of the equilibrium, shown in equation 26.15—that is, to maximize the yield of the alkene from the alcohol (right to left) or the alcohol from the alkene (left to right)—can be manipulated by adjusting the amount of water present in the reaction mixture. Large amounts of water (usually as aqueous acid) favour alcohol formation, whereas using concentrated acid and eliminating water favour alkene formation. By using these simple techniques, the alkene prepared in high yield.

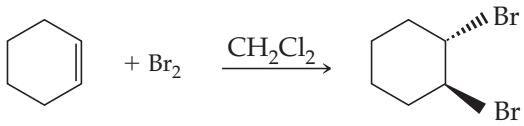
Halogenation: Addition of Br_2 and Cl_2

One of the easiest and most dramatic reactions in organic chemistry has to be the reaction of Br_2 with an alkene. Bromine is a dense orange liquid, whose colour persists if made into a solution in hexane. The addition of a slight excess of an alkene to this solution (**Figure 26.21**) at room temperature immediately turns the solution colourless. Undertaking this reaction in the presence of an alkane also demonstrates the large difference in reactivity between alkanes and alkenes towards bromination. This reaction and its dramatic colour change is a useful qualitative test for the presence of a C = C double bond in a compound.

The addition of bromine or chlorine to an alkene is an example of a **stereoselective reaction**: a reaction in which the product has one particular geometry in preference over another. Observe how in Equation 26.16 the two bromine atoms add to opposite sides of the plane of the cyclohexene molecule. Let us now investigate the reaction of bromine with cyclohexene, as an example of a halogenation, in more detail.

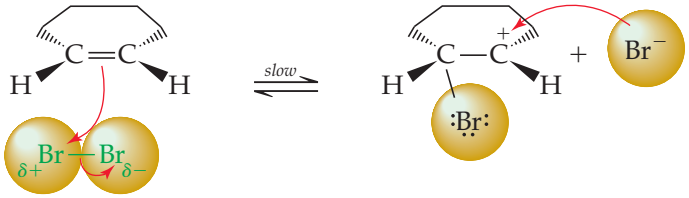


▲ **Figure 26.21 Bromine test for alkenes.** The bright orange colour of bromine solution is in contrast to the colourless solution produced by the addition of an alkene to the same solution.



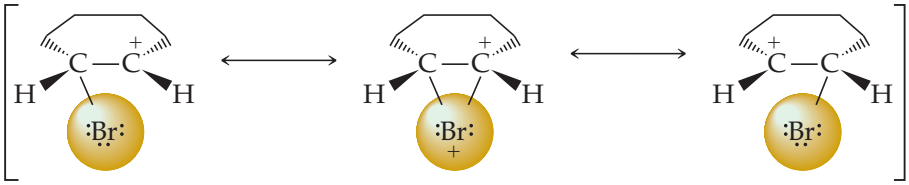
[26.16]

The reasons for the stereoselectivity observed in the bromination of alkenes involve both steric and electronic components. The enormous size of a bromine atom compared with a hydrogen atom means that the incoming nucleophile (Br^-) cannot attack the carbocation from the same face as the initial electrophile (as shown in Equation 26.17). In the case of a cyclic structure, restricted rotation about the C—C bonds ensures that only the *trans*-dihaloalkane is formed. Chlorination is not as stereoselective because of chlorine's comparatively smaller size.



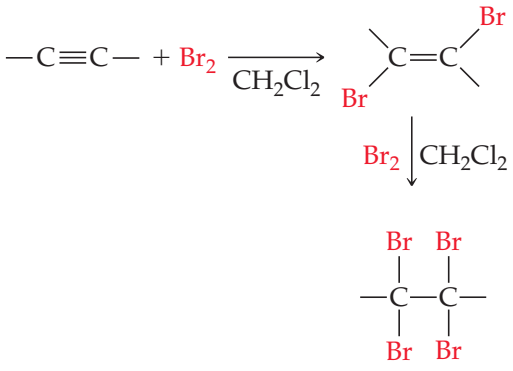
[26.17]

Three contributors to the resonance structure of the intermediate carbocation are possible because of the electron-rich nature of the bromine atom and its accessibility to the carbocation due to its size. Of these, the middle structure bearing the *bromonium ion* is the largest contributor to the intermediate's overall structure.



[26.18]

The bromination and chlorination of alkynes follows a similar mechanism. The stepwise addition of bromine, by way of example, is shown in Equation 26.19. In each step, dichloromethane (CH_2Cl_2) is the solvent.



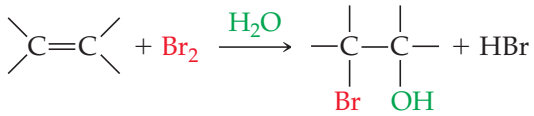
[26.19]

Addition of one equivalent of bromine leads to the formation of the dibromo-alkene in which the two bromo groups occupy a *trans* arrangement across the double bond as a result of the bromonium intermediate formed. A further equivalent of bromine leads to the tetrabrominated alkane in which all four positions around the carbon-carbon triple bond are occupied by halogen. Tetrahalogenation occurs when an excess of bromine or chlorine to the alkyne is used.

Halohydrin Formation

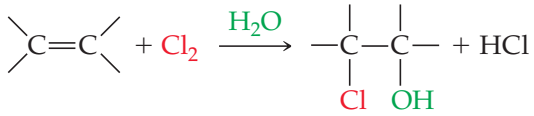
Let us now extend what we have learned about the mechanisms associated with the bromination and hydration of alkenes to more complicated additions. To do this, we will investigate the formation of the *halohydrins*—a class of compound containing halogen and OH functional groups. If the halogen and OH groups are on adjacent carbon atoms,

the compound is called a *vicinal halohydrin*. Equations 26.20 and 26.21 illustrate the reaction type:



[26.20]

a vicinal halohydrin

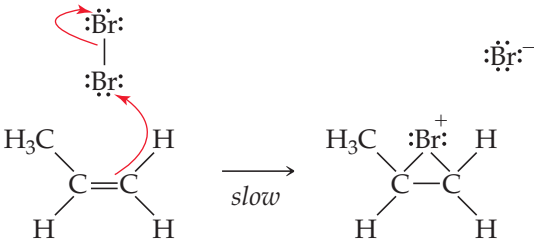


[26.21]

The halogen of the halohydrin originates from the source you are familiar with (being Br_2 or Cl_2) and the OH group of the halohydrin occurs typically through the introduction of water to the reaction. This can be achieved either by adding water to the solvent of choice or as the solvent, depending on practicality.

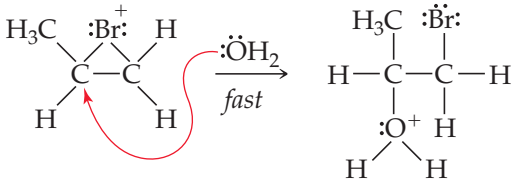
The mechanism of bromohydrin formation has three steps. Here we look at the formation of the bromohydrin derived from propene in more detail:

Step 1



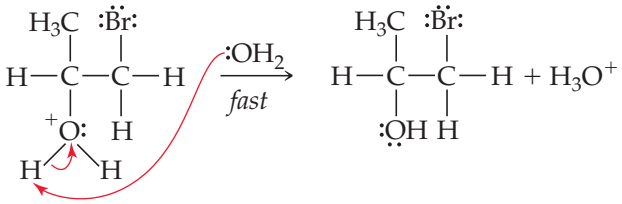
[26.22]

Step 2



[26.23]

Step 3



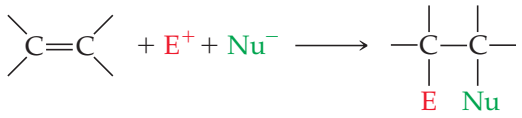
[26.24]

A cyclic bromonium ion is formed in the first step because Br^+ is the only electrophile in the reaction mixture (the corresponding cyclic chloronium ion would form if chlorine is used). This cyclic bromonium ion rapidly reacts with any nucleophile present. In the present case, two nucleophiles are present in solution. The two nucleophiles are Br^- and H_2O. But because H_2O is in the solvent, it is present in a higher concentration than Br^-. Consequently, reaction between the cyclic bromonium ion and H_2O is more likely. The protonated bromohydrin is a strong acid, and so reacts readily with water to form the halohydrin.

Notice throughout Equations 26.23–26.24 that the *regioselectivity* is well-defined with very little of the alternative bromohydrin formed. The product distribution follows *Markovnikov's rule,* as do all the additions we have studied so far. You may recall that for the addition of HCl across a double bond, the hydrogen adds to the side of the double bond with the most hydrogens. In the example of HCl addition, H^+ is considered to be the electrophile. In the case of halohydrin formation, the electrophile is Br^+, yet the outcome is still the same, that is, the electrophile adds to the side of the double bond with the most hydrogens.

While the major organic product of the reactions shown in Equations 26.20 and 26.21 is the vicinal halohydrin (called a bromohydrin or chlorohydrin, respectively), the corresponding dihalides are also formed to some extent. This is due to the competition between the two nucleophiles present, bromide ion and water.

Halohydrin formation suggests we can generalize addition reactions in the following way:



[26.25]

where the requisite nucleophile and electrophile can come from different starting materials. This means that provided you are able to identify a range of electrophiles (E^+) and nucleophiles (Nu^-) from a broad range of reagents, you will be able to convert alkenes into many highly functionalized compounds. **Table 26.2** lists some common electrophile (E^+) and nucleophile (Nu^-) combinations and the addition products.

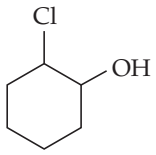
TABLE 26.2 Summary of addition reactions to an alkene by electrophile (E^+) and nucleophile (Nu^-) from Equation 26.25

Reagents	Electrophile	Nucleophile	Product
Br_2	Br_2	Br^-	—C(Br)—C(Br)—
H_2O/H_2SO_4	H_3O^+	H_2O	—C(H)—C(OH)—
Cl_2	Cl_2	Cl^-	—C(Cl)—C(Cl)—
Br_2/H_2O	Br_2	H_2O	—C(Br)—C(OH)—
NBS/H_2O	Br_2	H_2O	—C(Br)—C(OH)—
Cl_2/CH_3OH	Cl_2	CH_3OH	—C(Cl)—C(OCH_3)—
$Br_2/NaCl$	Br_2	Cl^-	—C(Br)—C(Cl)—
$Cl_2/NaBr$	Cl_2	Br^-	—C(Cl)—C(Br)—
NBS/NH_4Cl	Br_2	Cl^-	—C(Br)—C(Cl)—
NBS/NH_4F	Br_2	F^-	—C(Br)—C(F)—

Sample Exercise 26.7

Addition reactions leading to halohydrins

Indicate how the following alcohol can be prepared from an alkene:

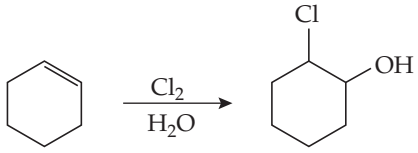


SOLUTION

Analyse We are asked to work backwards from a given structure to determine how we could make it from an alkene.

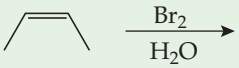
Plan Understand the differences between the starting alkene and the chlorohydrin product. Use our general equation [26.25] to determine from what reagents the electrophile and nucleophile are derived.

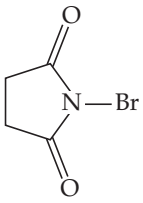
Solve The alkene required for this reaction is cyclohexene. This is deduced by placing the double bond between the positions occupied by the introduced Cl and OH functional groups. To get the addition of Cl and OH to the alkene, the reagents of choice must be Cl_2 and water. The water acts as both solvent and nucleophile.



Practice Exercise

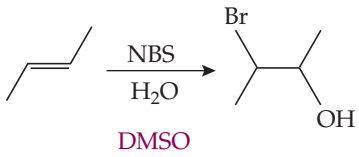
What are the major and minor products of the following reaction?





▲ **Figure 26.22** ***N*-Bromosuccinimide,** or NBS, can act as an electrophilic source of bromine by decomposing slowly in the presence of water to form a tiny amount of Br_2.

To develop the concept shown in Equation 26.22 further, let us now investigate another source of electrophilic bromine, which is *N*-bromosuccinimide (**Figure 26.22**). A general reaction utilizing *N*-bromosuccinimide (abbreviated NBS) as an electrophilic source of bromine is shown in Equation 26.26.

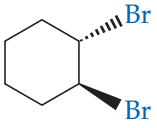


[26.26]

Here, the NBS reacts with an alkene in the presence of water and dimethylsulfoxide (DMSO) ($(CH_3)_2S{=}O$), which is a polar organic solvent miscible with water. Under these conditions, the NBS decomposes slowly to form a small amount of Br_2, which then undergoes reaction to form the bromohydrin. Because only a small amount of Br^- is ever generated, the concentration of water is always in excess and so the bromohydrin is always formed in high yield.

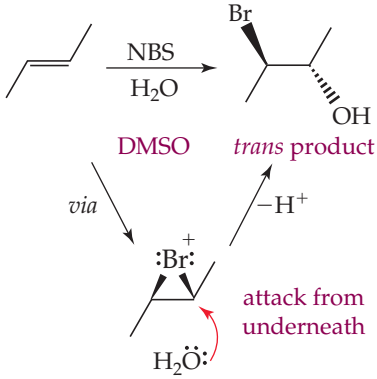
A CLOSER LOOK Stereochemistry in Halohydrin Formation

Stereoselectivity plays a part in the formation of the bromohydrin. Recall from Equation 26.16 that the product of the bromination of cyclohexene is the *trans* dibromide.



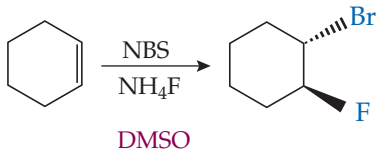
trans-1,2-dibromocyclohexane

Because the bridged halonium ion ring is opened by backside attack of H_2O in the halohydrin formation, addition of X and OH occurs in an *anti* (opposite) fashion and the *trans* product is most often formed.



[26.27]

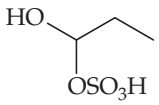
We can see the similarity more clearly in the following example where ammonium fluoride (NH_4F) provides a source of fluoride, which acts as the nucleophile, and DMSO acts as the solvent. Again, the *trans* product is formed.

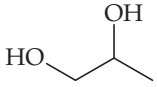


[26.28]

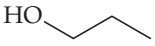
Self-Assessment Exercises

26.18 What is product formed from the addition of water in the presence of dilute sulfuric acid to propene?

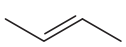
(a) 

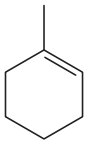
(b) 

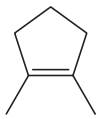
(c) 

(d) 

26.19 In the addition of HBr to the following alkenes, in which case do we need to apply Markovnikov's rule?

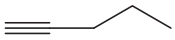
(a) 

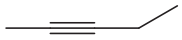
(b) 

(c) 

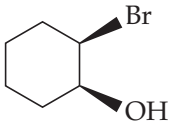
(d)

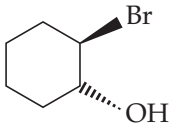
26.20 Which alkyne, when treated with excess HI, gives the exclusively 2,2-diiodopentane?

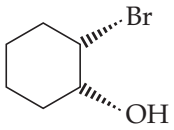
(a) 

(b) 

26.21 What product is formed when cyclohexene is treated with NBS in the presence of water?

(a) 

(b) 

(c) 

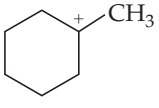
Exercises

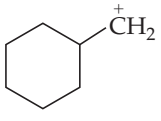
26.22 **(a)** Suggest a method of preparing *trans*-1,2-dichlorocyclohexane. **(b)** Suggest a method of preparing 1-chloro-2-fluorocyclohexane from cyclohexene.

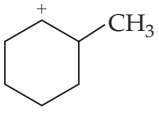
26.23 In the hydrohalogenation of but-1-ene with HCl, two alkyl halides can be formed. **(a)** Draw them. **(b)** Circle the major organic product and give an explanation for your choice, taking into account the stability of any intermediates.

26.24 Draw the intermediate that is thought to form in the addition of a hydrogen halide to an alkene, showing how it is formed and how it reacts, using cyclohexene as the alkene in your description.

26.25 Place the following carbocations in an increasing order of relative stability:

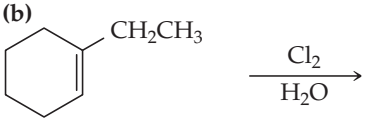
(a) 

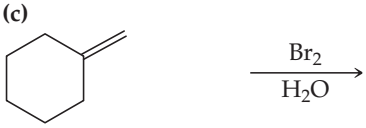
(b) 

(c) 

26.26 What is the major product of the following reactions?

(a) 

(b) 

(c) 

(d) 

26.27 Consider the dehydration and rehydration of 1-propanol. Is the product of the two reactions the same as the starting alcohol?

26.28 What would be the major organic product for the reaction of but-2-yne with excess bromine?

Answers to Self-Assessment Exercises

26.18 (c) **26.19** (b) **26.20** (a) **26.21** (b)

26.5 Alkanes from Alkenes: Catalytic Hydrogenation



Catalysts play a very important role in hydrocarbon chemistry. "Catalytic cracking" is used in oil refineries to convert high molecular weight hydrocarbons to the more useful, lower molecular weight, feedstock for the chemical industry. Catalysts are also used in the addition of hydrogen to alkenes and alkynes both in the research laboratory as well as for the manufacture of margarine from plant oils.

When you finish this section, you should be able to:

- Identify the conditions required to add hydrogen gas to an alkene or alkyne
- Understand the stereochemical outcome of hydrogenation of disubstituted cyclic alkenes

The reaction between an alkene and molecular hydrogen (H_2), referred to as hydrogenation, does not occur readily under ordinary conditions of temperature and pressure. One reason for the lack of reactivity of H_2 towards alkenes is the high bond enthalpy of the H_2 molecule. To promote the reaction, it is necessary to use a catalyst that assists in rupturing the H—H bond. The most widely used catalysts are finely divided metals capable of adsorbing H_2, such as Pt, Pd and Ni. The hydrogenation reaction is often called a **catalytic hydrogenation**, since only a small amount of the solid metal is necessary to promote the reduction of the alkene to the corresponding alkane in solution. Because the alkene and catalyst exist in different phases, this type of reaction undergoes *heterogeneous catalysis*.

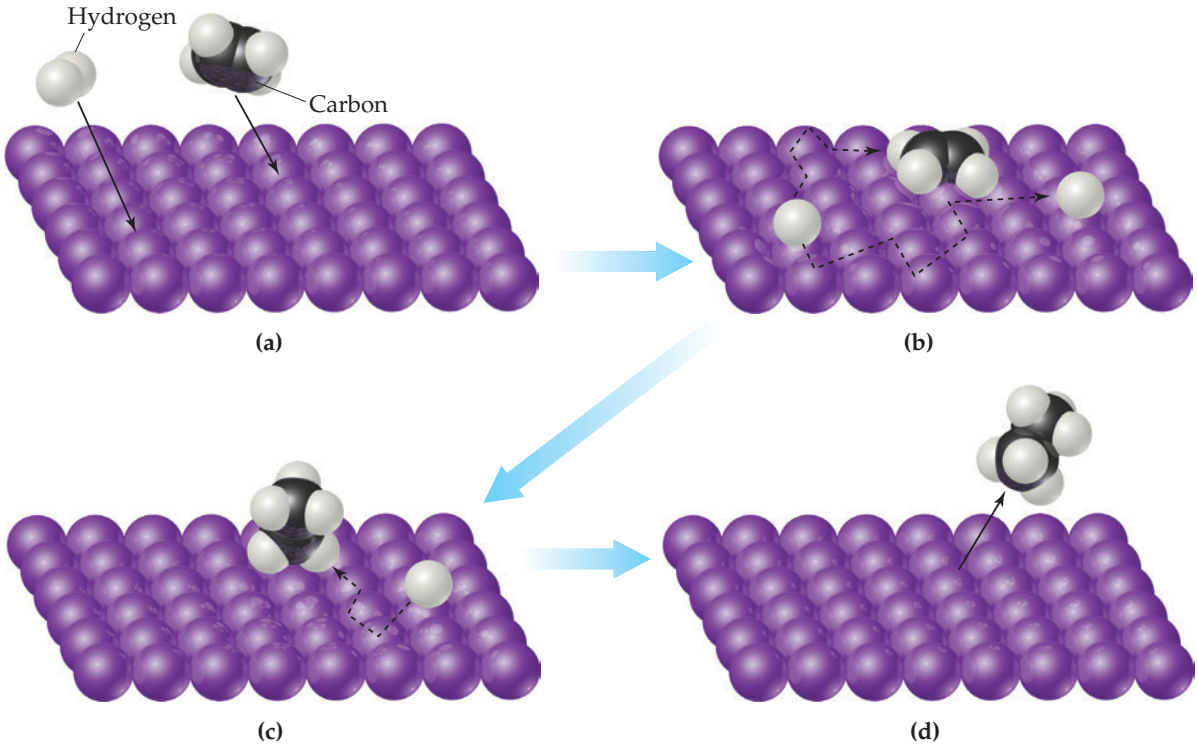
The reaction of hydrogen gas with ethene gas to form ethane gas provides an example of heterogeneous catalysis:

$$\underset{\text{ethene}}{C_2H_4(g)} + H_2(g) \xrightarrow{Pt} \underset{\text{ethane}}{C_2H_6(g)} \qquad \Delta H^\circ = -137\ \text{kJ/mol} \qquad [26.29]$$

We can understand the role of the catalyst in this process by considering the bond enthalpies involved (Table 8.3). In the course of the hydrogenation reaction, the H—H σ-bond and the carbon-carbon π-bond must be broken, and to do so requires the input of energy, which we can liken to the activation energy of the reaction. The formation of the new C—H σ-bonds *releases* an even greater amount of energy, making the reaction *exothermic*. When H_2 and C_2H_4 are bonded to the surface of the catalyst, less energy is required to break the bonds, lowering the activation energy of the reaction.

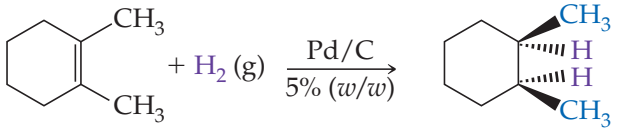
A CLOSER LOOK Hydrogenation

The mechanism by which the reaction is thought to occur is shown schematically in **Figure 26.23**. Both ethene and hydrogen are adsorbed on the metal surface (Figure 26.23(a)). Upon adsorption the H—H bond of H_2 breaks, leaving two H atoms that are bonded to the metal surface, as shown in Figure 26.23(b). The hydrogen atoms are relatively free to move about the surface. When a hydrogen atom encounters an adsorbed ethene molecule, it can form a σ-bond to one of the carbon atoms, effectively destroying the C—C π-bond and leaving an *ethyl group* (C_2H_5) bonded to the surface *via* a metal-to-carbon bond (Figure 26.23(c)). This bond is relatively weak, and when the other carbon atom also encounters a hydrogen atom, a second C—H σ-bond is readily formed and the resulting ethane molecule is released from the metal surface (Figure 26.23(d)). The site is ready to adsorb another ethene molecule and thus begin the cycle again.



▲ **Figure 26.23 Mechanism for reaction of ethene with hydrogen on a catalytic surface.** (a) The hydrogen and ethene are adsorbed at the metal surface. (b) The H—H bond is broken to give two adsorbed hydrogen atoms. (c) These hydrogens migrate to the adsorbed ethene and bond to the carbon atoms. (d) As C—H bonds are formed, the adsorption of the molecule to the metal surface is decreased and ethane is released.

Catalytic hydrogenations favour a *cis* stereochemistry. For example, the reaction of 1,2-dimethylcyclohexene with hydrogen in the presence of 5% (*w*/*w*) palladium on carbon (Pd/C) yields the alkane in 100% yield, with >75% of the alkane having the *cis* stereochemistry. Palladium on carbon is a standard synthetic catalyst for hydrogenation.



[26.30]

Sample Exercise 26.8

Identifying the product of a hydrogenation reaction

Write the structural formula for the product of the hydrogenation of 3-methyl-1-pentene.

SOLUTION

Analyse We are asked to predict the compound formed when a particular alkene undergoes hydrogenation (reaction with H_2).

Plan To determine the structural formula of the reaction product, we must first write the structural formula or Lewis structure of the reactant. In the hydrogenation of the alkene, H_2 adds to the double bond, producing an alkane. (That is, each carbon atom of the double bond forms a bond to an H atom, and the double bond is converted to a single bond.)

Solve The name of the starting compound tells us that we have a chain of five C atoms with a double bond at one end (position 1) and a methyl group on the third C from that end (position 3):

$$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3$$

Hydrogenation—the addition of two H atoms to the carbons of the double bond—leads to the following alkane:

$$CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}CH_3$$

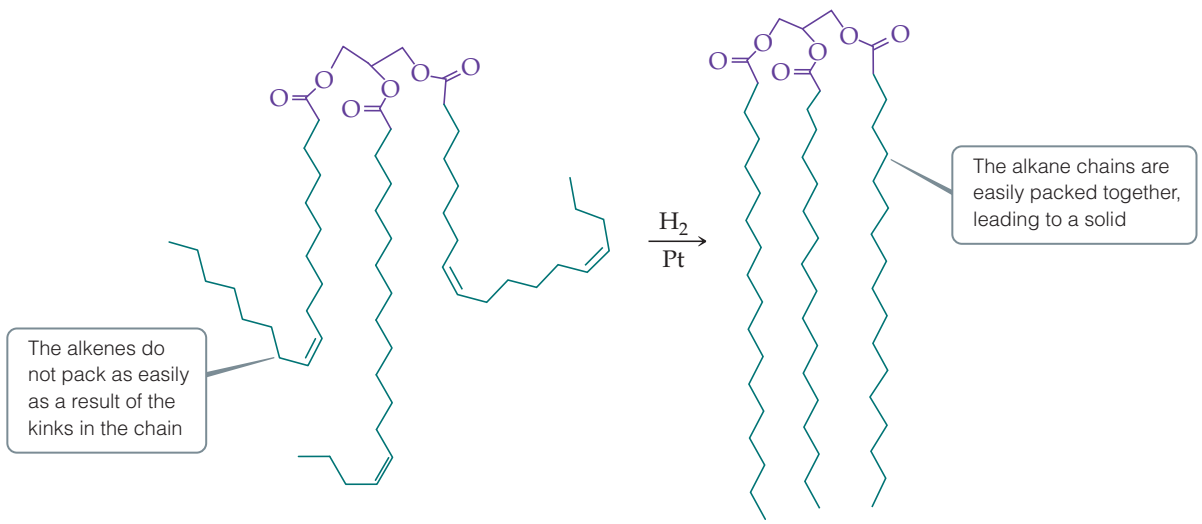
Comment The longest chain in the product alkane has five carbon atoms; its name is therefore 3-methylpentane.

Practice Exercise

Draw all the possible products (including stereochemistry) for the complete hydrogenation of the theoretical compound hexamethylcyclohexatriene, assuming 100% *cis* addition per double bond. Do not account for chair and boat conformations.

Hydrogenation is a useful commercial process for the preparation of fats from *polyunsaturated oils*. These oils, as the name suggests, contain many alkenes. Oils are generally **triglycerides** rich in linoleic ($C_{18}H_{32}O_2$), oleic ($C_{18}H_{34}O_2$), arachidonic ($C_{20}H_{32}O_2$) and other unsaturated fatty esters which, because of their structure, are liquids at room temperature (Section 26.2). Their conversion to stearic ($C_{18}H_{36}O_2$) and arachidic esters ($C_{20}H_{40}O_2$) by hydrogenation leads to **fats**, whose properties are more those of solids or semi-solids at room temperature. The reason for the change in physical properties has to do with the ease of packing the long alkyl chains over those chains that are "kinked" by the introduction of double bonds (Figure 26.24).

The process of converting oils to fats is called **hardening**. This process is especially relevant to the manufacture of margarine and cooking fats. The final hardened product is typically white. In the past, β-carotene was added to colour the margarine so that it looks like butter.



▲ **Figure 26.24 Hydrogenation of vegetable oil leads to a more solid product.**

Self-Assessment Exercises

26.29 What catalyst is required in the hydrogenation reaction of an alkene?

(**a**) H^+ (**b**) Fe (**c**) Pd/C

26.30 Partial hydrogenation of but-2-yne produces but-2-ene. What is the stereochemistry of the product?

(**a**) *Z* (**b**) *E* (**c**) a mixture of *Z* and *E* isomers

Exercises

26.31 Draw the products resulting from the catalytic hydrogenation of the following molecules.



26.32 How many moles of hydrogen are required to completely hydrogenate pent-1-en-3-yne?

26.33 Draw the structures of all possible alkenes and alkynes that could be used in a catalytic hydrogenation to form 2-methylbutane.

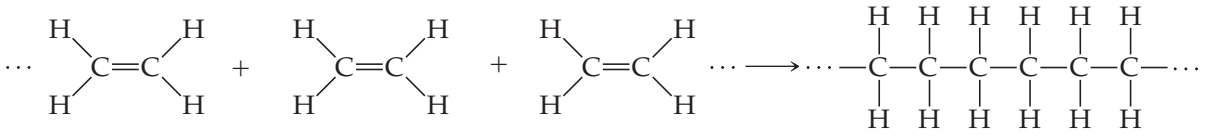
Answers to Self-Assessment Exercises

26.29 (c) **26.30** (a)

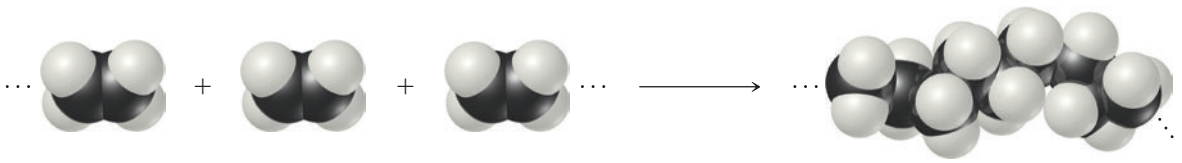
26.6 Addition Polymerization



In nature, we find many substances of very high molecular mass that make up much of the structure of living organisms and tissues. Some examples include starch and cellulose (which abound in plants) and proteins (found in both plants and animals). In 1827 Jons Jakob Berzelius (1779–1848) coined the word **polymer** (from the Greek *poly*, "many", and *meros*, "parts") to denote molecular substances of high molecular mass formed by the *polymerization* (joining together) of **monomers**, that is, molecules with low molecular mass. An example is the reaction of ethene monomers to form polyethene:



ethene polyethene

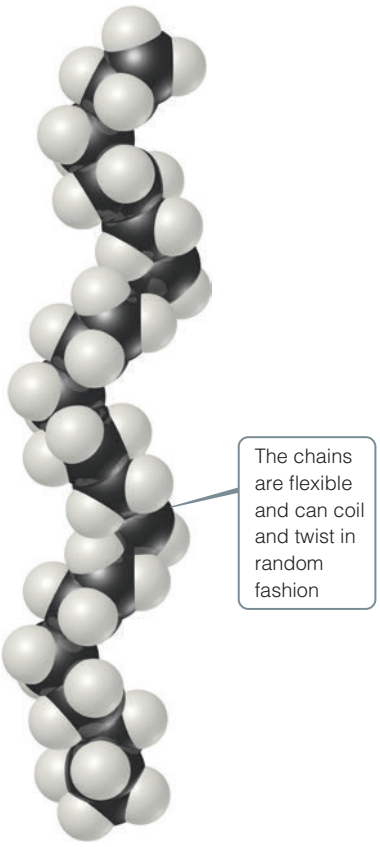


When you finish this section, you should be able to:

- Recognize the relationship between a monomer and a polymer
- Understand the three stages of addition polymerization
- Make the link between macroscopic properties such as density and the molecular level properties of crystallinity and cross linking

For a long time, humans have processed naturally occurring polymers, such as wool, leather, silk and natural rubber, into usable materials. Over the last century, however, chemists have learned to form synthetic polymers by polymerizing compounds through controlled chemical reactions. A great many of these synthetic polymers have a backbone of carbon–carbon bonds because carbon atoms have an exceptional ability to form strong stable bonds with one another.

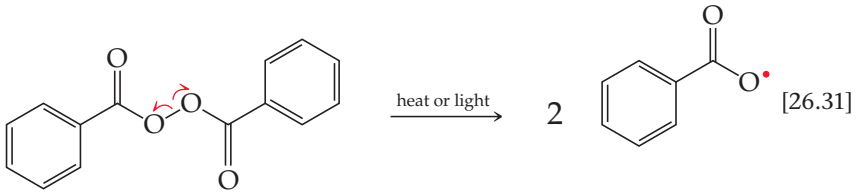
Plastics are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastic** materials can be reshaped. For example, plastic milk containers are made from a polymer known as *polyethene,* which has a high molecular mass. These containers can be melted down and the polymer recycled for some other use. In contrast, a **thermosetting plastic** is shaped through irreversible chemical processes and thus cannot be readily reshaped.



▲ **Figure 26.25 A segment of a polyethene chain.** The segment shown here consists of 28 carbon atoms. In commercial polyethene, the chain lengths range from about 10^3 to 10^5 CH_2 units.

Making Polymers

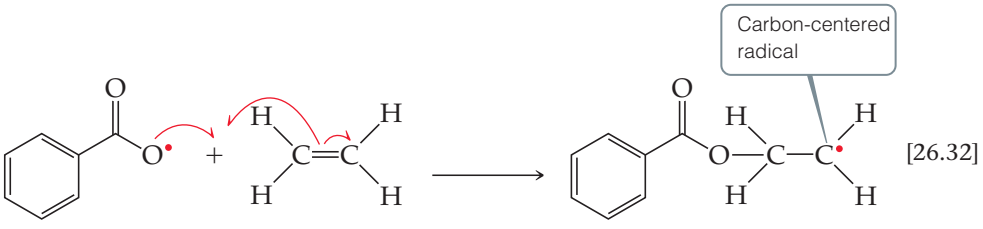
Polyethene (**Figure 26.25**) is a solid substance that is used to make thousands of plastic products, such as plastic bags, food containers and laboratory equipment. In making polyethene, a reactive center is formed that adds sequentially to the double bond in each ethene, extending the polymer chain and regenerating the reactive center. Such reactions are classified as chain-growth or **addition polymerizations** and polyethene is an **addition polymer**. In ethene polymerization, the reactive center is frequently a free radical, which can be derived from a radical initiator such as lauroyl peroxide. Peroxides dissociate to form two radicals upon heating or irradiation with light because of the very weak O—O bond:



[26.31]

Note the use of *fishhook arrows* in Equation 26.31. They differ from the arrows we have studied to date, which were "arrow"-headed. Fishhook arrows represent the movement of a single electron rather than an electron pair.

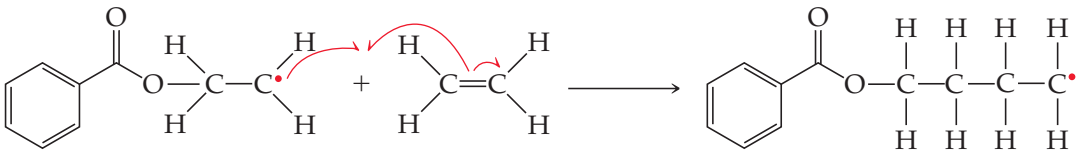
Once formed, the benzoyl radical can react with ethene to form a new carbon-centered radical. This step is called the **initiation** step. The relative stabilities of alkyl radicals follow a similar pattern to that of carbocations, namely 3° > 2° > 1° alkyl radicals.



[26.32]

The next stage of reaction is known as **propagation**. In this stage, the chain is extended by the consecutive addition of more ethene units through C—C bond formation:

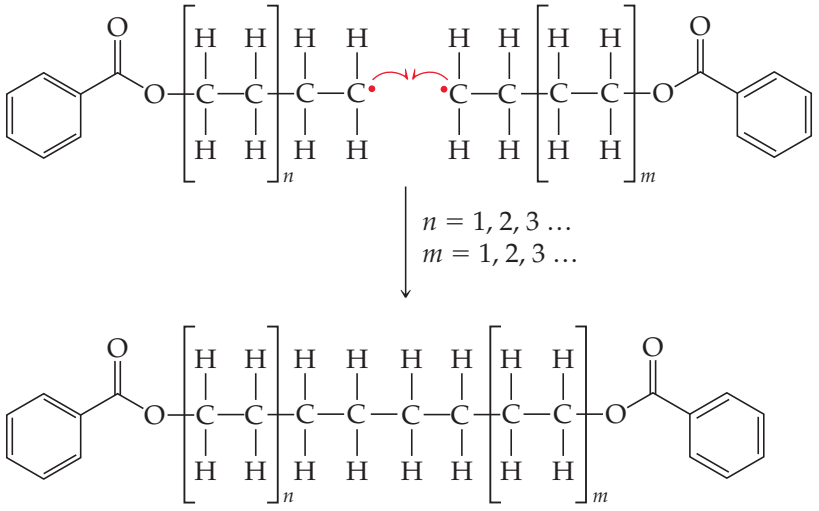
Propagation



[26.33]

The propagation continues until two radical polymer chains react to form a completed polymer by a final C—C bond formation that terminates the radical. This is known as the **termination** step. In Equation 26.34, *n* and *m* are normally large integers, which may or may not have the same value.

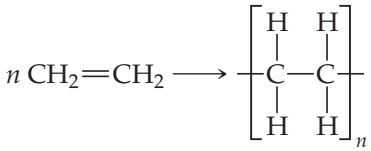
Termination



[26.34]

The reactive center in a chain-growth polymerization need not be a radical: depending on the monomer used, it may be an anion, cation or coordination complex. The most common process for polyethene production is *Ziegler–Natta* polymerization, named after the two scientists who developed the reaction in the 1950s. This process typically involves titanium and aluminum complexes, with a coordination complex as the reactive center, and is used in the formation of high-density polyethene (HDPE), a hard plastic. Radical polymerization of polyethene gives a polymer with occasional long branches, rather than simple straight chains, which makes it harder to pack the molecules together—this is low-density polyethene (LDPE), used in stretchy plastic wrap.

We can write the overall equation for the polymerization of ethene as follows:



[26.35]

Here, *n* represents the large number—ranging from hundreds to many thousands—of monomer molecules (ethene, in this case) that react to form one large polymer molecule. Within the polymer, a repeat unit (the unit shown in brackets in Equation 26.35) appears along the entire chain.

Polyethene is a very important commercial material; more than 10 billion kilograms are produced globally each year. Although its composition is simple, the polymer is not easy to make. Only after many years of research were the right conditions identified for manufacturing it. Today many different forms of polyethene, varying widely in physical properties, are known. Polymers of other chemical compositions provide still greater variety in physical and chemical properties. **Table 26.3** lists several other common polymers obtained by addition polymerization.

TABLE 26.3 Addition polymers of commercial importance

Monomers	Addition Polymer	Structure	Uses
$CH_2{=}CH_2$	Polyethene	$+CH_2{-}CH_2+_n$	Films, packaging, bottles
$CH_2{=}CH(CH_3)$	Polypropylene	$+CH_2{-}CH(CH_3)+_n$	Kitchenware, fibres, appliances
$CH_2{=}CH(C_6H_5)$	Polystyrene	$+CH_2{-}CH(C_6H_5)+_n$	Packaging, disposable food containers, insulation
$CH_2{=}CHCl$	Poly(vinyl chloride) (PVC)	$+CH_2{-}CHCl+_n$	Pipe fittings, clear film for meat packaging
$CH_2{=}C(CH_3)COOCH_3$	Poly(methyl methacrylate)	$+CH_2{-}C(CH_3)(COOCH_3)+_n$	Perspex, paints, moulded articles

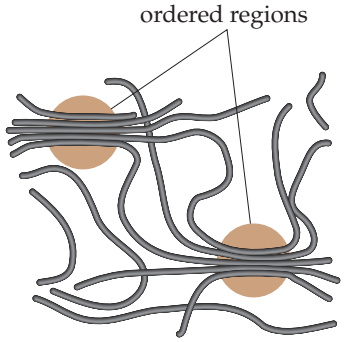
The names of polymers are simply derived from the monomers employed (Table 26.3). Poly(vinyl chloride) (PVC), for example, is made from vinyl chloride, poly(methyl methacrylate) is made from methyl methacrylate and polystyrene is made from styrene.

Structure and Physical Properties of Addition Polymers

The simple structural formulas given for polyethene and other polymers are deceptive. Since each carbon atom in polyethene is surrounded by four bonds, the atoms are arranged in a tetrahedral fashion, so that the chain is not straight as we sometimes depict it. Furthermore, the atoms are relatively free to rotate around the C—C single bonds. Thus rather than being straight and rigid, the chains of an addition polymer are very flexible, folding readily. The flexibility in the molecular chains can cause the polymer material itself to be very flexible

Both synthetic and naturally occurring polymers consist commonly of a collection of *macromolecules* (large molecules) of different molecular weights. Depending on the conditions of formation, the molecular weights may be distributed over a wide range or be closely clustered around an average value. In part, because of this distribution in molecular weights, polymers are largely amorphous (non-crystalline) materials. Rather than exhibiting a well-defined crystalline phase with a sharp melting point, they soften over a range of temperatures. They may, however, possess short-range order in some regions of the solid, with chains lined up in regular arrays, as shown in Figure 26.26. The extent of such ordering is indicated by the degree of **crystallinity** of the polymer. The crystallinity of a polymer can be enhanced with mechanical stretching, which aligns the polymer chains as the molten polymer is drawn out. Intermolecular forces between the polymer chains hold the chains together in the ordered crystalline regions, making the polymer denser, harder, less soluble and more resistant to heat. Table 26.4 shows how the properties of polyethene change as the degree of crystallinity increases.

The simple linear structure of polyethene is conducive to intermolecular interactions that lead to crystallinity. However, the degree of crystallinity in polyethene strongly



▲ **Figure 26.26 Interactions between polymer chains.** In the circled regions, the forces that operate between adjacent polymer-chain segments lead to ordering analogous to the ordering in crystals, though less regular.

TABLE 26.4 Properties of polyethene as a function of crystallinity

	Crystallinity				
	55%	62%	70%	77%	85%
Melting point (°C)	109	116	125	130	133
Density (g cm^{-3})	0.92	0.93	0.94	0.95	0.96
Stiffness* (MPa)	12	17	13	29	35
Yield stress* (MPa)	170	320	520	830	1140

* These test results show that the mechanical strength of the polymer increases with increased crystallinity. Discussion of the exact meaning and significance of these tests is beyond the scope of this text.

CHEMISTRY AND LIFE Recycling Plastics

If you look at the bottom of a plastic container, you are likely to see a recycle symbol (**Figure 26.27**) containing a number, as shown in **Table 26.5**. The number and letter abbreviation below it indicate the kind of polymer from which the container is made, as summarized in Table 26.5. These symbols make it possible to sort containers by composition. In general, the lower the number, the greater the ease with which the material can be recycled.



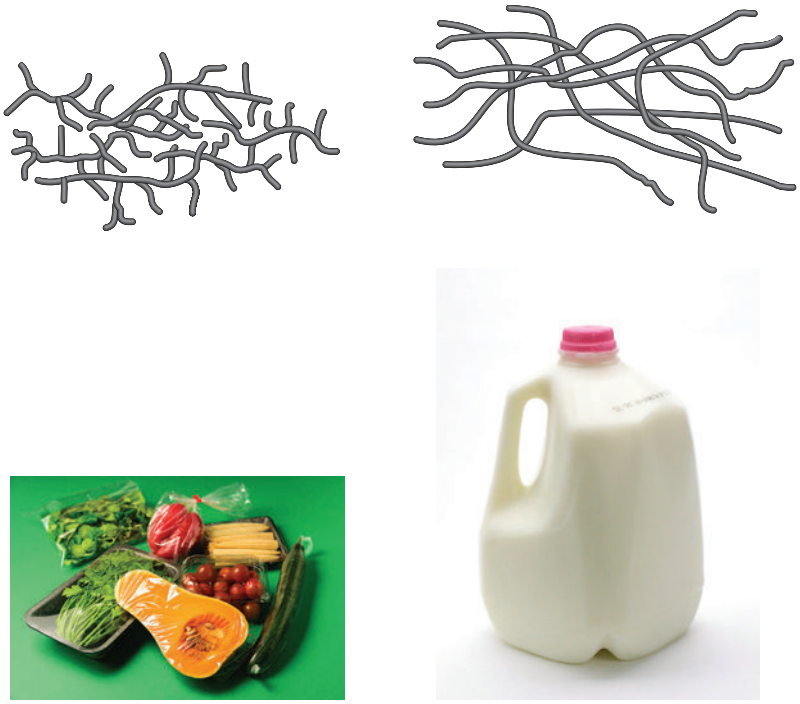
▲ **Figure 26.27** Recycling symbols.

TABLE 26.5 Categories used for recycling polymeric materials

Recycling number	Abbreviation	Polymer
1	PET or PETE	Polyethene terephthalate
2	HDPE	High-density polyethene
3	V	Polyvinyl chloride (PVC)
4	LDPE	Low-density polyethene
5	PP	Polypropylene
6	PS	Polystyrene
7	—	Others

depends on the average molecular mass. Polymerization results in a mixture of macromolecules with varying values of *n* and hence varying molecular masses. So-called low-density polyethene (LDPE), used in forming films and sheets, has an average molecular mass in the range of 10^4 u and has substantial chain branching. That is, side chains occur off the main chain of the polymer, much like spur lines that branch from a main railway line. These branches inhibit the formation of crystalline regions, reducing the density of the material. High-density polyethene (HDPE), used to form bottles, drums and pipes, has an average molecular mass in the range of 10^6 u. This form has less branching and thus a higher degree of crystallinity. Low-density and high-density polyethene are illustrated in **Figure 26.28**. Thus the properties of polyethene can be "tuned" by varying the average length, crystallinity and branching of the chains, making it a very versatile material.

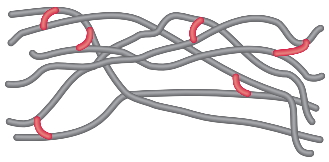
The physical properties of polymeric materials can be modified extensively by adding substances with lower molecular mass, called *plasticizers*, to reduce the extent of interactions between chains and thus to make the polymer more pliable. Poly(vinyl chloride) (PVC) (Table 26.3), for example, is a hard, rigid material of high molecular mass that is used to manufacture drainpipes. When blended with a suitable substance of lower molecular mass, however, it forms a flexible polymer that can be used to make rainboots and doll parts. In some applications, the plasticizer in a plastic object may be lost over time because of evaporation. As this happens, the plastic loses its flexibility and becomes subject to cracking.



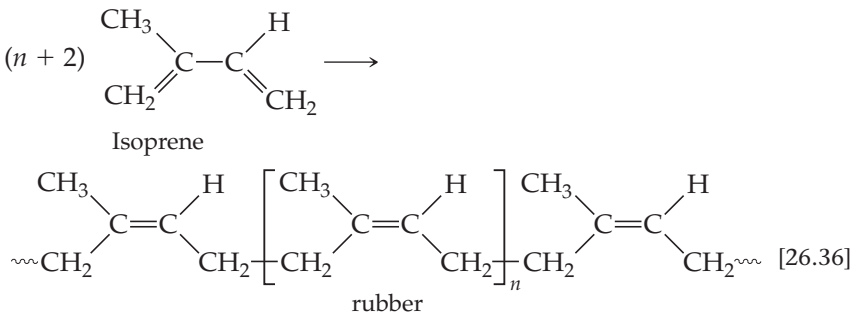
(a) (b)

▲ **Figure 26.28 Two types of polyethene.** (a) Schematic illustration of the structure of low-density polyethene (LDPE) and food-storage bags made of LDPE film. (b) Schematic illustration of the structure of high-density polyethene (HDPE) and containers formed from HDPE.

Polymers can be made stiffer by introducing chemical bonds between the polymer chains, as illustrated in **Figure 26.29**. Forming bonds between chains is called **cross-linking**. The greater the number of cross-links in a polymer, the more rigid the material. Whereas thermoplastic materials consist of independent polymer chains, thermosetting materials become cross-linked when heated. The cross-links allow them to hold their shapes. An important example of cross-linking is the **vulcanization** of natural rubber, a process discovered by Charles Goodyear in 1839 (see the Chemistry and Life, page 1246). Natural rubber is formed from a liquid resin derived from the inner bark of *Hevea brasiliensis,* or rubber tree. Chemically, it is a terpene, a polymer of isoprene, C_5H_8. In the process of vulcanization a controlled number of sulfur cross-links are introduced by reacting the carbon-carbon double bonds of adjacent chains with elemental sulfur in the presence of an accelerator and activator compound.

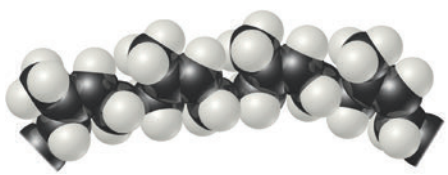


▲ **Figure 26.29 Cross-linking of polymer chains.** The cross-linking groups (red) constrain the relative motions of the polymer chains, making the material harder and less flexible than when the cross-links are not present.



Isoprene

rubber [26.36]



CHEMISTRY AND LIFE The Accidental Discovery of Teflon®

In 1938 a scientist at Du Pont named Roy J. Plunkett (1910–1994) made a rather curious observation: a tank of gaseous tetrafluoroethene ($CF_2{=}CF_2$) that was supposed to be full seemed to have no gas in it. Rather than discard the tank, Plunkett decided to cut it open. He found that the inside of the tank was coated with a waxy white substance that was remarkably unreactive towards even the most corrosive reagents. That compound was formed by the addition polymerization of tetrafluoroethene:

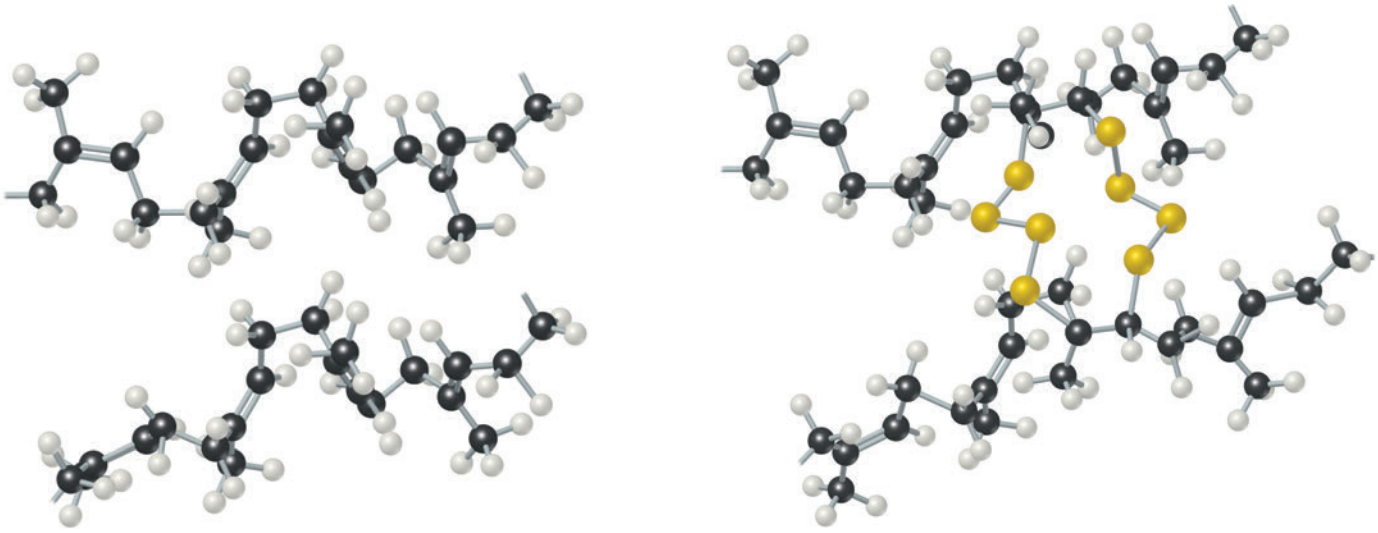
$$n CF_2{=}CF_2 \xrightarrow{\text{polymerization}} {+}CF_2{-}CF_2{+}_n$$

As it turned out, the properties of this material, called Teflon®, were ideal for an immediate and important application in the development of the first atomic bomb. Uranium hexafluoride (UF_6), which was used to separate fissionable ^{235}U by gaseous diffusion, is an extremely corrosive material. Teflon® was used as a gasket material in the gaseous diffusion plant. It is now used in a variety of applications, from non-stick cookware to space suits.

Plunkett's desire to know more about something that just didn't seem right is a wonderful example of how natural scientific curiosity can lead to remarkable discoveries.

CHEMISTRY AND LIFE Vulcanization

Natural rubber is not a useful polymer because it is too soft and too chemically reactive. Charles Goodyear (1800–1860) accidentally discovered that adding sulfur to rubber and then heating the mixture makes the rubber harder and reduces its susceptibility to oxidation or other chemical attack. The sulfur changes rubber into a thermosetting polymer by cross-linking the polymer chains through reactions at some of the double bonds, as shown schematically in **Figure 26.30**. Cross-linking of about 5% of the double bonds creates a flexible, resilient rubber. When the rubber is stretched, the cross-links help to prevent the chains from slipping, so that the rubber retains its elasticity. Nature also uses a sulfide crosslink to rigidify and preserve certain protein structures, such as insulin.

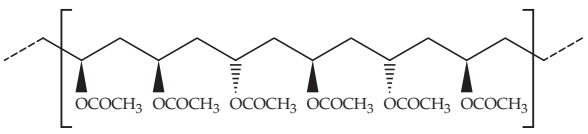


(a) (b)

▲ **Figure 26.30 Vulcanization of rubber.** (a) In natural rubber, carbon–carbon double bonds occur at regular intervals along the chain. (b) Chains of sulfur atoms have been added across two polymer chains, by the opening of a carbon–carbon double bond on each chain.

Self-Assessment Exercises

26.34 Identify the monomer unit in poly(vinyl acetate) from this fragment of the polymer chain.

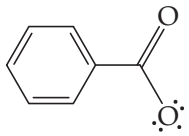


(a) $CH_2{=}CH{-}C(=O){-}O{-}CH_3$

(b) $CH_2{=}CH{-}O{-}C(=O){-}CH_3$

(c) $CH_3{-}CH_2{-}C(=O){-}O{-}CH_3$

26.35 A radical such as the benzoyloxy radical is often used in which stage of polymerization?



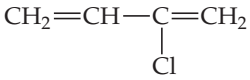
(**a**) Initiation (**b**) Propagation (**c**) Termination

26.36 A polymer with a high degree of cross-linking is likely to show which characteristics? **(a)** a soft flexible material **(b)** elasticity **(c)** a low melting point **(d)** a rigid structure

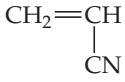
Exercises

26.37 Draw the structure of the monomer(s) employed to form each of the following polymers: **(a)** poly(vinyl chloride), **(b)** polystyrene, **(c)** polypropylene.

26.38 Write the chemical equation that represents the formation of **(a)** polychloroprene (neoprene) from chloroprene



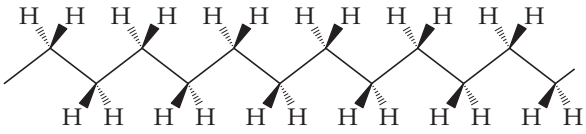
(Neoprene is used in road pavement seals, expansion joints, conveyor belts and wire and cable jackets.); **(b)** polyacrylonitrile



(Polyacrylonitrile is used in home furnishings, craft yarns, clothing and many other items.)

26.39 What molecular features make a polymer flexible? Explain how cross-linking affects the chemical and physical properties of the polymer.

26.40 Although polyethene can twist and turn in random ways, the most stable form is a linear one with the carbon backbone oriented as shown in this figure:

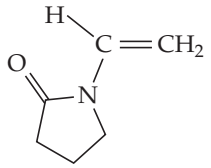


(a) What is the hybridization of orbitals at each carbon atom? What angles do you expect between the bonds?

(b) Now imagine that the polymer is polypropylene rather than polyethene. Draw the structures for polypropylene in which (i) the CH_3 groups lie on the same side of the plane of the paper (this form is called isotactic polypropylene), (ii) the CH_3 groups lie on alternating sides of the plane (syndiotactic polypropylene), and (iii) the CH_3 groups are randomly distributed on either side (atactic polypropylene). Which of these forms would you expect to have the highest crystallinity and melting point, and which the lowest? Explain in terms of intermolecular interactions and molecular shapes.

(c) Polypropylene fibres have been employed in athletic wear. The product is said to be superior to cotton clothing in wicking moisture away from the body through the fabric to the outside. Explain the difference between polypropylene and cotton (which has many –OH groups along the molecular chain), in terms of intermolecular interactions with water.

26.41 Poly(vinyl pyrrolidone) is commonly used in cosmetics and in wine clarification. Draw a representative segment of the polymer prepared from *N*-vinyl pyrrolidone:



26.42 How would you expect the properties of vulcanized rubber to vary as the percentage of sulfur increases?

Answers to Self-Assessment Exercises (a) **26.34** (b) **26.35** (d) **26.36**

Sample Integrative Exercise

Putting concepts together

In an example of an electrophilic addition reaction 1-butene reacts with hydrogen bromide to give 2-bromobutane. **(a)** Draw out the mechanism of this reaction including the carbocation intermediate. Show all the atoms attached to the double bond and use curved arrows to indicate electron-pair movements. **(b)** What are the hybridization and molecular geometry of the two atoms C1 and C2 in the starting material, intermediate and product? **(c)** Indicate the stereogenic carbon center in the product with *. **(d)** Explain why the product is formed as a racemic mixture.

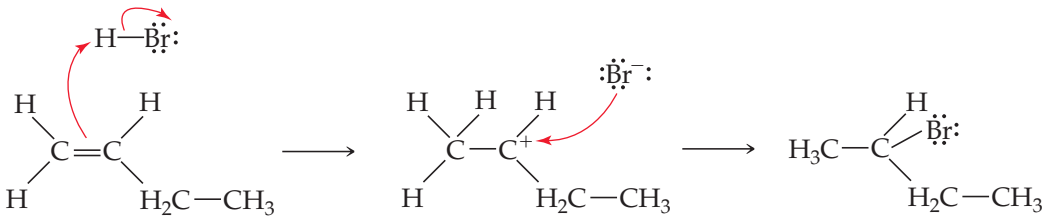
SOLUTION

Analyse In this problem we examine the mechanism of an electrophilic addition reaction and how the shape of the intermediate relates to the chirality of the product.

Plan First identify the structure of the starting material and product from the names given. Then draw the mechanism of the reaction and identify how the molecular geometry of C1 and C2 changes as the reaction progresses. Finally identify the features of the geometry change that result in a racemic mixture being produced.

Solve

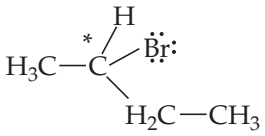
(a)



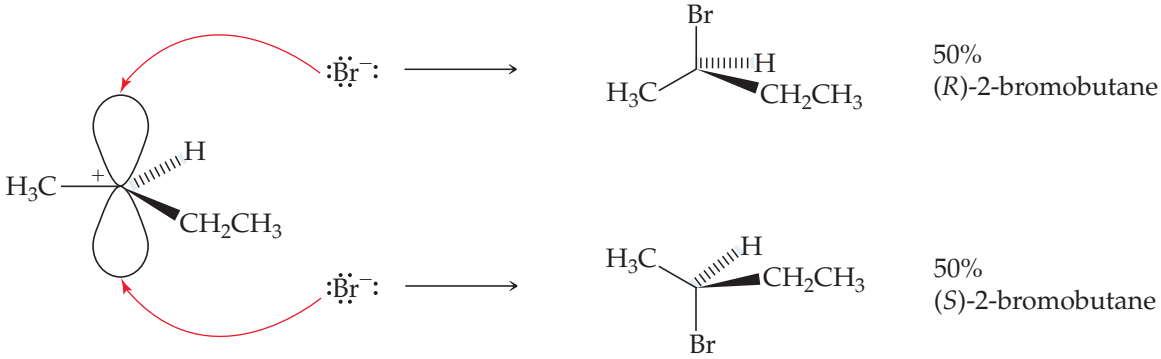
(b)

	Hybridization—C1	Geometry—C1	Hybridization—C2	Geometry—C2
Starting material	sp^2	Trigonal planar	sp^2	Trigonal planar
Intermediate	sp^3	Tetrahedral	sp^2	Trigonal planar
Product	sp^3	Tetrahedral	sp^3	Tetrahedral

(c)



(d) The carbocation is sp^2 hybridized and trigonal planar in shape. The positive charge may be thought of as an empty *p* orbital pointing above and below the plane containing the carbocation. The final stage of this reaction involves attack by the bromide ion on the carbocation and there is equal probability of this occurring to the top or the bottom face of the intermediate.



Chapter Summary and Key Terms

SECTION 26.1 **Unsaturated hydrocarbons** are those hydrocarbons that contain multiple bonds. Two main classes—**alkenes** and **alkynes**—are dealt with in this chapter. Alkenes contain one or more double bonds. Each double bond consists of one **σ-bond** and one **π-bond**. The π-bond is formed by the overlap of the unhybridized *p* orbitals on adjacent sp^2 hybridized carbon atoms. Alkynes contain one or more triple bonds. Each triple bond consists of one σ-bond and two π-bonds. The order of bond lengths is triple bond < double bond < single bond.

SECTION 26.2 The names of alkenes and alkynes are based on the longest continuous chain of carbon atoms that contains the multiple bond, and the location of the multiple bond is specified by a numerical prefix. The ***E,Z* system** is used to name the geometric isomers of alkenes and is based on the same priority system used in *R,S* nomenclature.

SECTION 26.3 Organic chemists use **curved arrow notation** to describe the redistribution of valence electrons. Arrow notation can also be used to describe resonance structures or to rationalize a reaction mechanism.

SECTION 26.4 Alkenes and alkynes readily undergo **addition reactions** to the carbon–carbon multiple bonds. There are three main classes of addition reactions: **halogenation**, **hydrohalogenation** and **hydration**. Additions of acids, such as HBr, proceed via a rate-determining step in which a proton is transferred to one of the alkene or alkyne carbon atoms, forming a **carbocation**. This addition follows **Markovnikov's rule**, which states that the hydrogen of HX (X = halogen, OH) adds to the side of the double bond with the most hydrogens. The carbocation is a form of **electrophile** that readily reacts with a **nucleophile**, in this case Br^-, to form the product. The addition of bromine to cyclohexene is an example of a **stereoselective reaction**.

SECTION 26.5 **Catalytic hydrogenation** can be used to convert alkenes or alkynes to alkanes using molecular hydrogen and a metal catalyst such as Ni, Pd or Pt. Oils are **triglycerides** that contain double bonds. They may be hydrogenated to **fats** in a process called **hardening**.

SECTION 26.6 **Polymers** are molecules of high molecular mass formed by joining together large numbers of smaller molecules, called **monomers**. In a chain growth or **addition polymerization** reaction, the molecules form new linkages by opening existing bonds. Polyethene is an example of an **addition polymer**. Three stages exist in this type of polymerization: **initiation**, **propagation** and **termination**.

Plastics are materials that can be formed into various shapes, usually by the application of heat and pressure. **Thermoplastics** can be reshaped, perhaps by heating, in contrast to **thermosetting plastics**, which are formed through an irreversible chemical process and cannot be reshaped.

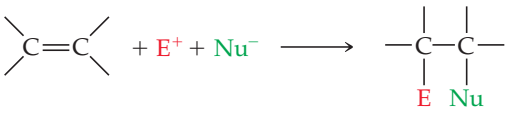
Polymers are largely amorphous, but some materials possess a degree of **crystallinity**. High-density polyethene, for example, with not much side-chain branching and a high molecular mass, has a higher degree of crystallinity than low-density polyethene, which has a lower molecular mass and a higher relative degree of branching. Polymer properties are also strongly affected by **cross-linking**, in which short chains of atoms connect the long polymer chains. Rubber is cross-linked by short chains of sulfur atoms in the process called **vulcanization**.

Key Skills

- Understand how to name alkenes and alkynes. In the case of alkenes, be able to determine *E, Z* isomerism. (Sections 26.1 and 26.2)
- Describe and understand the rules for using curved arrow notation and their application to describe the mechanism of a chemical reaction. (Section 26.3)
- Be able to draw the products of addition reactions using a range of reactants (e.g. Br_2, HCl) and understand their product distribution. (Sections 26.4 and 26.5)
- Understand the importance of alkenes to the industrial manufacturing of plastics. (Section 26.6)
- Be able to draw polymers formed by the addition polymerization of alkene monomers and understand some of their properties. (Section 26.6)

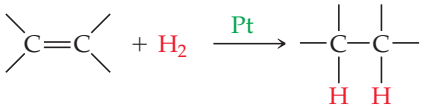
Key Equations

- Addition reactions



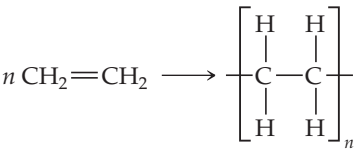
[26.25]

- Hydrogenation



[26.29]

- Addition polymerization

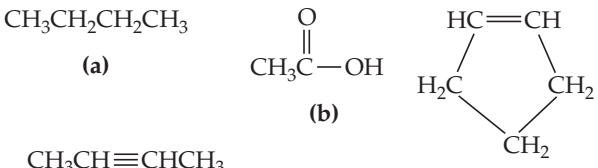


[26.35]

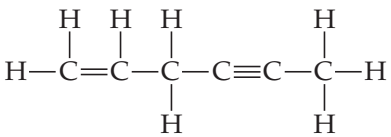
Exercises

Visualizing concepts

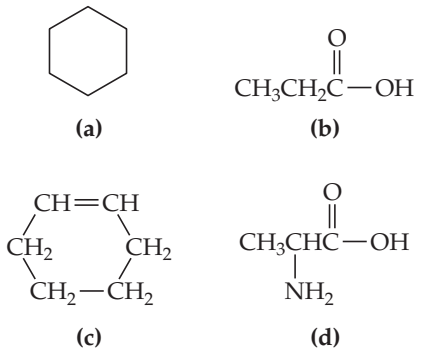
26.43 Which of the following molecules is unsaturated? [Section 26.1]



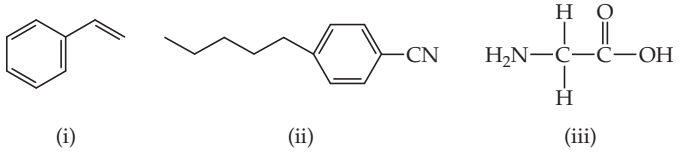
26.44 Consider the hydrocarbon drawn here. **(a)** What is the hybridization at each carbon atom in the molecule? **(b)** How many σ-bonds are there in the molecule? **(c)** How many π-bonds? [Section 26.1]



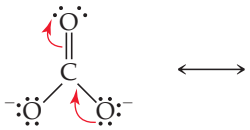
26.45 Which of the following molecules will most readily undergo an addition reaction? [Section 26.4]



26.46 Consider the molecules shown here. Which of these would be most likely to form an addition polymer? [Section 26.4]



26.47 Draw the product of the following valence electron movements. [Section 26.3]



Structure, Bonding and Naming (Sections 26.1, 26.2 and 26.3)

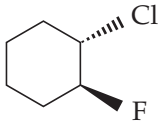
26.48 Give the general molecular formula for any cyclic alkene. What other general class of hydrocarbon has the same general formula?

26.49 What are the characteristic hybrid orbitals employed by **(a)** carbon in an alkane, **(b)** carbon in a double bond in an alkene, **(c)** carbon in a triple bond in an alkyne?

26.50 Name the following compounds systematically:

(a) *trans*-$CH_3CH{=}CHCH_2CH_2CH_3$

(b)



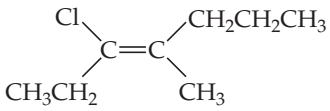
(c)



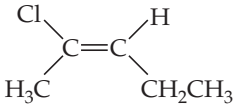
26.51 **(a)** Using butene as an example, distinguish between structural (constitutional) and geometric isomers. **(b)** The compound 4-chloropent-2-ene exists as four stereoisomers. Explain how these four isomers arise by drawing the structures of all four stereoisomers and showing the relationship between them.

26.52 Systematically name the following alkenes, assigning their geometry as *E* or *Z* where appropriate.

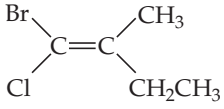
(a)



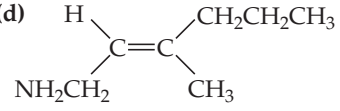
(b)



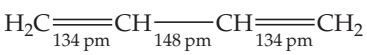
(c)



(d)



26.53 1,3-butadiene, C_4H_6, is a planar molecule that has the following carbon–carbon bond lengths:



(a) Predict the bond angles around each of the carbon atoms, and sketch the molecule. **(b)** Compare the bond lengths with the average bond lengths listed in Table 26.1. Can you explain any differences?

26.54 **(a)** What is the difference between a localized π-bond and a delocalized one? **(b)** How can you determine whether a molecule or ion will exhibit delocalized π-bonding? **(c)** Is the π-bond in NO_2^- localized or delocalized?

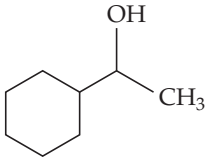
Addition Reactions of Unsaturated Hydrocarbons (Sections 26.4 and 26.5)

26.55 Using condensed structural formulas, write a chemical equation for each of the following reactions: **(a)** hydrogenation of cyclohexene; **(b)** addition of H_2O to *trans*-pent-2-ene, using H_2SO_4 as a catalyst (draw both likely products); **(c)** reaction of propene with bromine in water solvent.

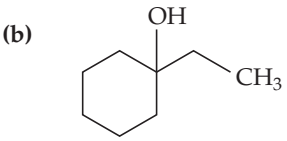
26.56 The rate law for the addition of Br_2 to an alkene is first order in Br_2 and first order in alkene. Does this fact prove that the mechanism of addition of Br_2 to an alkene proceeds in the same manner as for addition of HBr? Explain.

26.57 What alkenes would you hydrate to obtain the following alcohols?

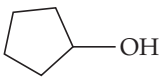
(a)



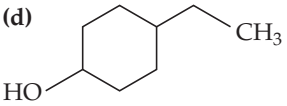
(b)



(c)



(d)

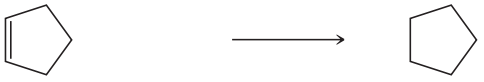


26.58 **(a)** When but-1-yne is hydrohalogenated with HCl a geminal dichloride is formed in preference. Draw its structure. **(b)** Give a reason for your choice.

26.59 **(a)** In the bromination of propene, a cyclic bromonium ion is formed in the first step. Draw it. **(b)** The addition of a nucleophile ($Nu^{\ominus}$) to this bromonium ion yields a single major product. Why is this the case and what product is formed? **(c)** Is this product chiral if Nu═OH? **(d)** What if Nu═Br?

26.60 Suggest suitable reagents for the following reactions:

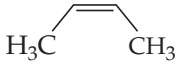
(a)



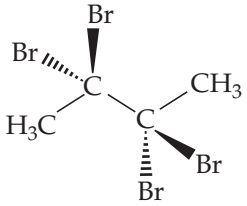
(b)



(c) $H_3C{-}C{\equiv}C{-}CH_3$ ⟶



(d) $H_3C{-}C{\equiv}C{-}CH_3$ ⟶



(e)



26.61 **(a)** Write the structural formula for the product of the hydrogenation of 3-methyl pent-1-ene. What is the systematic name of the product? **(b)** When D_2 reacts with ethene (C_2H_4) in the presence of a finely divided catalyst, ethane with two deuteriums, $CH_2D—CH_2D$, is formed. (Deuterium, D, is an isotope of hydrogen of mass 2.) Very little ethane forms in which two deuteriums are bound to one carbon (for example, $CH_3—CHD_2$). Use the sequence of steps involved in the reaction to explain why this is so.

Addition Polymerization (Section 26.6)

26.62 The structure of decane is shown in Table 24.3. Decane is not considered to be a polymer, whereas polyethene is. What is the distinction?

26.63 What is a monomer? Give three examples of monomers, taken from the examples given in this chapter.

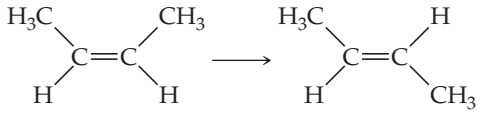
26.64 Teflon® is a polymer formed by the polymerization of $F_2C=CF_2$. Draw the structure of a section of this polymer. What type of polymerization reaction is required to form it?

26.65 What molecular structural features cause high-density polyethene (HDPE) to be denser than low-density polyethene (LDPE)?

26.66 Are high molecular masses and a high degree of crystallinity always desirable properties of a polymer? Explain.

Integrative Exercises

26.67 But-2-ene, C_4H_8, can undergo *cis–trans* isomerization:



cis-but-2-ene *trans*-but-2-ene

As discussed in the Chemistry and Life box on the chemistry of vision, such transformations can be induced by light and are the key to human vision. **(a)** What is the hybridization at the two central carbon atoms of but-2-ene? **(b)** The isomerization occurs by rotation about the central C—C bond. With reference to Figure 26.5, explain why the π-bond between the two central carbon atoms is destroyed halfway through the rotation from *cis*- to *trans*-but-2-ene. **(c)** Based on average bond enthalpies (Table 8.3), how much energy per molecule must be supplied to break the C—C π-bond? **(d)** What is the longest wavelength of light that will provide photons of sufficient energy to break the C—C π-bond and cause the isomerization? **(e)** Is the wavelength in your answer to part (d) in the visible portion of the electromagnetic spectrum? Comment on the importance of this result for human vision.

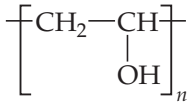
26.68 Ethene ($CH_2=CH_2$) reacts with hydrogen gas in the presence of a catalyst to give ethane (CH_3CH_3). **(a)** Draw the structures of the reactants and the product for this reaction and indicate the number of σ- and π-bonds that have been broken and have been formed in this reaction. Use average bond enthalpies in Table 8.3 to estimate **(b)** the enthalpy change for this reaction and **(c)** the average energy of a carbon–carbon σ-bond and π-bond. **(d)** Draw the electron distribution in a π-bond and explain why it is weaker than a σ-bond between the same atoms.

26.69 Consider the electrophilic addition of hydrogen chloride to propene. **(a)** Draw the reaction showing the primary and secondary carbocation intermediates and the products that arise from each intermediate. **(b)** Sketch an energy profile, similar to Figure 26.20, for the two possible pathways in this reaction showing the relative energies of the intermediates and indicating which carbocation is the more stable. **(c)** If the temperature of the reaction mixture was increased would the relative proportions of the two possible products change?

26.70 A sample of a polyunsaturated oil is hydrolysed to give either linoleic acid ($C_{18}H_{32}O_2$) or arachidonic acid ($C_{20}H_{32}O_2$) and you have to find out which one. You take a 1.0 g sample of the unknown acid and perform a hydrogenation reaction under catalytic conditions. This will hydrogenate the carbon–carbon double bonds present but not the carbon–oxygen double bond of the carboxylic acid group. **(a)** Calculate the double bond equivalents in linoleic acid and arachidonic acid. **(b)** Determine the number of carbon–carbon double bonds present in each of the acids. Your sample of unknown acid absorbs 299 cm^3 of hydrogen gas under STP conditions. **(c)** Calculate the number of moles of hydrogen gas used and identify which acid you have.

26.71 Acetylene (H—C≡C—H) can explosively form benzene (). **(a)** Write a chemical equation for this reaction and **(b)** calculate the heat of reaction given $\Delta_f H°$ (benzene) = 83 kJ mol^{-1} and $\Delta_f H°$ (acetylene) = 227 kJ mol^{-1}.

26.72 Polyvinyl alcohol is a polymer with the following structure.



(a) What intermolecular forces exist between polymer chains in polyvinyl alcohol? **(b)** Do you expect polyvinyl alcohol to be water soluble?

Design an Experiment

Many nuts, seeds and some fish are a good source of polyunsaturated fats in which the fat molecule contains two or more double bonds. These fats are liquid at room temperature (oils). Hydrogenation of some of the double bonds present increases the melting point of the fat and produces a semi-solid product that is easier to spread than a fully saturated fat such as butter. Imagine that you are an industrial chemist charged with monitoring the hydrogenation of an oil and stopping the reaction when some, but not all, of the double bonds have been saturated. In your experiment you take a small sample from the reaction mixture at regular time intervals after the hydrogenation commenced. (a) How would you ensure you took the same sized sample each time? (b) what type of solvent would you use to dissolve the sample? (c) What reagent can you think of that changes colour when it reacts with a double bond? (e) Can you think of a way of quantifying the amount of reagent you add and so relating it to the number of double bonds remaining in the sample.

27

ALCOHOLS, HALOALKANES, AND ETHERS

WHAT'S AHEAD

27.1 Alcohols: Structure, Properties, and Nomenclature

27.2 Haloalkanes

27.3 Ethers: Structure, Properties, and Nomenclature

27.4 Reactions of Alcohols

27.5 Nucleophilic Substitution Reactions of Haloalkanes

27.6 Haloalkanes to Alkenes: β-Elimination

27.7 Substitution versus Elimination

27.1 | Alcohols: Structure, Properties, and Nomenclature



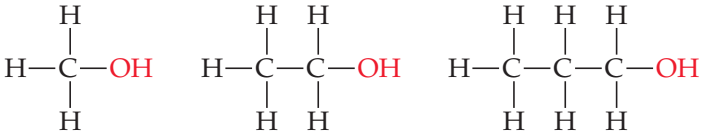
Whether white, red, or something in between, wine is a complex mixture of chemicals. One of the main constituents of wine is, of course, ethanol. Produced by the yeast fermentation of the sugars within the fruits from which it is made, much of the popularity of wine comes from its intoxicating effect. The science of wine and wine making is called *oenology*, and today it helps sustain a multibillion-dollar industry worldwide.

Currently, ethanol is valued more than ever. Its uses are as diverse as a substitute for, or additive in, petrol; as a solvent in the manufacture of varnishes and perfumes; as a fluid in thermometers; in the manufacture of acetic acid; in the preparation of essences and flavorings and as a disinfectant. Ethanol is miscible with water in all proportions. Absolute ethanol contains >99% *v/v* ethanol and is purified from industrial ethanol by first applying fractional distillation, which produces a liquid that is 95% *v/v* ethanol, then by azeotropic distillation.

In this section, we take an introductory look at the structure of alcohols, some of their physical properties, and how to name them. By the end of the section, you should be able to:

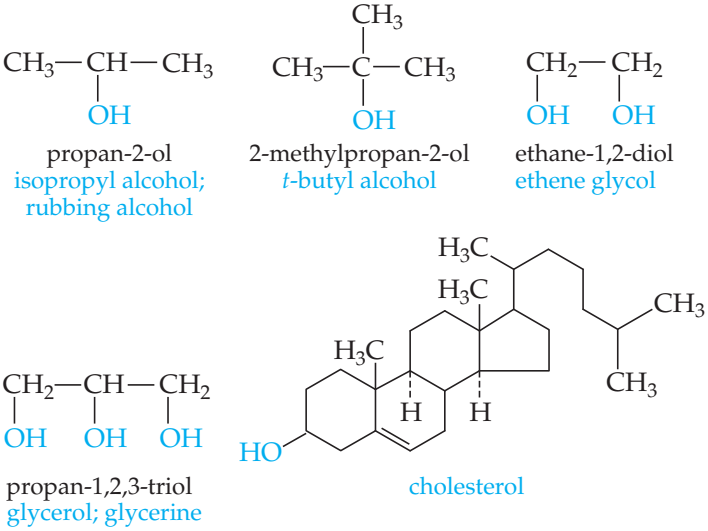
- Have an idea of the solubility of alcohols in water or hydrocarbons
- Be able to name simple alcohols
- Recognize the classification of an alcohol as primary, secondary, or tertiary

Alcohols are hydrocarbon derivatives in which one or more hydrogens have been replaced by a *hydroxyl* group, OH. **Figure 27.1** shows the structural formulas and names of the three simplest straight-chain alcohols together with five other important alcohols. The simple alcohols are named by changing the last letter in the name of the corresponding alkane to *-ol*; for example, ethan*e* becomes ethan*ol*. Where necessary, the location of the OH group is designated by an appropriate numeral prefix that indicates the position of the OH group (Figure 27.1).

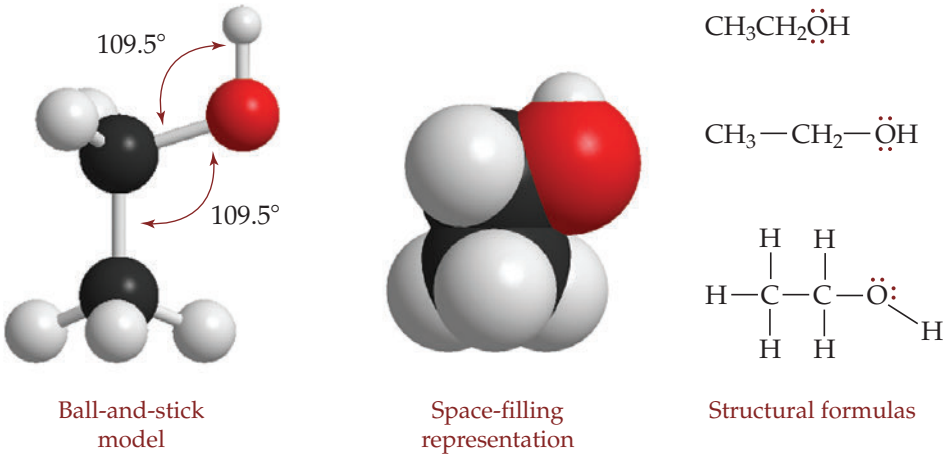


The oxygen atom of the hydroxyl group is sp^3 hybridized, having a tetrahedral arrangement of its bonds and lone pairs (**Figure 27.2**). Two of the sp^3 hybrid orbitals of the oxygen atom form σ-bonds with carbon and hydrogen. Each of the other two orbitals contain a pair of unshared electrons, or **lone pair**. The bond angles about the oxygen atom of an alcohol are very similar to those around sp^3 carbon centers. Any variation from the ideal 109.5° bond angle is due to the comparatively large size of the lone pairs.

▼ Figure 27.1 Structural formulas of six important alcohols. Common names are given in blue.

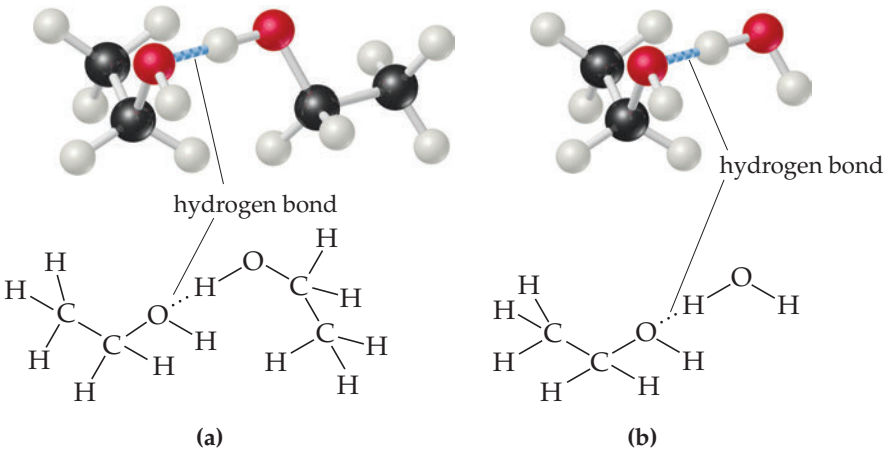


The properties of alcohols are very different from those of the alkanes from which they are derived. For example, methane, ethane and propane are all colorless gases under normal conditions, whereas methanol, ethanol, and propanol are colorless liquids. The reason for the difference in physical properties lies in the fact that the O—H bond is polar, with the difference in electronegativity values between the oxygen and hydrogen atoms being 1.4. As a result, the —OH functional group can participate in intermolecular hydrogen bonding, which increases the attractive forces between the molecules of the alcohol. The strength of a hydrogen bond is approximately 20 kJ/mol, which is considerably weaker than an O—H covalent bond (about 460 kJ/mol); however, it is strong enough to have a significant effect on the alcohol's physical properties. As a result, the boiling points of alcohols are much higher than those of their parent alkanes. The ability of alcohols to form hydrogen bonds is also why they are much more soluble in polar solvents such as water, than in the corresponding



◀ **Figure 27.2 The structure of ethanol.** A number of representations for ethanol are shown.

Go Figure What is the maximum number of hydrogen bonds a single ethanol molecule could possess?



▲ **Figure 27.3 Hydrogen-bonding interactions.** (a) Between two ethanol molecules and (b) between an ethanol molecule and a water molecule.

hydrocarbons (**Figure 27.3**). For example, the solute–solute, solvent–solvent and solute–solvent forces are not greatly different within a mixture of CH_3CH_2OH and H_2O. As a result, there is no major change in the environments of the molecules as they are mixed.

Liquids that mix completely in another liquid are said to be *miscible*, whereas solids that dissolve in a liquid are said to be *soluble* in that liquid. Pairs of liquids, such as ethanol and water, that mix in all proportions are miscible; those that do not mix are *immiscible*. For example, hexane (C_6H_{14}) is immiscible in water. The attraction between the polar water molecules and the nonpolar hexane molecules is not sufficiently strong to allow the formation of a solution.

The number of carbon atoms in an alcohol affects its solubility in water. As the length of the carbon chain increases, the polar OH group becomes an ever-smaller part of the molecule, and the compound behaves more like a hydrocarbon. The solubility of the alcohol in water decreases correspondingly. By contrast, the solubility of the alcohol in a nonpolarsolvent like hexane increases as the nonpolar hydrocarbon chain increases in length. The series of alcohols in **Table 27.1** demonstrates that polar liquids tend to be miscible in other polar liquids and nonpolar liquids in nonpolar ones. This phenomenon is simply stated as "*like dissolves like*".

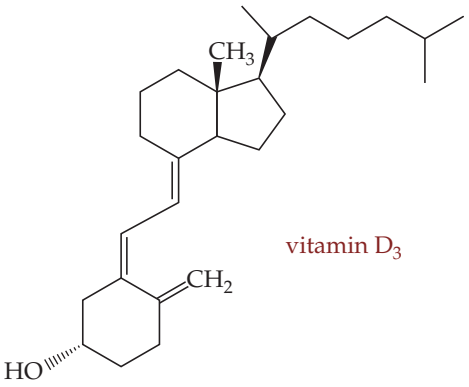
TABLE 27.1 Solubilities of some alcohols in water and in hexane*

Alcohol	Solubility in H_2O	Solubility in C_6H_{14}
CH_3OH (methanol)	∞	0.12
CH_3CH_2OH (ethanol)	∞	∞
$CH_3CH_2CH_2OH$ (propan-1-ol)	∞	∞
$CH_3CH_2CH_2CH_2OH$ (butan-1-ol)	0.11	∞
$CH_3CH_2CH_2CH_2CH_2OH$ (pentan-1-ol)	0.030	∞
$CH_3CH_2CH_2CH_2CH_2CH_2OH$ (hexan-1-ol)	0.0058	∞
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2OH$ (heptan-1-ol)	0.0008	∞

* Expressed in mol alcohol/100 g solvent at 20 °C. The infinity symbol indicates that the alcohol is completely miscible with the solvent.

CHEMISTRY AND LIFE Vitamin D

Vitamin D, an alcohol, is a steroid hormone derived from cholesterol. The biologically active form of the hormone is vitamin D_3 whose primary function is to regulate calcium and phosphorus homeostasis and maintain bone density in the body. Food provides us with a precursor molecule which is converted to vitamin D_3 under the skin by the action of sunlight. Hence it is sometimes called the sunshine vitamin (Figure 27.4). Milk is fortified with vitamin D as a dietary safeguard in countries where outdoor exposure is often limited. Recent evidence suggests there is a need, for children especially, to spend more time outdoors. The "stay out of the sun" campaigns, in conjunction with the great popularity of computer games, have been linked to an increased risk of vitamin D deficiency and the resulting underdevelopment of bone in children, called *rickets*. Rickets is characterized by improper mineralization during the development of bones and results in soft bones, curved spines, and knock-knees. Nevertheless, a sensible approach to sun exposure is also required.



vitamin D_3



Food sources:
Cheese
Margarine
Butter
Fortified milk
Healthy cereals
Fatty fish



▲ Figure 27.4 Vitamin D and its food sources.

Sample Exercise 27.1

Predicting Solubility Patterns in Organic Compounds

Predict whether the following compounds are more likely to dissolve in water or hexane (C_6H_{14}) solvent: cyclohexanol ($C_6H_{11}OH$), acetic acid (CH_3COOH), chloroform ($CHCl_3$), heptane (C_7H_{16}), and glycerol (Figure 27.1).

SOLUTION

Analyze We are asked to differentiate between various compounds by their solubility or miscibility in either hexane or water.

Plan *Like dissolves in like.*

Solve Although cyclohexanol contains an OH group, the addition of the C_6 ring system would make its properties comparable with 1-hexanol. Given the choice of solvents, cyclohexanol dissolves better in hexane because the molecule is more "alkane-like".

Acetic acid is a very polar compound, containing little alkane character. This compound dissolves better in water as a solvent.

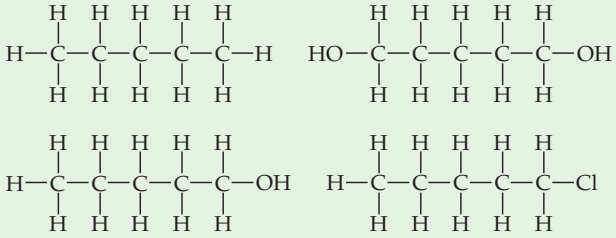
Chloroform is a moderately polar liquid because of its tetrahedral geometry. Chlorine atoms are poor hydrogen-bonding groups, however, and so this compound would be more miscible with hexane.

Heptane is an alkane, so it is nonpolar. This compound is miscible with hexane.

Glycerol is a small organic compound containing three OH groups. It is very soluble in water.

Practice Exercise

Arrange the following substances in order of increasing solubility in water:



Common Alcohols

Figure 27.5 shows several commercial products that consist entirely or in part of an alcohol. Let's consider how some of the more important alcohols are formed and used. The simplest alcohol, methanol, has many important industrial uses and is produced on a large scale. Carbon monoxide and hydrogen are heated together under pressure in the presence of a metal oxide catalyst:

$$CO(g) + 2\,H_2(g) \xrightarrow[400\ ^\circ C]{200-300\ bar} CH_3OH(g) \qquad [27.1]$$

Because methanol has a very high octane rating as a car fuel, it is used as a petroleum additive and as a fuel in its own right.

Ethanol is a product of the fermentation of carbohydrates such as sugar and starch. In the absence of air, yeast cells convert carbohydrates into a mixture of ethanol and CO_2, as shown in Equation 27.2. In the process, yeast derives energy necessary for growth.

$$C_6H_{12}O_6(aq) \xrightarrow{\text{yeast}} 2\,C_2H_5OH(aq) + 2\,CO_2(g) \qquad [27.2]$$

This reaction is conducted under carefully controlled conditions to produce beer, wine, and other beverages in which ethanol is the active ingredient.

Many polyhydroxyl alcohols (those containing more than one OH group) are known. The simplest of these is ethane-1,2-diol (ethylene glycol, $HOCH_2CH_2OH$). This substance is the major ingredient in car radiator coolant. Another common polyhydroxyl alcohol is propane-1,2,3-triol (glycerol, $HOCH_2CH(OH)CH_2OH$). This is a viscous liquid that dissolves readily in water and is widely used as a skin softener in cosmetic preparations. It is also used in foods and confectionary to keep them moist.

Cholesterol is classed as a *steroid* but here we will look at it as a biochemically important alcohol. The OH group forms only a small component of this rather large molecule, so cholesterol is virtually insoluble in water (0.2 g per 100 cm^3 of H_2O) and has a waxy feel. Cholesterol is an essential component of our bodies; when present in excessive amounts, however, it may precipitate from solution. If it precipitates in the gall bladder, it may form crystalline lumps called *gallstones*. Cholesterol may also precipitate against the walls of veins and arteries and thus contribute to high blood pressure and other cardiovascular problems. The amount of cholesterol in our blood is determined not only by how much cholesterol we eat but also by total energy intake. There is evidence that excessive caloric intake leads the body to synthesize excessive amounts of cholesterol.



▲ **Figure 27.5 Everyday alcohols.** Many of the products we use every day—from rubbing alcohol and throat lozenges to hair spray and radiator coolant— are composed either entirely or mainly of alcohols.

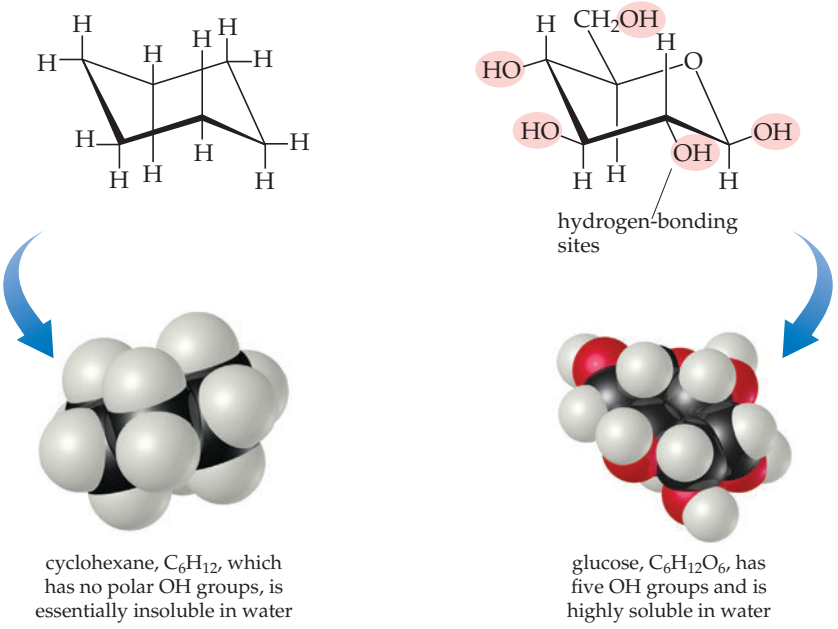
Naming Alcohols

Alcohol nomenclature is based on selecting the longest chain containing the OH group. This chain is numbered to give the OH group the lowest possible number. Alcohols that are *normal*—that is, they contain the OH functional group on the first carbon of a straight-chain alkyl group—are listed in Table 27.1. Sometimes, you may see these compounds named as *n*-butanol, *n*-hexanol, and so on. In these cases, the *n* stands for normal.

CHEMISTRY AND LIFE The Solubility Nexus

The solubility of organic molecules is an important issue, especially in the area of medicine. Not only must a drug be effective, but it must have sufficient solubility in water for aqueous administration in the blood. These two criteria are seldom satisfied collectively and are complicated further by the need for a drug candidate to pass through hydrophobic cell membranes and/or the blood–brain barrier.

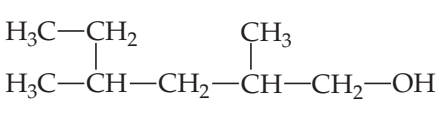
One way to enhance the solubility of a substance in water is to increase the number of polar groups it contains. For example, increasing the number of OH groups along a carbon chain of a solute increases the extent of hydrogen bonding between that solute and water, thereby increasing solubility. Glucose ($C_6H_{12}O_6$) has five OH groups, which makes the molecule very soluble in water (83 g dissolves in 100 cm^3 of water at 17.5 °C). Glucose is shown in **Figure 27.6** and is compared structurally with cyclohexane, its hydrocarbon analogue. The solubility of cyclohexane in water is extremely low due to its inability to hydrogen-bond to water. The second approach to increasing polarity is to add charge. As we will see in Chapters 29 and 31, negative charge can be added through *carboxylate groups* and positive charge through *ammonium salts*. Both are proven and common ways to make drugs soluble in water.



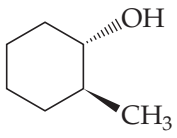
▲ **Figure 27.6 Hydrogen bonding and aqueous solubility.** The presence of OH groups capable of hydrogen bonding with water enhances the aqueous solubility of organic molecules.

It is more appropriate, however, to use IUPAC nomenclature, which names these compounds using a positional prefix—for example, butan-1-ol, hexan-1-ol. Note that methanol and ethanol do not need a prefix.

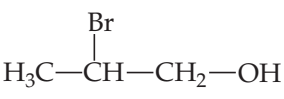
The names of some simple alcohols are given here. Each molecule contains extra functionality or branching, yet all the names are derived from the name of the alcohol. Their names illustrate, to some extent, the hierarchy of nomenclature.



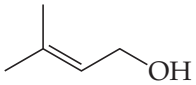
2,4-dimethylhexan-1-ol



(*1S,2S*)-2-methylcyclohexanol is better than *trans*-2-methylcyclohexanol



2-bromopropan-1-ol



3-methyl-2-buten-1-ol

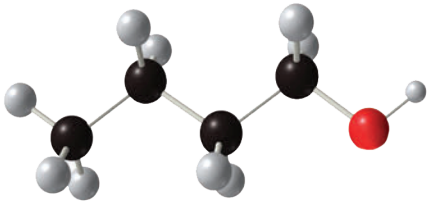
Systematic naming using the IUPAC conventions does not distinguish between, for example, 1-hexanol and hexan-1-ol as the most satisfactory way to name a functionalized

alcohol. Both methods unambiguously describe the position of the OH group and could be used. The latter naming style is better suited to molecules that contain an alkene as well as the OH group. In such cases, "*an*" would be replaced by "*en*" to represent the incorporation of the alkene. Compounds of this type are called *unsaturated alcohols*.

The 2-methylcyclohexanol example illustrated earlier demonstrates two nomenclature principles. The alcohol functional group, when bonded to a cyclic structure, is assigned position 1, based on the arguments we used to discuss the nomenclature of cycloalkenes (Section 26.2). Although *trans* satisfactorily describes the orientation of the OH and CH_3 groups, it does not unambiguously describe the molecule (there is another enantiomer with a *trans* arrangement—can you draw it?). In this case, the absolute stereochemistry at each position should be described.

The OH group is not always located at position 1. **Figure 27.7** illustrates the different $C_4H_{10}O$ alcohols that are possible, as well as their systematic and common names. Alcohols, like alkanes, are classified as primary, secondary or tertiary. We discuss this in more detail in the following section.

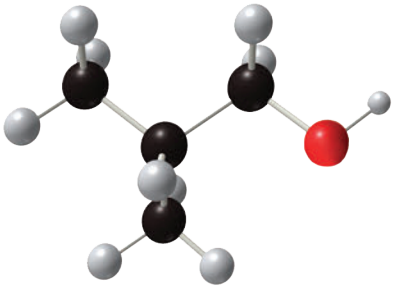
Go Figure Which of the alcohols shown in this figure are chiral?



$H_3C—CH_2—CH_2—CH_2—OH$

butan-1-ol
(*n*-butanol)

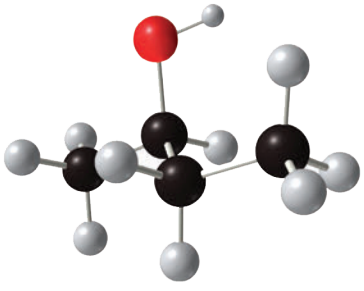
Classification: 1°



$H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_2—OH$

2-methylpropan-1-ol
(isobutyl alcohol)

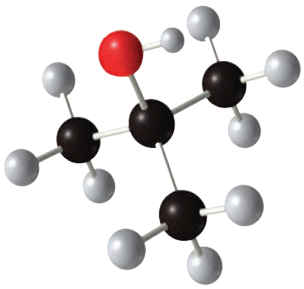
Classification: 1°



$H_3C—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_2—CH_3$

butan-2-ol
(*sec*-butanol)

Classification: 2°



$H_3C—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}—OH$

2-methylpropan-2-ol
(*tert*-butanol)

Classification: 3°

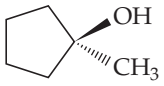
▲ **Figure 27.7 Isomeric alcohols.** The structure, names and classifications of the four isomeric alcohols related to butanol.

Sample Exercise 27.2

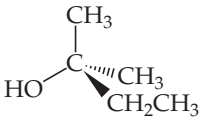
Naming Alcohols

Systematically name the following alcohols, taking stereochemistry into account where appropriate.

(a)



(b)



SOLUTION

Analyze We are given two structures and asked to name them.

Plan Name each compound using the longest chain possessing the OH group. Assign stereochemistry based first on symmetry then on the Cahn–Ingold–Prelog rules in Chapter 25.

Solve

(a) This example has no stereochemical consequence because a plane of symmetry exists within the molecule. The compound is derived from cyclopentane. Its systematic name is 1-methylcyclopentanol.

(b) This example also has no stereochemical consequences because a plane of symmetry exists within the molecule. The compound is derived from butanol, as the longest chain bearing the OH group is four carbons long. Its systematic name is 2-methylbutan-2-ol.

Practice Exercise

Draw the structures corresponding to the following names: **(a)** (*R*)-4-methylpentan-2-ol **(b)** (*Z*)-3-penten-1-ol

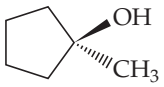
Alcohols containing two or three OH groups are called **diols** and **triols**, respectively. Common examples are shown in Figure 27.1.

Sample Exercise 27.3

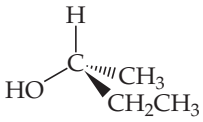
Classifying Alcohols

Classify each of the following alcohols as primary, secondary or tertiary.

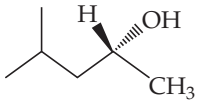
(a)



(b)



(c)



SOLUTION

Analyze We are given the structures of three alcohols and asked to classify them.

Plan Locate the carbon bearing the OH group and determine the number of carbons attached to this carbon.

Solve

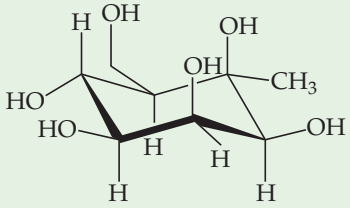
(a) The carbon bearing the OH group has three carbons attached to it: two from the ring and one from the methyl group. Therefore, this is a tertiary alcohol.

(b) The carbon bearing the OH group has two carbons attached to it, one from the methyl group and the other from the ethyl group. This compound can be classed as a secondary alcohol.

(c) The carbon bearing the OH group has two other carbons attached. Hence it too is secondary.

Practice Exercise

Classify all alcohol functional groups in the following molecule as 1°, 2° or 3°.



Classifying Alcohols

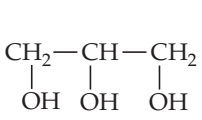
The classification and notation used to distinguish between types of alcohols are:

Primary (1°) alcohol:	The carbon atom bearing the OH group is bonded to only one other carbon atom.
Secondary (2°) alcohol:	The carbon atom bearing the OH group is bonded to two carbon atoms.
Tertiary (3°) alcohol:	The carbon atom bearing the OH group is bonded to three carbon atoms.

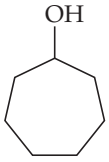
Figure 27.7 illustrates this classification within a series of butanol isomers. There is a big difference in reactivity between 1°, 2°, and 3° alcohols. An important part of your understanding of the chemistry of alcohols is the ability to recognize an alcohol's class and to use this knowledge to predict the product of a reaction. Each classification of alcohol—namely primary, secondary and tertiary—reacts differently to a range of reactants. As we see in the following chapters, this classification allows us to predict the type of product and/or the necessary reagents with which to undertake certain functional-group manipulations.

Self-Assessment Exercises

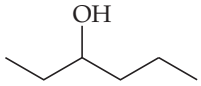
27.1 Which of the following molecules would you expect to be miscible in water?



(a)

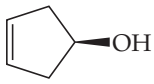


(b)



(c)

27.2 Give the full systematic name of the following alcohol:



(a) Cyclopent-1-en-3-ol
(b) Cyclopent-1-en-4-ol
(c) Cyclopent-3-enol
(d) (*R*)- Cyclopent-3-enol

27.3 Which of the structures in self-assessment exercise 27.1 contains a primary alcohol?

Exercises

27.4 Suppose the hydrogens on the OH group of glycerol (Figure 27.1) were replaced with methyl groups, CH_3. Would you expect the solubility in water of the resulting molecules to be higher than, lower than or about the same as the solubility of glycerol?

27.5 Write the structural formulae for as many alcohols as you can think of that have the empirical formula C_3H_6O.

27.6 Explain why propan-1-ol is miscible with water yet hexan-1-ol is not.

27.7 Write the condensed structural formula for each of the following compounds: **(a)** butan-2-ol, **(b)** 1,2-ethanediol, **(c)** diethyl ether.

27.8 Classify the isomeric alcohols with molecular formula $C_4H_{10}O$ as primary, secondary or tertiary.

Answers to Self-Assessment Exercises

27.1 (a) **27.2** (c) **27.3** (a)

27.2 | Haloalkanes



A class of haloalkanes you may be familiar with are the **chlorofluorocarbons**, or **CFCs**. Compounds of this category were typically used as refrigerants, as propellants in aerosols, and as industrial solvents. They were usually marketed under the name *Freon*. CFCs are odorless, non-toxic, non-flammable, and non-corrosive compounds and so found great industrial utility. During the mid-1970s, however, research into CFCs showed they had a harmful effect on the environment. Being relatively chemically inert means that CFCs can persist in the atmosphere for a long time. Thus, they are not broken down in the troposphere but find their way into the stratosphere, where they are decomposed by the action of ultraviolet (UV) radiation. In this process, a reaction sequence is initiated that depletes the ozone layer—a thin layer of the Earth's atmosphere that acts as a shield against excess UV radiation. The attributed result is not only a greater prevalence in skin cancer, but also a higher risk of global warming as chlorofluorocarbons are also much more effective as greenhouse gases than carbon dioxide. In the late 1980s, the United Nations Environment Program put in place a number of agreements to phase out the use of CFCs by 1996. For their work in this area and for their forewarning of the implications, Sherwood Rowland, Mario Molina, and Paul Crutzen were awarded the 1995 Nobel Prize in Chemistry.

In this section, we will introduce haloalkanes with some examples and names. By the end of the section, you should be able to:

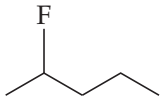
- Write the name of simple haloalkanes

Aliphatic or cyclic hydrocarbons containing a halogen directly bonded to an sp^3 hybridized carbon are called **haloalkanes**. They are generally written as:

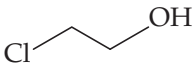
$$R—X \qquad \text{where } X = F, Cl, Br, I$$

Haloalkanes are also commonly referred to as alkyl halides.

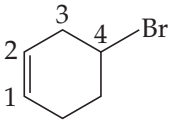
Haloalkane nomenclature is derived from the longest chain bearing the halogen. The position number is taken to be the lowest possible, bearing all other substituents in mind. Halogen substituents are indicated by the prefixes fluoro-, chloro-, bromo- and iodo-. The derived name places these substituents in alphabetical order:



2-fluoropentane



2-chloroethanol



4-bromocyclohexene

We should also note here that the halogen functional group is second only to alkyl groups as the lowest functional group in the nomenclature hierarchy. All other substituents take precedence in deriving a compound's name, and the numbering used is determined by the location of the other group. For example, 2-chloroethanol is named as the alcohol and not the haloalkane. 4-Bromocyclohexene is named by taking into account the position of the double bond before the halogen.

Many haloalkanes have common names. Some examples are:



methylene chloride
(dichloromethane)



chloroform
(trichloromethane)



vinyl chloride
(chloroethene)

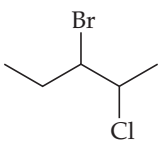
Compounds such as dichloromethane and chloroform are useful solvents in organic synthesis. Compounds of the form CHX_3 are often called **haloforms**, of which chloroform is an example. Perfluorinated compounds (in which all hydrogens are replaced by fluorine) are also very useful. One example we are all familiar with is Teflon™ (polytetrafluoroethene, $(CF_2CF_2)_n$) with its application in non-stick cookware among others.

Having properties very different from both water and hydrocarbons, perfluorinated compounds have been used as solvents since they are easily partitioned from both water and most organic solvents. The polar structure also has application in medicine. For example, perfluorocarbons are able to dissolve oxygen at levels greater than blood. As a result, they are undergoing trials in dramatic experiments as blood substitutes in cases where trauma results in severe blood loss with no time to match blood types.

Haloalkanes have a wealth of chemistry associated with them. We have already seen how they can be formed from alkenes and alkanes. Later in this chapter we will explore two reaction types in detail—nucleophilic substitution (Section 27.5) and β-elimination (Section 27.6)—in which haloalkanes are reactants. Later, in Chapter 28, we will explore the use of haloalkanes for the preparation of Grignard reagents.

Self-Assessment Exercises

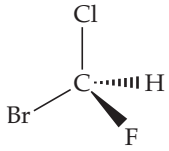
27.9 Write the systematic name of:



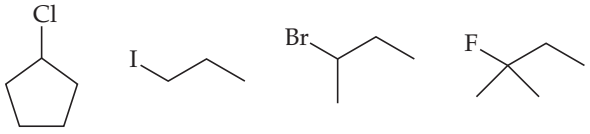
(a) 3-bromo-4-chloropentane
(b) 4-chloro-3-bromopentane
(c) 2-chloro-3-bromopentane
(d) 3-bromo-2-chloropentane

Exercises

27.10 Give the full name, including stereochemical descriptor of:



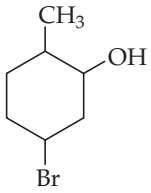
27.11 Name and classify the following haloalkanes as primary, secondary or tertiary.



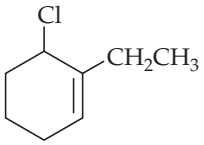
(a) **(b)** **(c)** **(d)**

27.12 Give the IUPAC name for the following structures:

(a)



(b)



Answers to Self-Assessment Exercise

27.9 (d)

27.3 Ethers: Structure, Properties, and Nomenclature



Diethyl ether, originally called just "ether", was used in medicine for the treatment of some illnesses more than 200 years ago. However, it was not until 1846, when Boston dentist William T G Morton administered its vapors to a patient and extracted a tooth, apparently painlessly, that its potential for use in surgery was quickly realized, and the era of modern anesthetics began. The word anesthesia comes from the Greek for "without sensation". Nowadays, there are many safer anesthetics and ether is no longer used.

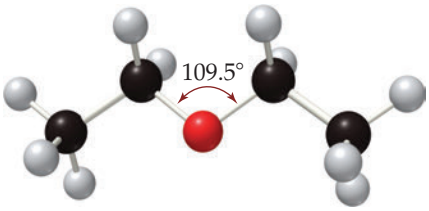
In this section, we introduce you to the ether functional group and its nomenclature. By the end of this section, you should be able to:

- Name alkyl ethers

We can think of alcohols as compounds in which one hydrogen atom and one hydrocarbon group are bonded to an oxygen atom. Compounds in which two hydrocarbon groups are bonded to one oxygen atom are called **ethers**. As for alcohols, the oxygen atom is sp^3 hybridized with the two C—O bonds subtending an angle of approximately 109.5°. Two of the sp^3 hybrid orbitals of the oxygen atom form σ-bonds with two carbon atoms adjacent to them. Each of the other two hybridized orbitals contains a pair of unshared electrons. **Figure 27.8** illustrates the Lewis structure and other molecular model representations of diethyl ether, the most commonly used of all the ethers.

Ethers are polar molecules, but because of the steric hindrance due to the alkyl groups attached, only weak dipole–dipole interactions exist between molecules. As a result of having alkyl groups bonded to the central oxygen atom, there is no opportunity for hydrogen bonding or other strong electrostatic interactions, so the physical properties of ethers are closer to those of alkanes than to those of alcohols. This moderate polarity is, however, advantageous as it allows ethers to dissolve a wider range of organic compounds than hexane would as a comparative solvent.

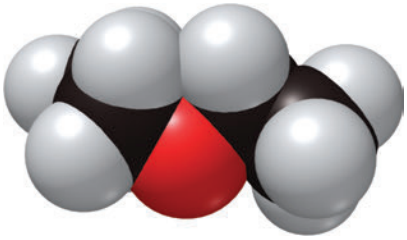
Ethers resemble hydrocarbons in their inertness to chemical reactions. As a consequence, ethers make excellent solvents in which to undertake chemical reactions. Two commonly used solvents are diethyl ether and tetrahydrofuran (THF). Diethyl ether, as we have already seen, is an acyclic ether (Figure 27.8), whereas THF (**Figure 27.9**) is a cyclic ether derived, as the name suggests, from furan, that has a structure given here.



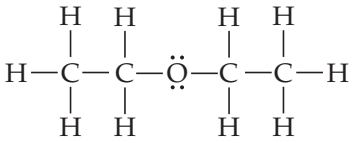
Ball-and-stick model

$CH_3CH_2\ddot{O}CH_2CH_3$

$H_3C-CH_2-\ddot{O}-CH_2-CH_3$

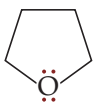


Space-filling representation

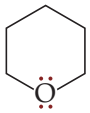


Structural formulae

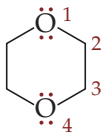
◀ **Figure 27.8 The structure of diethyl ether.** A number of representations for diethyl ether are shown.



tetrahydrofuran (THF)

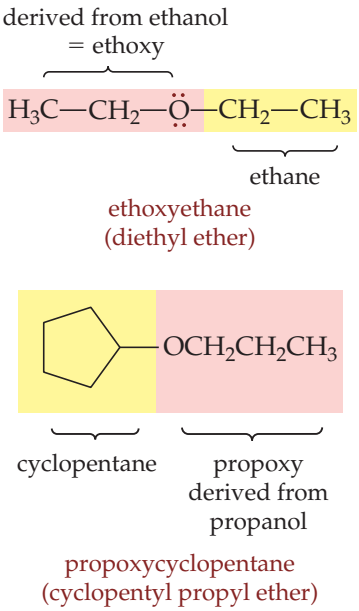


tetrahydropyran (THP)



1,4-dioxane

◀ **Figure 27.9 Cyclic ethers.** Simple cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane are excellent solvents. Tetrahydropyrans (THP) are useful reagents in organic synthesis.



▲ **Figure 27.10 Ether nomenclature.** Systematic names are derived from the longest alkyl chain present that is attached to the ether oxygen and the residual alkoxy group. Examples of common names are shown in brackets.

TABLE 27.2 Physical properties of the constitutional isomers butan-1-ol and diethyl ether

Compound	Structure	Melting point	Boiling point	Density g/cm^3
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	−90 °C	118 °C	0.81
diethyl ether	$CH_3CH_2OCH_2CH_3$	−116 °C	35 °C	0.70

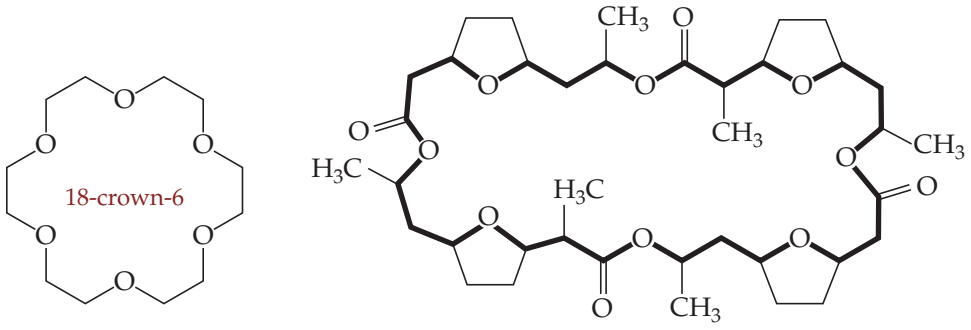
The structural difference between alcohols and ethers has a marked effect on the properties and chemical reactivity. Butanol and diethyl ether are constitutional isomers and representative molecules within their respective classes. Table 27.2 illustrates the differences in three of their principal properties.

Naming Ethers

Acyclic ethers are named systematically by selecting the longest chain and adding to it the name of the attached **alkoxy** (–OR) **group**. Common names are used more freely with this class of compounds, as the IUPAC method leads to lengthy names quite quickly. These common ether names are derived from the two alkyl groups that are attached to the ether oxygen. Figure 27.10 illustrates how to derive the systematic and common names of acyclic ethers.

Cyclic ethers, such as tetrahydrofuran, are **heterocyclic compounds** whose names are derived in some instances from the parent heterocycle. Heterocyclic compounds are derivatives of cyclic hydrocarbons in which one of the ring carbons is replaced with another atom, usually O or N, but many other hetero atoms have also been incorporated (for example, S, Se, P). Figure 27.9 showed the structure of the most common cyclic ethers.

Cyclic polyethers such as 18-crown-6 (Figure 27.11) are useful in organic synthesis as phase transfer catalysts and metal ion complexation agents. Discovered and developed by Charles Pedersen in the 1960s, **crown ethers** are a synthetic analogue of naturally occurring antibiotics such as nonactin.



▲ **Figure 27.11 Macrocyclic ethers.** Naturally occurring cyclic ethers like nonactin can transport ions across biological membranes. In doing so, they act as potent antibiotics. Crown ethers such as 18-crown-6 are synthetic analogues of nonactin that are also useful for the separation of heavy metal salts from waterways, as catalysts of reactions involving carbanions and as phase transfer catalysts.

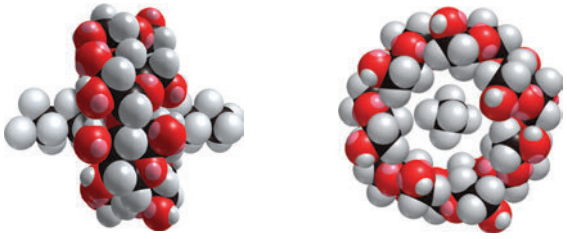
A CLOSER LOOK Crown Ethers

Supramolecular chemistry, also known as "chemistry beyond the molecule", is a multidisciplinary science that came to prominence in the late 1980s. This was in part due to the award of the 1987 Nobel Prize in Chemistry to Charles Pedersen (1904–1989), Donald Cram (1919–2001) and Jean-Marie Lehn (b 1939), three of the founders and early developers of supramolecular chemistry. This field began with Pedersen's pioneering work on crown ethers and their metal ion complexes (**Figure 27.12**). The potential of supramolecular chemistry to bridge the gap between chemistry and biology, thereby finding applications in medicine, materials and environmental science, biotechnology and nanotechnology, has seen interest in this field grow rapidly over the past 10–15 years.

Supramolecular chemistry is seen by some as either a molecular art form or as *molecular engineering*. During its development throughout the 1980s and 1990s, supramolecular chemistry was used as a tool to create the most unlikely molecular topologies. For example, rotaxanes (*rota*, wheel; *axa*, axle) are a chemical curiosity containing two molecular components (**Figure 27.13**). The molecular shapes of the two components differ, one resembling a wheel and the other an axle. The axle component is threaded through the center of the wheel component, and is usually terminated by bulky groups to stop the wheel falling off. The use of the bulky stoppers means that the wheel and axle components are mechanically interlocked—they cannot be removed from each other without breaking a covalent bond. Rotaxanes are being investigated as molecular electronic switching and optical binary devices due to their ability to undergo conformational isomerism.



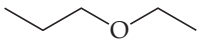
▲ **Figure 27.12** **18-crown-6 complex of K^+.**



▲ **Figure 27.13** **Rotaxanes are mechanically interlocked molecules.** In this illustration, the axle component, a simple alkane, is threaded through the wheel or ring component, a cyclodextrin.

Self-Assessment Exercise

27.13 What is the systematic name of the following structure?

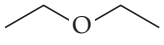


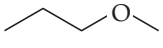
(a) Ethyl propyl ether
(b) Propyl ethyl ether
(c) Propoxy ethane
(d) Ethoxy propane

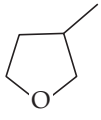
Exercises

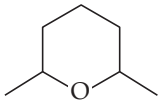
27.14 Explain why the boiling point of ethanol (78 °C) is much higher than that of its isomer, dimethyl ether (−25 °C), and why the boiling point of CH_2F_2 (−52 °C) is far above that of CF_4 (−128 °C).

27.15 Give names for the following ethers (ignore stereochemistry):

(a)


(b)


(c)


(d)


27.16 Write the structures for all the isomeric ethers with molecular formula $C_5H_{12}O$ and give a name for each.

27.17 List two criteria that would make a liquid a good solvent in which to undertake chemical reactions.

27.18 What properties of 18-crown-6 make it possible to complex metal ions such as Na^+ or K^+?

Answers to Self-Assessment Exercise

27.13 (d)

27.4 Reactions of Alcohols

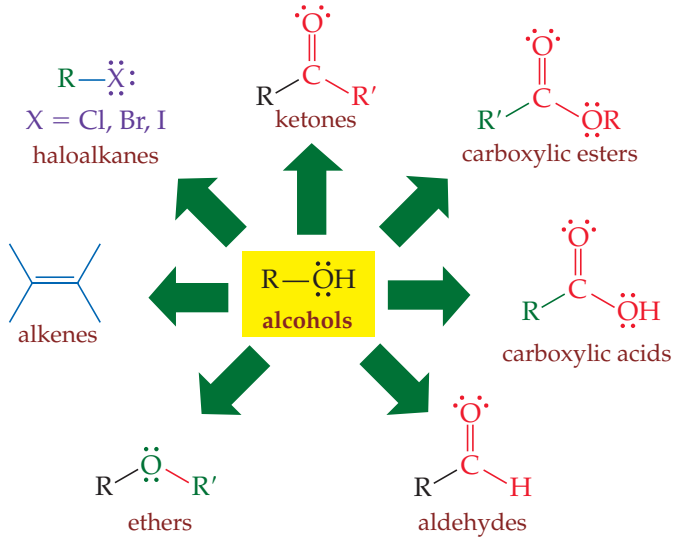


In this section, we start to examine some of the reactions that alcohols can undergo and begin to see how functional groups may be interconverted. Some reactions show a visible change. For instance, when sodium metal reacts with ethanol to form a solution of sodium ethoxide, the metal dissolves and bubbles of hydrogen are evolved. Other reactions take place entirely within the solution phase, but a knowledge of the chemistry involved allows us to predict the outcome of the reaction.

When you finish this section, you should be able to

- Know the conditions to convert an alcohol to an alkoxide
- Recognize two different reagents commonly used to transform alcohols to haloalkanes
- Understand the mechanism of a dehydration reaction

Alcohols are central to organic chemistry. **Figure 27.14** illustrates the relationships between alcohols and the other seven major classes of functional groups introduced in this text.



▲ **Figure 27.14** **Functional group interconversion.**

Four of these functional groups, highlighted in red, can be arrived at through oxidation of a suitable alcohol.

In this section we explore further the interconversion of alcohols to alkenes and haloalkanes. Ethers are formed by taking advantage of the high reactivity of the conjugate base of an alcohol, called an **alkoxide**. Alkoxides are as strong a base as hydroxide and also make excellent nucleophiles.

Alkoxides

Alcohols react with alkali metals to form alkoxides in the same way that water reacts with alkali metals to form hydroxide. The reaction is irreversible, since the other product of the reaction, hydrogen gas, is evolved.

$$2\,H_2O + 2\,Na \longrightarrow 2\,HO^-Na^+ + H_2(g) \qquad [27.3]$$

sodium hydroxide

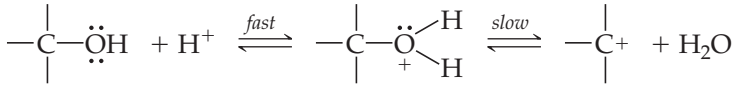
$$2\,ROH + 2\,K \longrightarrow 2\,RO^-K^+ + H_2(g) \qquad [27.4]$$

potassium alkoxide

The name of the alkoxide is derived from the alcohol undergoing reaction. For example, the reaction of ethanol with sodium gives sodium ethoxide, the reaction of *tert*-butanol (2-methyl-2-propanol) with potassium metal yields potassium *tert*-butoxide. Reactions involving alkoxides invariably use the corresponding alcohol as the solvent for ease of preparation.

Basicity of Alcohols

The ability of an alcohol's OH group to accept a proton is an important property that is important in the context of dehydration (loss of $-H_2O$). An alcohol can act as a weak base, forming an oxonium ion under acidic conditions. The oxonium ion ($pK_a \sim -2$) is a slightly better acid than the hydronium ion (H_3O^+, $pK_a \sim -1.7$), but of greater importance to organic synthesis is the ability of the oxonium ion to lose water, forming a carbocation intermediate:



an oxonium ion a carbocation [27.5]

As we discussed in the context of Markovnikov's rule, the stability of the carbocation intermediate is an enormous driving force for the reactivity of a species, and even dictates the reaction pathway.

Alcohols to Haloalkanes

Alcohols can be converted into haloalkanes by treatment of a halogenating agent, usually under acidic conditions. In this reaction, the OH group of the alcohol is substituted by a halogen. The reaction is classed as a **nucleophilic substitution (S_N) reaction** and we will see much more of this in the next section.

A nucleophilic substitution reaction is any reaction in which one nucleophile is substituted for another.

In using mineral acids (e.g. HCl, HBr, HI) as the halogenating agent, the first stage of substitution is protonation of the alcohol to form an oxonium ion. This is followed by elimination of water to form the intermediate carbocation as indicated in Equation 27.5. This last step is rate-determining, being faster for formation of a 3° carbocation than 2° and 1°.

The stability of the intermediate carbocation is the major factor allowing the substitution reaction to dominate for 3° alcohols. For example, the conversion of 2-methyl-2-propanol to 2-bromo-2-methylpropane using HBr is a reaction that occurs readily at room temperature using HBr.

$$(CH_3)_3COH + HBr \longrightarrow (CH_3)_3CBr + H_2O \qquad [27.6]$$

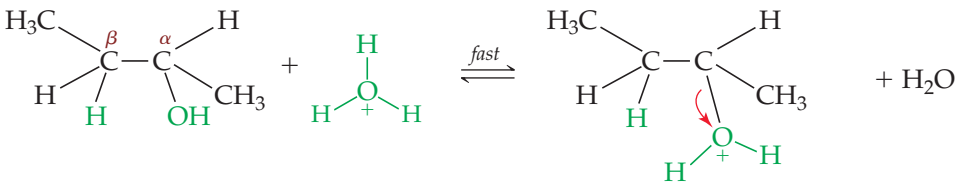
Secondary alcohols also undergo substitution using mineral acids, but they require heating and longer reaction times. Primary alcohols require extreme conditions to substitute using this method, and are impractical. The most efficient way of achieving this conversion is to react the primary alcohol with thionyl chloride:

$$\underset{\text{butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + \underset{\text{thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{sulfur dioxide}}{SO_2(g)} + HCl \qquad [27.7]$$

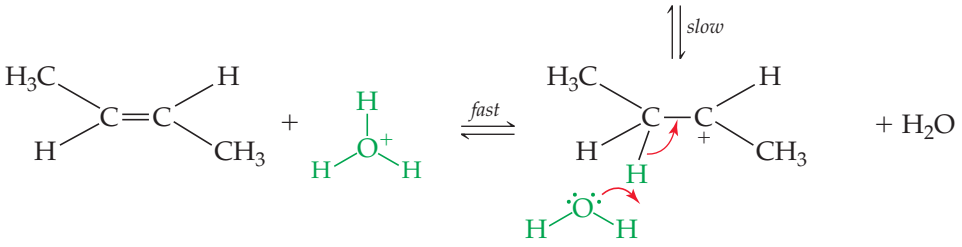
The reason this reaction works well is that one of the products (SO_2) is gaseous, so once it is liberated the reaction goes to completion.

Dehydration of Alcohols

We have already indicated that alcohols can be dehydrated to form alkenes (see Equation 26.15). Equation 27.8 illustrates the accepted mechanism. This acid-catalyzed dehydration process has, as one of its intermediates, an oxonium ion. The rate-determining step is the elimination of water to form the corresponding carbocation. Removal of a small group from a larger molecule, as in this case, is called an *elimination reaction*. Water is classed as a *good leaving group* because of its stability and relatively unreactive nature. Hydroxide ion, however, does not eliminate easily and so is classed as a *poor leaving group*.



[27.8]



Leaving groups can be classified as good or poor based on their reactivity. In general, the better leaving groups are those that are conjugate bases of strong acids. A relative order of leaving group is:

$$\underset{\text{Good leaving group}}{I^- > H_2O > Br^- > Cl^-} \gg \underset{\text{Poor leaving group}}{F^- > CH_3COO^- > OH^- > NH_2^-}$$

Once water has been eliminated from the oxonium ion in Equation 27.8, the reaction proceeds rapidly to the formation of the alkene by the loss of a proton from a carbon atom located in a neighboring position (called the β-position) to the original C—OH bond. The two electrons that once formed the C_β—H bond will now form the π-bond of the alkene. Without the β-hydrogen atom, the dehydration reaction does not proceed.

The nature of the equilibrium is such that removal of water or distillation of the alkene (which generally will have a lower boiling point than the corresponding alcohol) will maximize the formation of the alkene by driving the equilibrium in the forward direction.

Self-Assessment Exercises

27.19 Can you use an aqueous solution of ethanol to form sodium ethoxide?

(a) Yes

(b) No

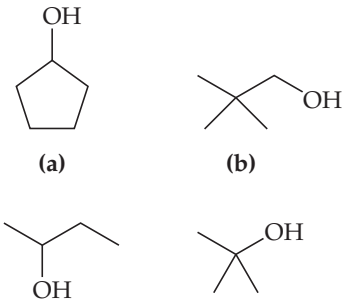
27.20 Which is the reagent of choice to convert butan-1-ol to 1-chlorobutane?

(a) Cl_2

(b) HCl

(c) $SOCl_2$

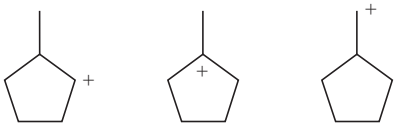
27.21 Which of the following molecules would *not* undergo a dehydration reaction?



(a) **(b)** **(c)** **(d)**

Exercises

27.22 Which of the following carbocations is most stable? Which is least stable?



(a) **(b)** **(c)**

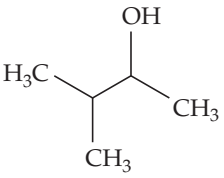
27.23 **(a)** Write a chemical equation for the substitution reaction of butan-2-ol with HBr. **(b)** Write a stepwise mechanism for this reaction. **(c)** Would butan-1-ol undergo the substitution reaction more quickly or more slowly than butan-2-ol?

27.24 **(a)** Which of the following is the *best* leaving group: (i) fluoride, (ii) iodide, (iii) hydroxide, (iv) chloride or (v) bromide? **(b)** Why, in a polar protic solvent, is iodide a better nucleophile than fluoride?

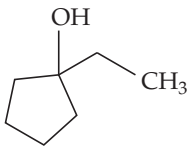
27.25 The addition of water to an alkene in the presence of H_2SO_4 leads to the formation of an alcohol, as shown in Equation 26.15. This reaction is in equilibrium with the dehydration of the newly formed alcohol to re-form the alkene. Describe a way of controlling the equilibrium so as to improve the yield of the alcohol.

27.26 What alkenes are formed as the major products from the dehydration of the following alcohols?

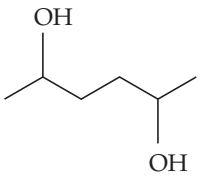
(a)



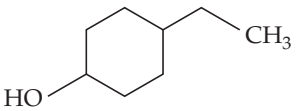
(b)



(c)



(d)



How many sets of stereoisomers are formed in each product case?

Answers to Self-Assessment Exercises

27.19 (b) **27.20** (c) **27.21** (b)

27.5 Nucleophilic Substitution Reactions of Haloalkanes

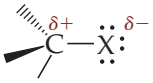


Between 20% and 30% of pharmaceuticals currently on the market have fluorine in their structure. These substances are active in a wide range of physiological situations, including cholesterol regulation (eg Lipitor®), antidepressant medication (eg Prozac®), for treatment of some cancers (fluorouracil), and are also present in many broad-spectrum antibiotics and in inhaled anesthetics (isoflurane). The strong carbon–fluorine bond resists metabolism and delays excretion from the body allowing for longer time periods between doses. The presence of fluorine also makes the substance more lipophilic, a useful property for anesthetics. In contrast, the bond between carbon and chlorine, bromine or iodine, is more reactive than a typical carbon–carbon single bond, which makes these haloalkanes excellent intermediates in chemical synthesis.

By the end of this section, you will be able to:

- Appreciate the scope of reactions undergone by haloalkanes.

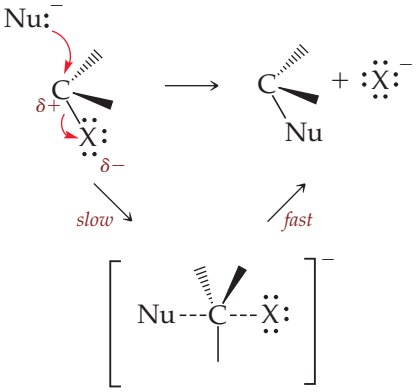
The conversion of alcohols to haloalkanes by substitution opens up a large library of functional group manipulation, limited only by imagination. The reactivity of haloalkanes manifests itself from the difference in electronegativity between carbon (2.5) and the halogens (2.6–4.0), which means the carbon bearing the halogen is susceptible to nucleophilic attack.



Where X = F, Cl, Br, I

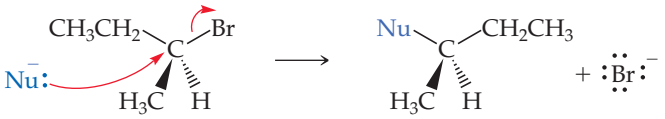
Nucleophilic substitution reactions of haloalkanes proceed by attack of the nucleophile (Nu:) at the carbon bearing the halogen. The trigonal-bipyramidal transition state formed in this reaction has long Nu—C and C—X bonds, signifying the strengthening bond formation of the incoming nucleophile and the weakening C—X bond of the outgoing halide. One of the driving forces for this reaction is the stability of the halide ion, which is an excellent leaving group.

As you can see in (Figure 27.15), the transition state that leads to the product involves both the haloalkane and the nucleophile in the rate-determining step. As such, this reaction is classed as $\mathbf{S_N2}$ for bimolecular (2), nucleophilic (N) substitution (S) reaction.



▲ Figure 27.15 Nucleophilic substitution reactions.

If the starting haloalkane is chiral about the carbon bearing the halogen, then the S_N2 reaction shown in Equation 27.9 usually proceeds with inversion of stereochemistry:

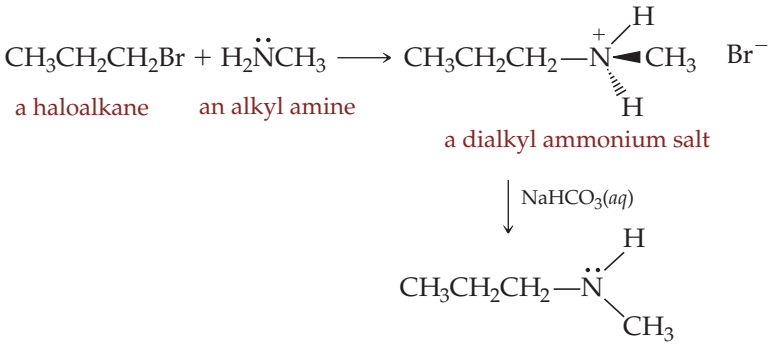


(*S*) stereochemistry (*R*) stereochemistry [27.9]

Inversion of stereochemistry can be thought of as the inversion of an umbrella that happens on a windy day (**Figure 27.16**). In this analogy, consider the umbrella canopy as three groups around a tetrahedral center that do not participate in an S_N2 reaction. Upon nucleophilic attack, the canopy is inverted, with some strain, to yield a new conformation.

However, the inversion of stereochemistry depends on the nature of the nucleophile and leaving group, the substituents about the stereocenter and the reaction conditions (for example, the solvent used).

Table 27.3 lists common nucleophiles employed in nucleophilic substitution reactions, as well as the classes of organic compound formed by the substitution. We have already investigated some of these in detail. Two nucleophile classes we have yet to discuss in any detail involve amines (which are neutral molecules) and the cyanide ion (CN^-). The addition of ammonia to a haloalkane, for example, leads initially to an **alkyl ammonium salt**. Such salts are characterized by four groups around nitrogen of which at least one is an alkyl group. Provided the ammonium ion is of the form R_3NH^+, $R_2NH_2^+$ or RNH_3^+, they are easily transformed into **amines** by the addition of base.



a haloalkane an alkyl amine a dialkyl ammonium salt

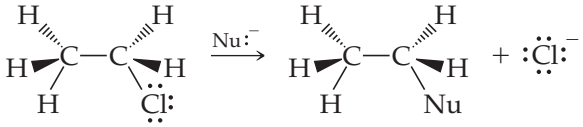
a dialkyl amine

N-methyl-1-propanamine [27.10]



◀ **Figure 27.16** The mechanism of an S_N2 reaction is analogous to an umbrella on a windy day.

TABLE 27.3 Common nucleophilic substitution reactions based on the reaction:



Nucleophile	Product	Class of compound
$^{-}$:ÖH	CH_3CH_2OH	an alcohol
$^{-}$:ÖR	CH_3CH_2OR	an ether
$^{-}$:Ï:	CH_3CH_2I	an alkyl iodide
$^{-}$:CN	CH_3CH_2CN	a nitrile
:NH_3	$CH_3CH_2NH_3^+X^-$	an alkyl ammonium salt
ÖH_2	CH_3CH_2OH	an alcohol

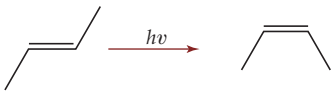
A CLOSER LOOK Molecularity

The molecularity of a reaction describes the number of atoms or molecules of reactant taking part in an elementary reaction. Remember that an overall reaction mechanism is composed of several elementary reactions. Most elementary reactions involve one (*unimolecular*) or two (*bimolecular*) species. Though most reactions are monitored by the loss of reactants or the formation of products, ultimately it is the molecularity of the rate-determining step that defines the observed kinetics of the overall reaction and hence whether a reaction is unimolecular or bimolecular. Molecularity should not be confused with reaction order.

Simple unimolecular reactions include decomposition of chlorine by homolytic bond cleavage or isomerization reactions. In both cases, the rate of reaction depends directly on the concentration of the only reactant. In this case, it is easy to see why this is a unimolecular reaction.

homolytic bond cleavage $Cl_2 \xrightarrow{h\nu} 2Cl\cdot$

isomerization

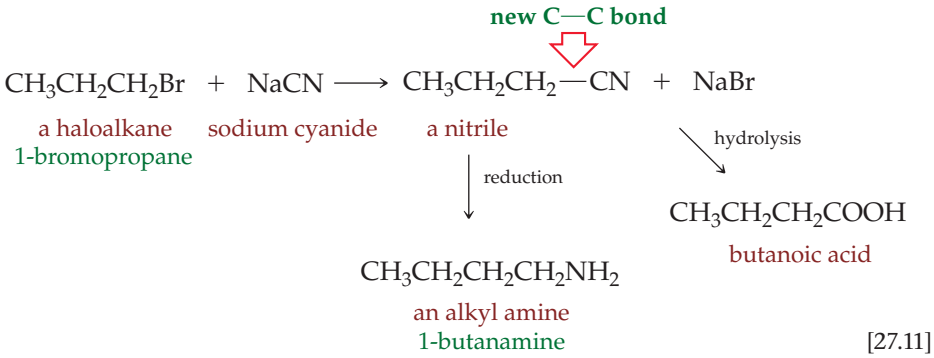


In a bimolecular reaction, two species are required to give rise to the product, for example the dimerization of $NO_2^{\cdot}$ or the addition of HCl to an alkene. In each case, the rate of reaction depends directly on the concentration of the two reactants, which need to collide before reaction can proceed.

$2NO_2 \longrightarrow N_2O_4$



The reaction of cyanide ion (CN^-) with a haloalkane (producing a **nitrile**) is extremely useful in organic synthesis despite the obvious toxicity problems, due to its ability to form a new C—C bond upon substitution. Reduction of the nitrile yields an alkyl amine which differs from the starting haloalkane by the addition of an extra CH_2 group, as well as the change in functional group.

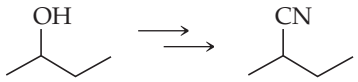


[27.11]

Sample Exercise 27.4

Nucleophilic Substitution Reactions

Using 2-butanol as a starting material, design a synthesis of 2-methylbutyronitrile in two steps:

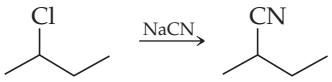


SOLUTION

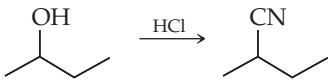
Analyze We are asked to design a substitution reaction for replacing a secondary OH group by CN.

Plan For a synthesis problem like this, it is usually helpful to consider the sequence of steps starting from the product you want. You know from Table 27.3 that nitriles can be synthesized from the haloalkane by substitution.

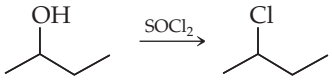
Solve In the following example the chloride is chosen, although the bromide is just as efficient:



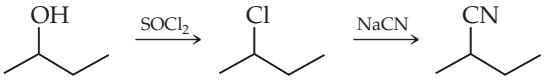
Formation of the alkyl chloride from the alcohol can occur in two ways. Since 2-butanol is a secondary alcohol, reaction with either HCl or thionyl chloride, $SOCl_2$, will yield 2-chlorobutane.



or

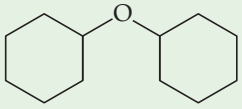


Thus the overall two-step reaction sequence is:



Practice Exercise

Describe how you would prepare this ether from cyclohexanol.



Self-Assessment Exercise

27.27 What is the product of the reaction between (*S*)-2-bromobutane and the hydroxide nucleophile, OH^-?

(a) butan-1-ol

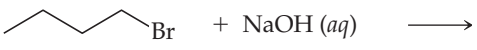
(b) (*S*)-butan-2-ol

(c) (*R*)-butan-2-ol

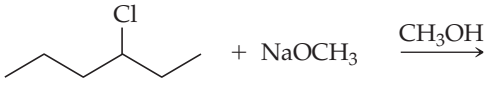
Exercises

27.28 Write the structure of the major organic product expected from the following reactions:

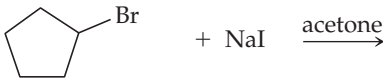
(a)



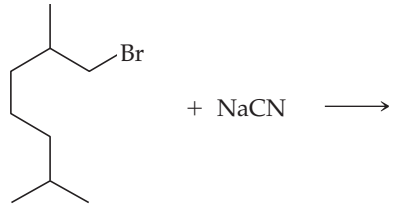
(b)



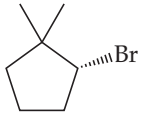
(c)



(d)



27.29 Name the product formed when methoxide reacts with:



27.30 Draw the mechanism of the reaction of chloroethane with cyanide. Use curly arrows where appropriate and show the structure of the trigonal bipyramidal transition state.

27.31 Hydroxide, OH^-, can act as both a base and a nucleophile. Explain the difference between these two terms and give a reaction to illustrate each case.

27.32 Design a synthesis of methoxymethane (CH_3OCH_3) starting from methanol as the only carbon containing compound.

Answers to Self-Assessment Exercise

27.27 (c)

27.6 Haloalkanes to Alkenes: β-Elimination



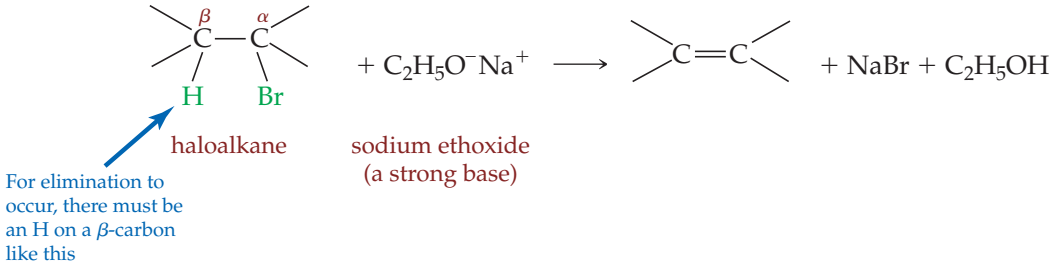
In the laboratory, there is often more than one way to approach the synthesis of a target molecule. The way chosen will depend on a range of factors including availability of starting materials, cost, what byproducts are formed, and the compatibility of the transformation with other functional groups that may be present. We have already seen that alkenes may be formed by the acid catalyzed dehydration of alcohols, they may also be formed from haloalkanes in an elimination reaction.

By the end of this section, you should be able to:

- Recognize which haloalkanes undergo elimination and predict the product formed.

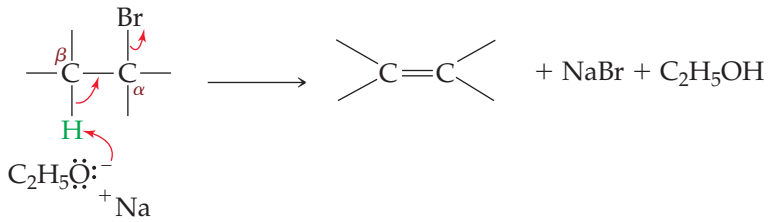
The process of eliminating a good leaving group, as outlined for the dehydration of an alcohol, is quite general. For example, haloalkanes undergo elimination under basic conditions. This process, called a ***β*-elimination reaction**, involves the *dehydrohalogenation*

of the haloalkane—that is, the loss of a hydrogen atom and a halogen atom from the same molecule. For the reaction to proceed, a hydrogen atom on the carbon atom adjacent to the carbon bearing the halide (that is, the β-carbon) must be present and be removed.



[27.12]

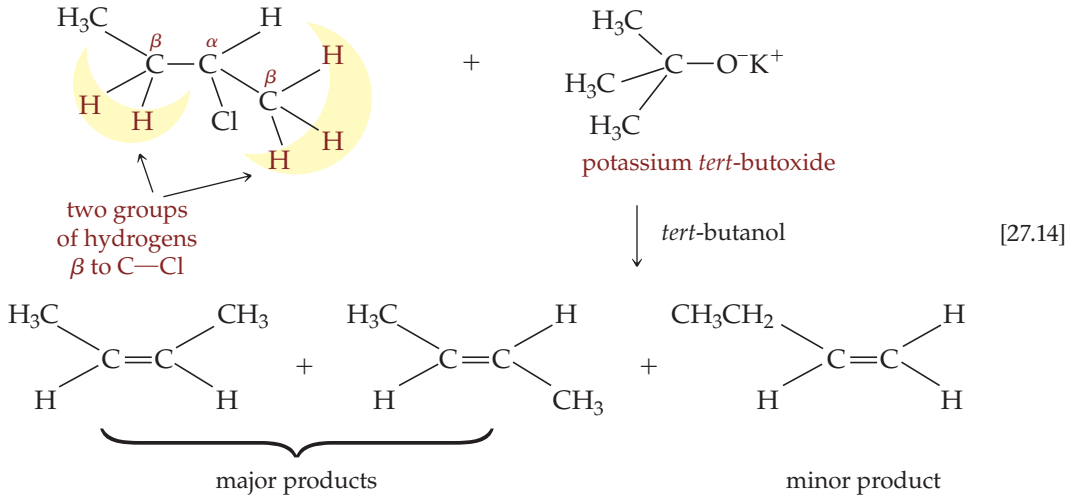
The reaction is not as fast as the corresponding dehydration of an alcohol, requiring the use of a strong base (for example, sodium ethoxide) to proceed. The mechanism can be shown to occur in a single (and essentially irreversible) step:



[27.13]

Typically, the hydrogen atoms of hydrocarbons do not react in this way. However, the inductive effect of the halogen atom on the α-carbon draws electron density out of the C—H bond, causing the β-hydrogen to become more acidic by weakening the C—H bond. Because this reaction involves the haloalkane and strong base in the rate-determining step, this **elimination reaction** is known as an **E2** or bimolecular (2) elimination (E) reaction.

Let us now consider the reaction of 2-chlorobutane with potassium *tert*-butoxide, another strong organic base:

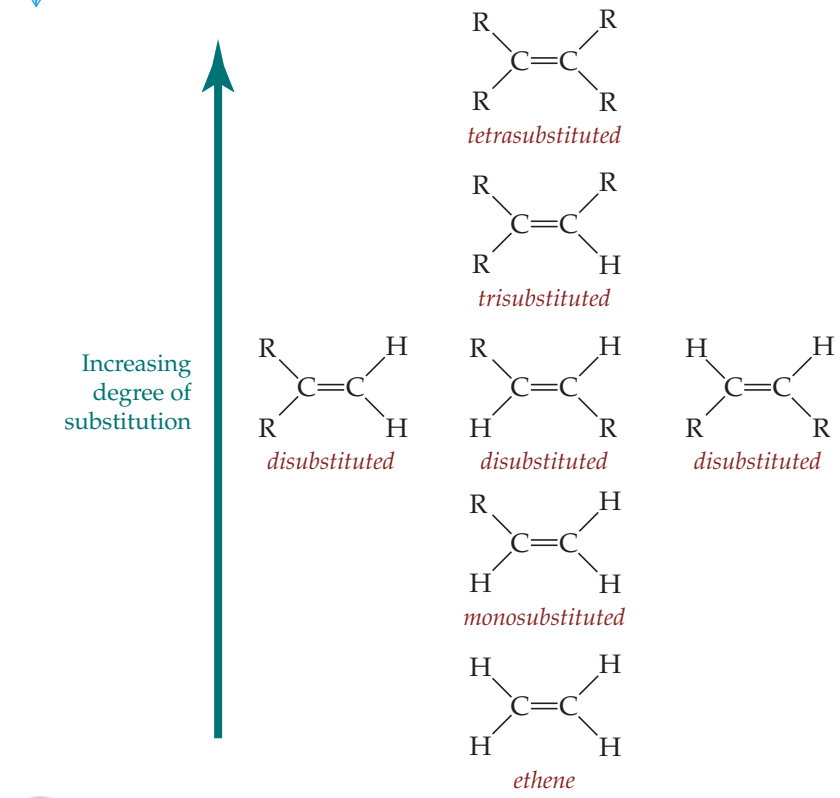


[27.14]

In this case, there are two sets of β-hydrogens as highlighted in Equation 27.14. Although β-elimination can lead to the formation of two alkenes, one elimination product is formed in preference to the other.

The major alkene formed by dehydrohalogenation is the one containing the more substituted double bond. This preference is known as **Zaitsev's rule**. The more substituted double bond is the one with the greater number of substituents (excluding hydrogen) attached to the two carbons of the double bond. For example, the but-2-ene formed in Equation 27.14 has two methyl groups connected to the carbons of the double bond, whereas but-1-ene has a single ethyl group connected. Because but-2-ene has two non-hydrogen substituents, it is the more substituted of the two alkenes formed. **Figure 27.17** illustrates what is meant by a substituted alkene.

Go Figure Which of these alkenes are isomers?



▲ **Figure 27.17** **Substituted alkenes in which R is a non-hydrogen atom, typically being carbon.**

Sample Exercise 27.5

β-Elimination in Haloalkanes

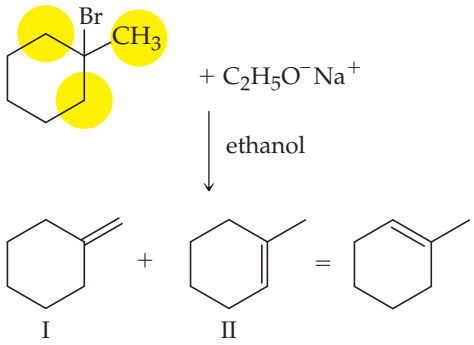
Draw the structural formula for the major product formed when 1-bromo-1-methylcyclohexane is reacted with sodium ethoxide in ethanol. Systematically name the major product.

SOLUTION

Analyze We are asked to determine the product of the reaction of a sterically hindered haloalkane with a strong base.

Plan Begin by structurally identifying the compounds involved. Look for β-hydrogens then determine the types of alkenes possible.

Solve



There are two different sets of β-hydrogens highlighted in yellow, those on the methyl group and two equivalent sets on the cyclohexane ring. Hence two different alkenes, I and II, are formed. The major product will be the one that satisfies the criterion of Zaitsev's rule. The more substituted double bond is found in II, and so it is formed in preference.

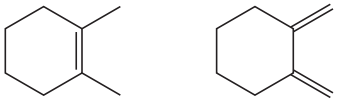
Alkene II is named *1-methylcyclohexene*.

Practice Exercise

2-Methylpent-2-ene can be formed by the reaction of potassium *tert*-butoxide and which bromoalkane?

Self-Assessment Exercise

27.33 What product is formed from the *β*-elimination reaction of 1,2-dibromo-1,2-dimethylcyclohexane?



(a) **(b)**



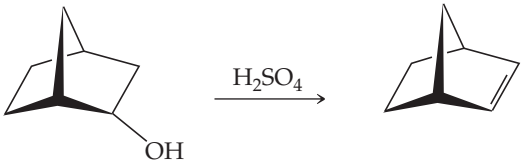
(c) **(d)**

Exercises

27.34 2-Methylpent-2-ene can be formed by the reaction of potassium *tert*-butoxide and which bromoalkane?

27.35 Dec-2-ene can be formed by the reaction of potassium *tert*-butoxide and which two chloroalkanes? Which chloroalkane would you use to maximize your yield?

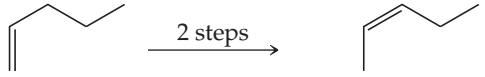
27.36 The dehydration of norborneol yields none of the Zaitsev product. Why is this so? [*Hint:* Think about the geometry of the products.]



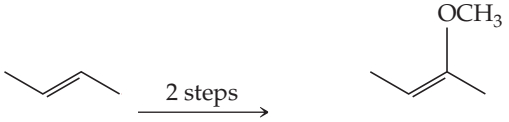
27.37 What is the structure of the major alkene product formed when 2-methylpropane is reacted consecutively with Br_2, in the presence of light, and then potassium *tert*-butoxide? [*Hint:* You will need to recall the regioselectivity of free-radical bromination, covered in Chapter 24.]

27.38 Insert the missing reagents or products in the multi-step reactions shown here.

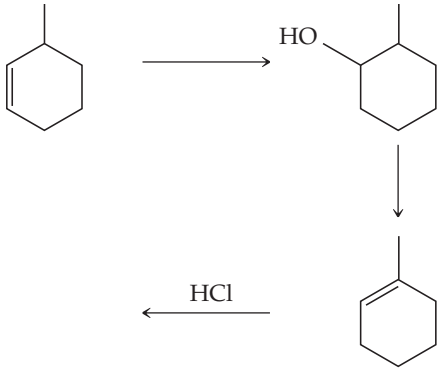
(a)



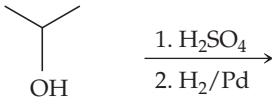
(b)



(c)



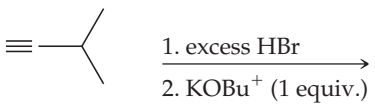
(d)



(e)



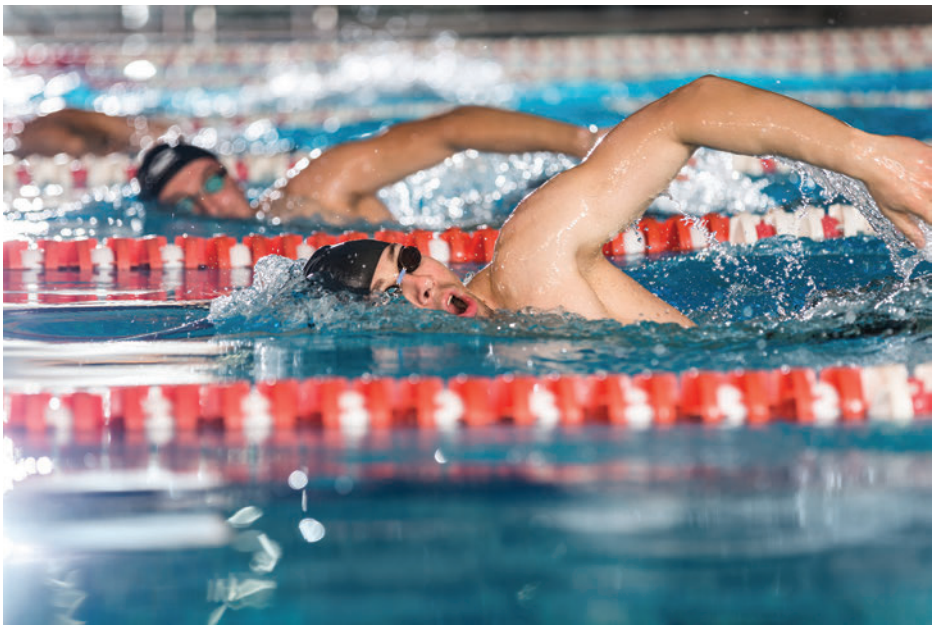
(f)



Answers to Self-Assessment Exercise

27.33 (d)

27.7 | Substitution versus Elimination

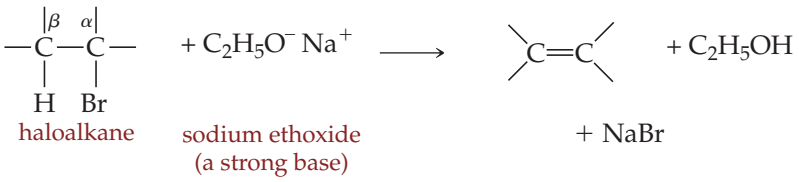


There are many situations in chemistry where two or more reaction pathways compete to give different products. One of the skills we introduce in this section is to recognize the molecular structures, choice of reagents, solvents, and conditions that favor one pathway over a different one. In this way, we optimize the formation of the compound we want and minimize waste. By the end of this section, you should be able to:

- Identify the features that distinguish substitution and elimination pathways.

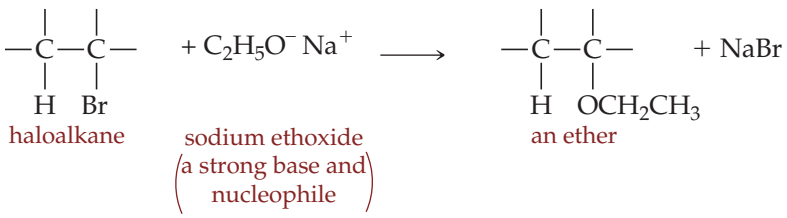
We consider four types of reactions in this section, E1, E2, S_N1 and S_N2. We have already encountered two of these formally (E2 and S_N2). As we will see, each reaction type does not operate in isolation, but together they form a competing process. Which direction a reaction proceeds in depends on several factors, including starting material and reagents, type of solvent, and electronic and steric effects.

We have already seen in this chapter that alkoxides are a strong base, able to deprotonate haloalkanes in a β-elimination reaction.



[27.15]

However, as we saw in Section 27.5, alkoxides are able to react with haloalkanes in another way. Instead of providing a means of elimination, alkoxides can also interact with haloalkanes to form ethers. The classic example is the *Williamson ether synthesis*, in which the halide is replaced by the alkoxide in a substitution reaction.



[27.16]

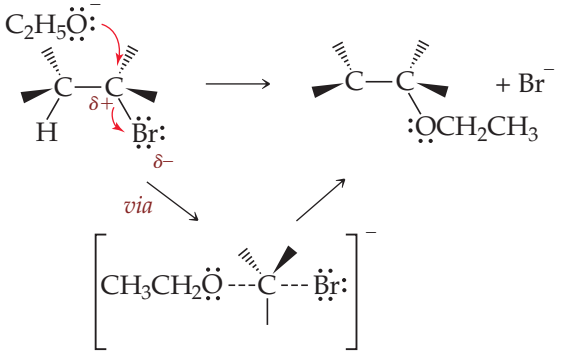
A CLOSER LOOK Nucleophile or Lewis Base?

Whether a reaction follows an elimination or substitution pathway is dependent on whether the added reagent acts as a Lewis base or nucleophile, respectively. Recall that a Lewis base is an electron-pair donor, the same as a nucleophile. In broader definitions, a Lewis base can donate its electron pair to something other than H^+. By this definition, both a nucleophile and Lewis base can form new covalent bonds. So what's the difference?

The answer is nothing. We usually invoke the term Lewis base when there is a proton abstraction process, as in an elimination reaction, and the term nucleophile in all other cases. So, a Lewis base can be a good nucleophile if there are no sterically bulky groups around the electron donor.

Related Exercise: 27.68

The mechanism for this substitution reaction involves attack of the nucleophilic alkoxide on the weakly electrophilic carbon atom bearing the halide. Note that strong bases are typically good nucleophiles. The carbon atom bearing the halogen is made more electrophilic by the inductive effects of the halogen. This reaction type is called a *nucleophilic substitution (S_N) reaction*. The reaction goes through a trigonal-planar carbon state with elongated bonds for the incoming alkoxide and the outgoing halide. Eventual loss of Br^- yields the ether. The reaction shown in Equation 27.17 can be further defined as an S_N2 reaction, since the rate-determining step requires the addition of the alkoxide in concert with the loss of halide.

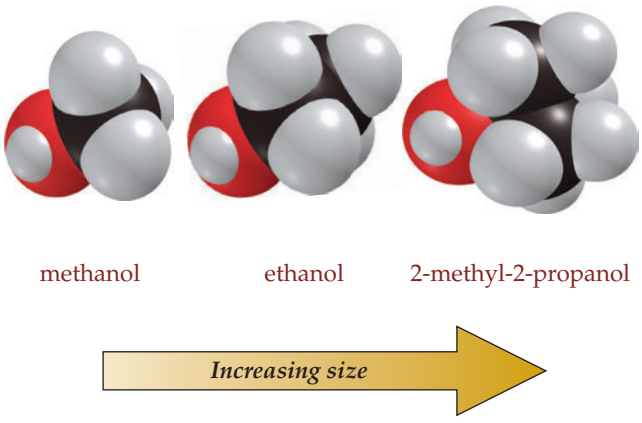


[27.17]

The β-elimination reaction (Equation 27.12) is in fact in competition with the substitution reaction. Generally, *S_N2 reactions are in competition with E2 reactions*. Which mechanism predominates in the reaction is dictated by a variety of factors:

1. The size of the alkoxide: the bulkier the alkoxide, the more elimination is favored. **Figure 27.18** illustrates this change in size. Alkoxides such as that generated from 2-methyl-2-propanol (*tert*-butanol) favor E2 because of their large size, while those generated from methanol favor S_N2.
2. The accessibility of the carbon bearing the halogen: the more accessible it is, the more substitution is favored.
3. The accessibility of the hydrogen atom in the β-position: the more accessible it is, the more elimination is favored.

Any alkyl groups positioned off the α-carbon of the haloalkane tend to favor β-elimination. This is particularly true of the larger halogens, Br and I.



▲ **Figure 27.18** Size increases with substitution.

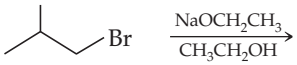
E1 and S_N1 Reactions

In Section 27.4 we discovered that generating a carbocation intermediate leads rapidly to formation of the alkene. The stability of the carbocation formed in the dehydration is also the driving force for that reaction. That is, the conditions needed to dehydrate a tertiary alcohol are much milder than those needed to dehydrate a primary alcohol, due to the relative stabilities of the intermediate tertiary and primary carbocations, respectively. In this case, the rate-determining step is the loss of water to form the carbocation intermediate as shown in Equation 27.5. As such, this elimination reaction is *unimolecular*

Sample Exercise 27.6

Predicting Substitution or Elimination

What is the major organic product from the following reaction? Indicate whether this is an S_N2 or E2 reaction.

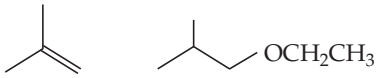


SOLUTION

Analyze We are given the reaction of a haloalkane with a strong base also capable of acting as a good nucleophile. We are asked to determine the product and the mechanism.

Plan We need to consider both elimination and substitution products in our deliberation, as well as the nature of the base and whether a β-hydrogen is present and accessible.

Solve The elimination and substitution products are:



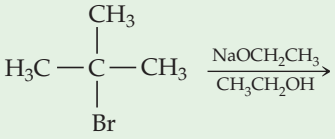
elimination product | substitution product

The α-carbon in the starting bromoalkane is essentially unhindered despite the bulk of the two methyl groups nearby and the bromine atom. This implies that substitution would occur readily. In contrast, the β-hydrogen is more restricted by the same steric groups. This factor suggests that substitution predominates. The substitution follows an S_N2 mechanism.

This practice exercise shows how the yield of alkene may be optimized.

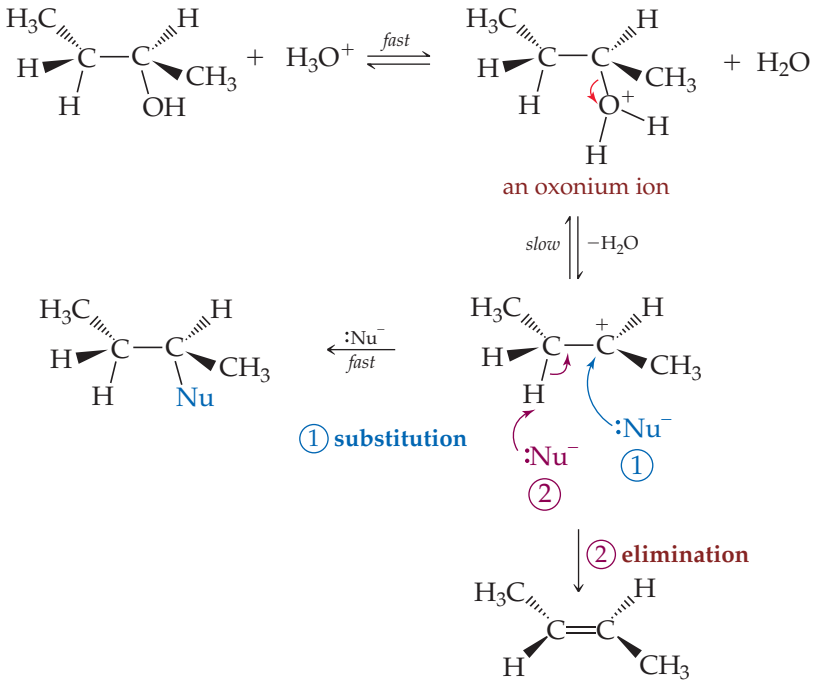
Practice Exercise

What is the major organic product from the following reaction?



and is designated as an **E1** mechanism. A summary of this mechanism and its competing substitution reaction is shown in Figure 27.19.

The β-elimination reaction, shown as route 2 in Figure 27.19, is also in competition with a nucleophilic substitution reaction, shown as route 1 in Figure 27.19. If a nucleophile is present within the reaction mixture, then substitution is also likely. The equilibrium arrows shown in Figure 27.19 between the oxonium ion and the carbocation in fact display this very principle. In this case, water acts as the leaving group in one reaction direction

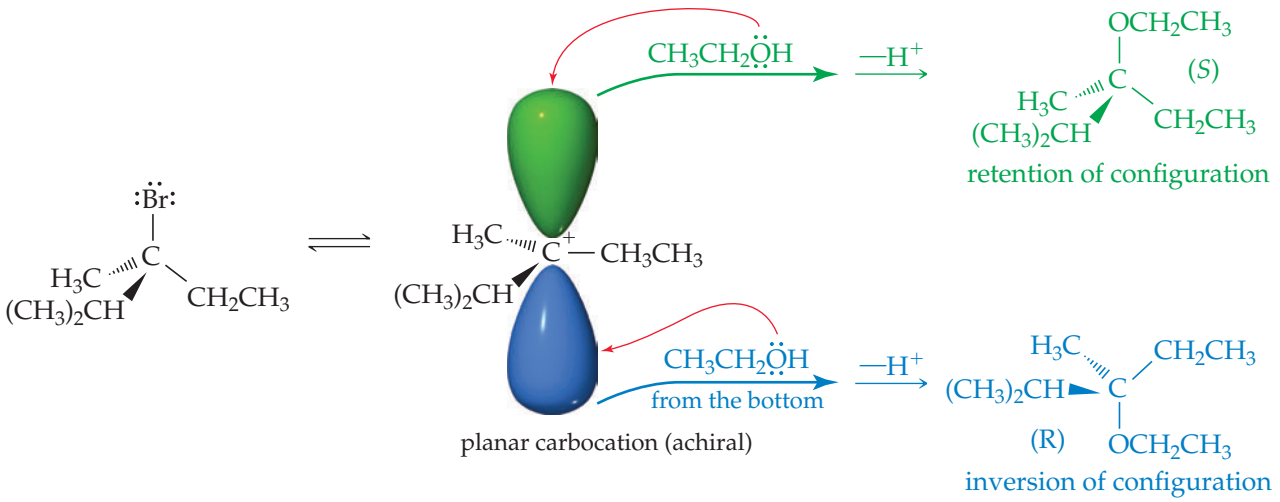


▶ **Figure 27.19 Substitution and elimination reactions.** The rate-determining step is the generation of the carbocation intermediate common to both reactions.

(from top to bottom) and as the nucleophile in the other direction (from bottom to top). The result of the latter reaction leads only to formation of more of the starting alcohol. However, what if another nucleophile, such as Cl^-, is also present? The result is the formation of a haloalkane. Since the rate-determining step is still the same (and unimolecular), this type of substitution is known as an **S_N1** reaction.

As opposed to the typical inversion of stereochemistry seen in S_N2 reactions, S_N1 reactions result in, a racemic mix—or at the very least a less optically pure compound than the starting material. This is because in the S_N1 mechanism the carbocation intermediate is sp^2 hybridized and planar (**Figure 27.20**). A nucleophile can attack the carbocation from either face leading to retention or inversion of stereochemistry.

Table 27.4 summarizes the important parameters for substitution and elimination reactions discussed in this chapter.



▲ **Figure 27.20** **S_N1 Racemization.**

TABLE 27.4 General patterns of reactivity for substitution and elimination reactions at a sp^3 carbon

Property	S_N2	S_N1
Rate of reaction Reason:	$1° > 2° \gg 3°$ Steric	$3° > 2° \gg 1°$ Carbocation stability
Products	Substitution (major) E2 (minor)	Substitution (major) E1 (major)
Stereochemistry	Stereospecific, inversion	Racemic product
Kinetics	2nd order (substrate, base)	1st order (substrate)
Leaving group	Important	Important
Nucleophile effect on rate	Important	No effect
	E2	**E1**
Rate of reaction Cause:	$3° > 2° \gg 1°$ Steric	$3° > 2° \gg 1°$ Carbocation stability
Products	Alkene (major), S_N2 (minor)	Most stable alkene
Kinetics	2nd order (substrate, base)	1st order (substrate)
Leaving group	Important	Important
Effect of base on rate	Strongest base fastest	No base necessary

Self-Assessment Exercise

27.39 Is the reaction of 1-chloro-2,2-dimethylpropane with hydroxide S_N1, S_N2, E1 or E2?

(a) S_N1

(b) S_N2

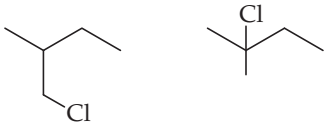
(c) E1

(d) E2

Exercises

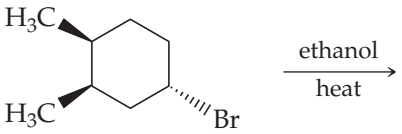
27.40 When sodium ethoxide ($NaOCH_2CH_3$) reacts with an haloalkane, two types of products are likely. Illustrate this point by drawing the *major* organic products when sodium ethoxide acts as a base or as a nucleophile in its reaction with 2-chlorobutane.

27.41 Which of the following haloalkanes gives the *slowest* S_N2 reaction? Why?



27.42 **(a)** Which is more nucleophilic, methoxide or *tert*-butoxide? Why? **(b)** Show the best way to prepare $CH_3OCH(CH_3)_2$ by an S_N2 reaction.

27.43 **(a)** Provide the structure of the major organic products that result in the following reaction (including stereochemistry). **(b)** What mechanism predominates?



27.44 When 1-iodo-1-methylcyclohexane is treated with sodium ethoxide, the more highly substituted alkene product predominates. When potassium *tert*-butoxide is used instead, the less substituted alkene predominates. Why?

27.45 **(a)** Which of the following halides is most reactive in an E2 reaction with sodium methoxide? **(b)** Which is least reactive in an E2 reaction?

(i) $(CH_3)_3CCH_2I$

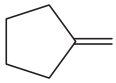
(ii) $(CH_3)_2CHCHICH_3$

(iii) $(CH_3)_2CHCH_2Br$

(iv) $(CH_3)_2CHCH_2Cl$

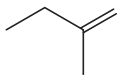
27.46 Supply the missing haloalkane reactant in the followings elimination reactions.

(i) CH_3CH_2ONa, ethanol, heat →



(ii) CH_3CH_2ONa, ethanol, heat → $CH_3CH{=}CHCH_2CH_3$

(iii) CH_3CH_2ONa, ethanol, heat →



Answers to Self-Assessment Exercise

27.39 (b)

Sample Integrative Exercise

Putting Concepts Together

An unknown organic product was characterized by combustion analysis. You find the compound contains 59.96 % carbon and 13.42 % hydrogen and the remainder is oxygen.

(a) Determine the empirical formula of the compound. **(b)** If the molar mass is found to be 60.09 g mol^{-1}, draw and name all possible constitutional isomers of the compound and identify the functional groups present. **(c)** Your compound is not very soluble in water and has a boiling point close to room temperature; suggest the identity of the compound. **(d)** How would you synthesize this compound?

SOLUTION

Analyze This question provides some data which we use to obtain the formula of an unknown compound. Using Lewis structures we represent the structure of the possible compounds and, with the aid of some observations of the physical properties, we are asked to suggest the identity of the compound.

Plan Combustion analysis gives the empirical formula of a compound. This, together with a molar mass, enables us to determine the molecular formula from which we can construct all constitutional isomers. This allows us to identify the functional groups present and relate them to likely physical properties of the material.

Solve

(a) The percentage of oxygen in the compound is 100% − (59.96 + 13.42)% = 26.62%. The number of moles of each element in 100 g of the compound is;

$$\text{Moles of C} = \frac{59.96\ \text{g}}{12.01\ \text{g mol}^{-1}} = 4.992\ \text{mol C}$$

$$\text{Moles of H} = \frac{13.12\ \text{g}}{1.008\ \text{g mol}^{-1}} = 13.31\ \text{mol H}$$

$$\text{Moles of O} = \frac{26.62\ \text{g}}{16.00\ \text{g mol}^{-1}} = 1.664\ \text{mol O}$$

Dividing by the smallest number of moles present (1.664) gives the whole number ratio of the elements.

$$\text{Moles of C : H : O} = \frac{4.992\ \text{mol}}{1.664\ \text{mol}} : \frac{13.31\ \text{mol}}{1.664\ \text{mol}} : \frac{1.664\ \text{mol}}{1.664\ \text{mol}}$$
$$= 3 : 8 : 1$$

So the empirical formula is C_3H_8O.

(b) The molar mass of C_3H_8O is 60.09 g mol^{-1} which is the same as that determined for the unknown compound so we can conclude the molecular formula of the compound is also C_3H_8O. There are three possible constitutional isomers.

$H_3C—CH_2—CH_2—OH$

1-propanol

$H_3C—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

2-propanol

$H_3C—CH_2—O—CH_3$

methoxyethane

The first two structures are alcohols (a primary alcohol and secondary alcohol, respectively) and the final structure is an ether.

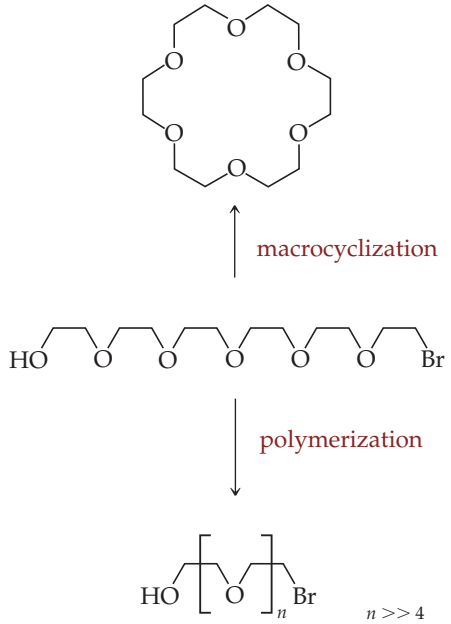
(c) Boiling point and solubility are directly related to the intermolecular forces present. As all the molecules have the same formula we assume the strength of the dispersion forces are similar in the three cases. Two compounds contain an alcohol functional group which can form hydrogen bonds and the third compound is an ether which, when pure, shows no hydrogen bonds between molecules. As a consequence of the hydrogen bonds the alcohols are likely to display an appreciably higher boiling point and greater solubility in water than the ether. The unknown compound is likely to be methoxyethane.

(d) A Williamson ether synthesis of iodomethane and ethanol in the presence of sodium metal would form methoxyethane. Note that forming the product from iodoethane and methanol will lead to the formation of ethene as a side product. This occurs through an elimination of HI using the sodium methoxide generated *in situ* as a base.

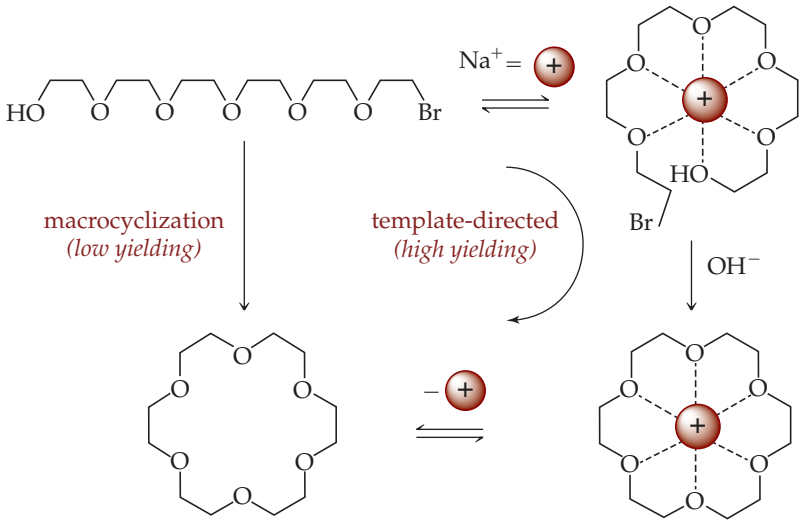
CHEMISTRY AND LIFE Polymerization versus Macrocyclization

The preparation of cyclic ethers (Section 27.3) has always involved two competing processes: the desired macrocyclization and an unwanted polymerization. **FIGURE 27.21** illustrates these two processes using the crown ether, 18-crown-6, as the example. Intramolecular reaction of the OH group on the bromide in the presence of base yields the crown ether, 18-C-6, via substitution. Intermolecular reaction of the OH group on the bromide of a *second* molecule in the presence of base yields the polyether, also via substitution. Since both processes are competing, the result has always been a low (<20%) isolated yield of the macrocycle. Intramolecular processes are usually faster than intermolecular processes because of the proximity of reactive functional groups; however, this is true only of small molecules. In the example of crown ether synthesis shown in Figure 27.21 the longer the starting acyclic polyether, the lower the yield of the crown ether.

We can, however, take advantage of the affinity of polyethers for metal cations to bias the reaction outcome. In this case, the spherical cation acts as a *template* to promote the formation of the cyclic crown ether by allowing the polyether to wrap around the cation (**FIGURE 27.22**). In this orientation, the carbon bearing the bromine atom and the OH group are brought into close proximity, enabling the intramolecular substitution reaction to occur in preference to the polymerization upon the addition of base—for example, hydroxide ion. Removal of the cationic template yields the macrocycle in 60–80% yield. This very practical reaction is analogous to the approach taken by nature in the formation of highly complex and functioning molecules such as DNA, in which a template strand is necessary to build the double helix using DNA polymerases I and II.



▲ **Figure 27.21** Competition between (formation of) a crown ether and a polymer.



▲ **Figure 27.22** The template effect.

Chapter Summary and Key Terms

SECTION 27.1 **Alcohols** are hydrocarbon derivatives containing one or more OH groups. Alcohols are more **miscible** with water than ethers of comparable size, due to their ability to hydrogen-bond as a result of the **lone pairs** on oxygen. Alcohols that have two or three OH groups, such as ethene glycol and glycerol, are called **diols** and **triols**, respectively. Alcohols are classed as **primary** (1°), **secondary** (2°) or **tertiary** (3°). Short-chain alcohols are miscible with water.

SECTION 27.2 **Haloalkanes** are hydrocarbons containing one or more halogens, usually generalized as RX (X = F, Cl, Br, I). They are also commonly referred to as alkyl halides. Compounds of the form CHX_3 are often called **haloforms**, of which chloroform is an example. **Chlorofluorocarbons**, or **CFCs**, are odorless, non-toxic, non-flammable and non-corrosive compounds that were typically used as refrigerants, propellants in aerosols and industrial solvents before being phased out due to their harmful effects on the ozone layer in the atmosphere.

SECTION 27.3 **Ethers** contain a bridging oxygen atom between two hydrocarbon chains. Cyclic ethers are a subclass of a large group of organic compounds known as **heterocyclic compounds**. Ethers contain both alkyl and **alkoxy** groups. Larger **cyclic polyethers** such as the **crown ethers** are able to complex metal ions within their cavity. Ethers make good solvents.

SECTION 27.4 The reaction of sodium metal with an alcohol leads to an **alkoxide**. Alkoxides are as strong a base as hydroxide. Potassium *tert*-butoxide and sodium ethoxide are examples cited frequently in this chapter. Alcohols act as a weak base, generating an oxonium ion under acidic conditions. Alcohols can be converted into haloalkanes by treatment of a halogenating agent, usually under acidic conditions. In this reaction, the OH group of the alcohol is substituted by a halogen in a **nucleophilic substitution (S_N) reaction**. Alcohols can also dehydrate to form alkenes.

SECTION 27.5 Nucleophilic substitution reactions of haloalkanes proceed by attack of the nucleophile at the carbon bearing the halogen. Because of the difference in electronegativity between carbon and any of the halides, this bond is polarized such that the carbon becomes mildly electrophilic. If the transition state that leads to the product involves both the haloalkane and the nucleophile in the rate-determining step, the reaction is classed as an **S_N2** or bimolecular (2), nucleophilic (N), substitution (S) reaction. The reaction of haloalkanes with **amines** leading to **alkyl ammonium salts,** is one such example. **Nitriles** are formed when haloalkanes are reacted with cyanide.

SECTION 27.6 Alkenes are readily formed from haloalkanes through a process called a ***β*-elimination reaction**. An **elimination reaction** involves the removal of a small group from a larger molecule. An **E2** reaction is a bimolecular (2) elimination (E) reaction. The alkene that forms in preference is the one that follows **Zaitsev's rule**, which states that the more substituted double bond predominates.

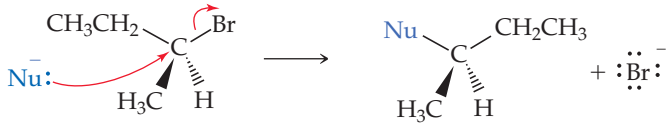
SECTION 27.7 Substitution and elimination reactions are competing reactions. Bimolecular substitution reactions (S_N2) compete against bimolecular elimination reactions (E2); which mechanism predominates in the reaction is dictated by a variety of steric factors. Tertiary alcohols undergo unimolecular reactions in which the rate-determining step is the elimination of water leading to a carbocation intermediate. In this case **E1** or **S_N1** reactions are likely depending on the reaction conditions.

Key Skills

- Understand how to derive the names of simple alcohols, ethers and haloalkanes. Learn the common names for the simplest cases. Learn how to classify alcohols as 1°, 2° or 3°. (Sections 27.1, 27.2 and 27.3)
- Learn the basic functional group manipulation shown in Figure 27.14. (Section 27.4)
- Be able to explain the difference between S_N1, S_N2, E1 and E2 mechanisms and have a qualitative understanding of when one predominates over another to predict reaction outcomes. (Sections 27.5, 27.6 and 24.7)

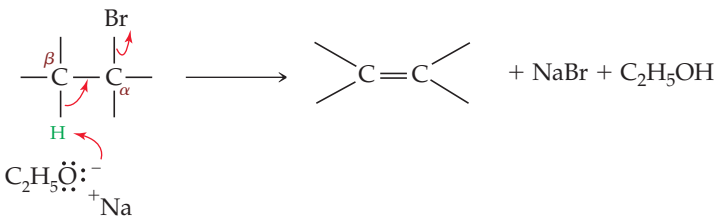
Key Equations

- Substitution



[27.9]

- β-Elimination



[27.13]

Exercises

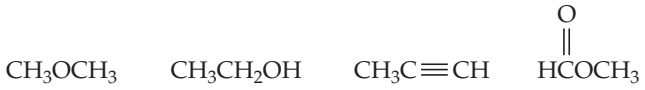
Visualizing Concepts

27.47 Propan-1-ol ($CH_3CH_2CH_2OH$) and propan-2-ol (also known as isopropyl alcohol $(CH_3)_2CHOH$), whose space-filling models are shown, have boiling points of 97.2 °C and 82.5 °C, respectively. Explain why the boiling point of propan-1-ol is higher, even though both have the molecular formula of C_3H_8O. [Section 27.1]



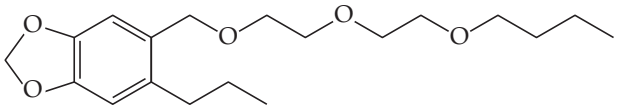
propan-1-ol propan-z-ol

27.48 What features must a molecule have to participate in hydrogen bonding with other molecules of the same kind? Which of the following compounds would you expect to **(a)** have the highest boiling point, **(b)** be least soluble in water? Explain. [Section 27.1]



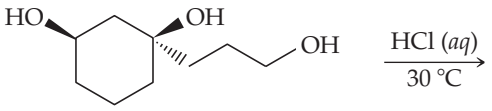
(i) (ii) (iii) (iv)

27.49 Piperonyl butoxide is used commercially as an additive to pyrethrum-based insecticides to enhance their effect. Copy the structure and highlight the atoms that constitute the cyclic ether and the acyclic polyether. [Section 27.3]



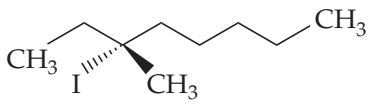
piperonyl butoxide

27.50 Draw the carbocation that triol 1 would form under the indicated conditions. Explain your answer. [Section 27.4]



1

27.51 How many distinct alkene products (including stereochemistry) are possible when the iodoalkane shown here undergoes E2 elimination? [Section 27.5]



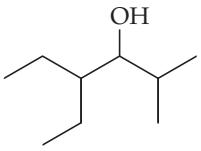
Alcohols: Structure, Properties, and Nomenclature (Section 27.1)

27.52 Two oxygen-containing compounds have the same empirical formula. One substance is a gas, the other is a liquid. How is it possible for two substances with the same empirical formula to have markedly different properties?

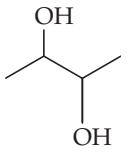
27.53 Draw the structures of **(a)** hexan-2-ol, **(b)** propane-1, 2, 3-triol, **(c)** 4,4-dimethylcyclohexanol, **(d)** *cis*-1, 2-cyclopentanediol, **(e)** 2-methylpropan-2-ol.

27.54 Name the following alcohols, ignoring stereochemistry:

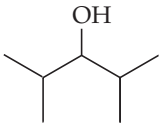
(a)



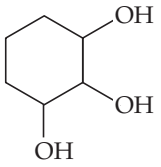
(b)



(c)

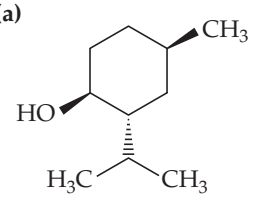


(d)



27.55 Classify the following alcohols as primary, secondary, or tertiary.

(a)



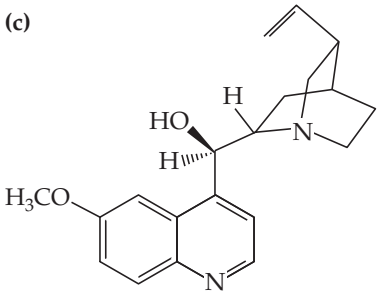
menthol

(b)



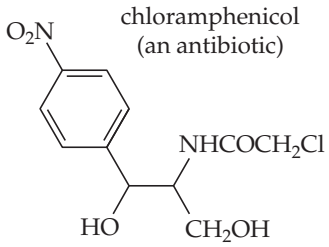
patchoulol

(c)



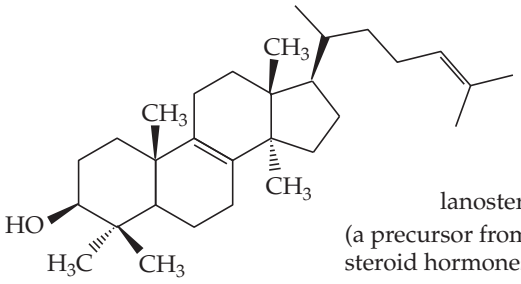
quinine
(an antimalarial drug)

(d)



chloramphenicol
(an antibiotic)

(e)



lanosterol
(a precursor from which all steroid hormones are made)

Haloalkanes (Section 27.2)

27.56 Eight isomers have the molecular formula $C_5H_{11}Cl$. How many of these are tertiary chloroalkanes?

27.57 Describe the carbon–chlorine bond of chloroalkanes as polar or nonpolar. Why?

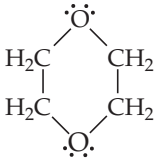
Ethers: Structure, Properties, and Nomenclature (Section 27.3)

27.58 Ethene glycol ($HOCH_2CH_2OH$), the major substance in antifreeze, has a normal boiling point of 198 °C. By comparison, ethanol (CH_3CH_2OH) boils at 78 °C at one atmospheric pressure. Ethene glycol dimethyl ether ($CH_3OCH_2CH_2OCH_3$) has a normal boiling point of 83 °C, and ethyl methyl ether ($CH_3CH_2OCH_3$) has a normal boiling point of 11 °C. **(a)** Explain why replacement of a hydrogen on the oxygen by CH_3 generally results in a lower boiling point. **(b)** What are the major factors responsible for the difference in boiling points of the two ethers?

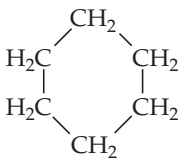
27.59 **(a)** Give the empirical formula and structural formula for the cyclic ether containing four carbon atoms in the ring. **(b)** Write the structural formula for a straight-chain compound that is a structural isomer of your answer to part (a).

27.60 Why do ethers make good solvents, whereas alcohols usually make poor solvents in which to undertake a chemical reaction? When might an alcohol make an appropriate solvent?

27.61 Which would you expect to be more soluble in water, cyclohexane or dioxane? Explain.



dioxane

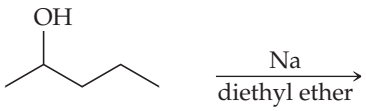


cyclohexane

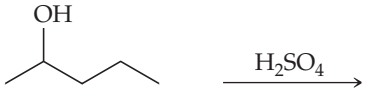
Reactions of Alcohols and Haloalkanes (Sections 27.4 and 27.5)

27.62 Suggest a possible stable reaction product for each of the following reactions:

(a)



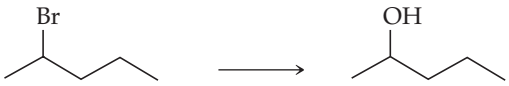
(b)



27.63 Sodium wire is normally used to "dry" tetrahydrofuran before distillation and use in water-sensitive reactions. **(a)** Write an equation for the reaction of sodium metal with water. **(b)** This reaction is very exothermic and care should be taken as to how "wet" the tetrahydrofuran is. What alternative to water might you use to destroy excess sodium, and what precautions should you take?

27.64 Suggest ways of conducting the following transformations.

(a)



(b)



(c)



(d)

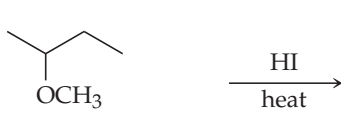


27.65 Provide the structure of the major organic product of the following reactions.

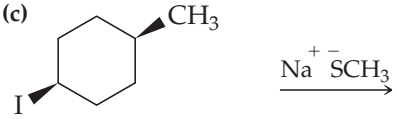
(a)



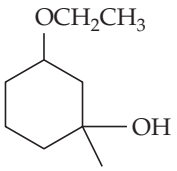
(b)



(c)



27.66 Describe a synthesis of A starting from 3-methylcyclohexene-3-ol.



A

Haloalkanes to Alkenes: β-Elimination (Section 27.6)

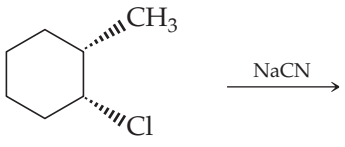
27.67 When sodium ethoxide ($NaOCH_2CH_3$) reacts with 2-chlorobutane, a haloalkane and three unsaturated products are likely (including stereochemistry). **(a)** Draw them. **(b)** Which ones are likely to be formed in higher yield?

27.68 Which base, sodium ethoxide or potassium *tert*-butoxide, would you employ for the efficient dehydrohalogenation of 1-bromo-2-ethylbutane. Why?

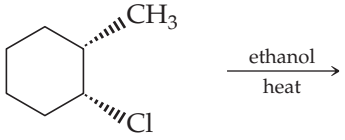
27.69 **(a)** Define bimolecular. **(b)** Using diagrams, give an example of a bimolecular reaction using diagrams.

27.70 What is the major product formed in the following reactions and what mechanisms predominate?

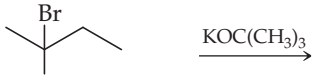
(a)



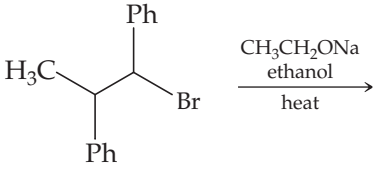
(b)



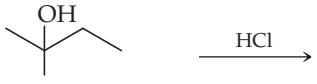
(c)



(d)



(e)

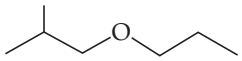


Substitution versus Elimination (Section 27.7)

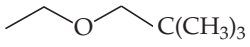
27.71 When haloalkanes react with alkoxides a competition exists between elimination and substitution reactions. Which product is formed can be biased by the judicious choice of haloalkane and alkoxide. The following ethers can only be prepared in high yield by the combination of one alkoxide ion and one haloalkane.

What is the correct combination in each case?

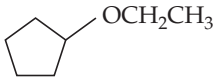
(a)



(b)



(c)



27.72 **(a)** What is the substitution product of the following reaction? **(b)** What is the elimination product of this reaction?

$CH_3CH_2Br + HO^- \rightarrow$

27.73 Which of the following S_N2 reactions is the *fastest*? Why?

(a) $CH_3CH_2CH_2I + HO^- \rightarrow CH_3CH_2CH_2OH + I^-$

(b) $CH_3CH_2CH_2Br + HO^- \rightarrow CH_3CH_2CH_2OH + Br^-$

(c) $CH_3CH_2CH_2I + H_2O \rightarrow CH_3CH_2CH_2OH + HI$

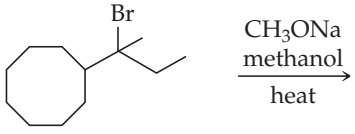
(d) $CH_3CHICH_3 + HO^- \rightarrow CH_3CHOHCH_3 + I^-$

27.74 The reaction of a tertiary bromoalkane with iodide follows. **(a)** Assuming no other changes, what is the effect of *doubling* the concentration of the haloalkane? **(b)** Assuming no other changes, what is the effect of doubling *only* the concentration of the nucleophile?



27.75 When 2-bromo-3-methyl-1-phenylbutane is treated with sodium methoxide, why is the major product 3-methyl-1-phenyl-1-butene?

27.76 What is the major organic product of the following reaction? Why?

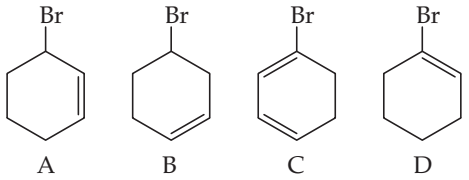


Additional Exercises

27.77 Consider the following experimental data for the rate of an elimination reaction for a tertiary bromide. What is the mechanism for the reaction?

Experiment No.	[Bromoalkane]	[Base]	Rate
1	0.01	0.01	1
2	0.02	0.01	2
3	0.01	0.02	1

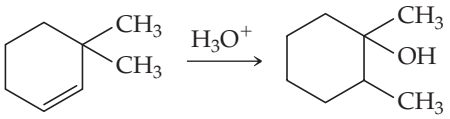
27.78 Which of the following bromides forms the most stable carbocation? Why?



27.79 **(a)** Dehydrohalogenation of 2-bromobutane in the presence of a strong base proceeds via which mechanistic pathways? **(b)** Why is the E1 not a likely mechanism when 1-chloropentane is heated in ethanol? **(c)** Predict the two most likely mechanisms (substitution and elimination) for the reaction of 2-iodohexane with sodium ethoxide and give the products of these reactions. **(d)** Can primary haloalkanes react by S_N2, S_N1, E2 and E1 mechanisms? Are any of these mechanisms prohibited? What conditions favor a particular mechanism?

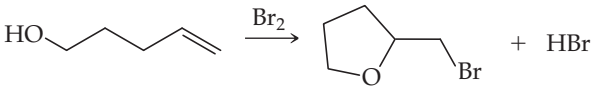
Integrative Exercises

27.80 This question relates to the hydration of 3,3-dimethylcyclohexene and the development of an appropriate mechanism to account for the formation of 1,2-dimethoxy-1-cyclohexanol.



(a) Draw a mechanism leading to the first carbocation intermediate. **(b)** The next step involves a methyl migration from carbon 3 to carbon 2. Draw this intermediate and comment on why this is favored. **(c)** Use water as a nucleophile and draw the next step of the mechanism. **(d)** Complete the mechanism to generate the product. What does this mechanism tell you about the requirement of acid?

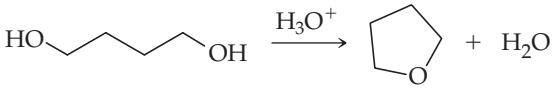
27.81 Provide a detailed, step-by-step mechanism for the following reaction.



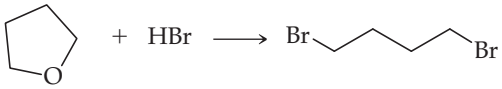
27.82 Describe a way of converting but-2-ene into but-2-yne using a bromination as the first step.

27.83 Describe a way of converting hex-3-ene into hex-3-yne.

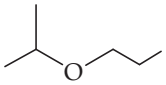
27.84 Propose a mechanism for the following reaction:



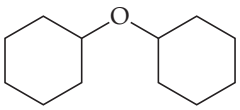
27.85 Propose a mechanism for the following reaction:



27.86 Starting with propan-1-ol as the only organic material, synthesize isopropyl propyl ether.

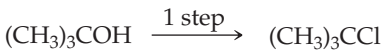


27.87 Describe how you would prepare this ether from cyclohexene.

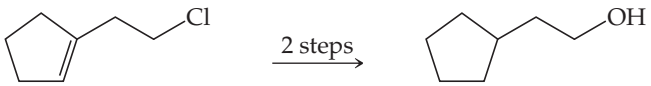


27.88 How would you accomplish the following transformations?

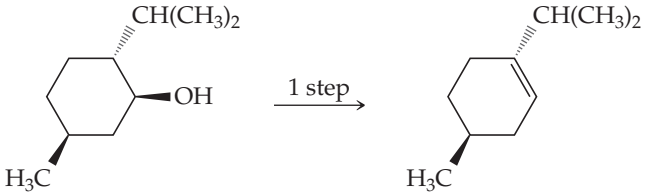
(a)



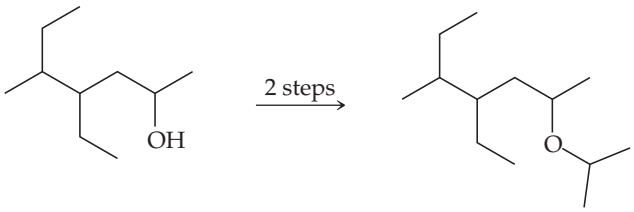
(b)



(c)



(d)



27.89 Consider the three alkenes: ethene, propene and 2-methylpropene. **(a)** For each alkene, draw the reaction showing the acid-catalyzed hydration to form one major product. Include the carbocation intermediate in each case. **(b)** Write the systematic name of the alcohols produced. Classify the intermediate carbocations and the alcohol products as *primary, secondary* or *tertiary*. **(c)** What is the connection between the classification of the carbocations and the alcohols that arise from them?

27.90 In the S_N2 reaction of 1-bromobutane with hydroxide ions we imagine a smooth interchange between the leaving group and the attaching nucleophile, while the S_N1 reaction of 2-bromo-2-methylpropane involves the formation of a carbocation intermediate. Sketch the energy profile (similar to Figure 15.17) for the two mechanisms. Use labels to show which part of your sketch represents a transition state, which an intermediate and which energy changes represents E_a and ΔH for the reaction.

27.91 The conversion of 2-methyl-2-propanol to 2-bromo-2-methylpropane using concentrated hydrobromic acid occurs at room temperature. As the reaction proceeds, the reaction mixture separates into two layers. **(a)** Why does this occur? Treatment of the product, 2-bromo-2-methylpropane, with sodium ethoxide gives 2-methylpropene. **(b)** What is the geometry and hybridization observed for the central carbon atom in both the haloalkane and alkene? 2-Methylpropene is a gas at room temperature. **(c)** What is the maximum volume of gas produced, at 25 °C and 101.3 kPa, if 5.0 g of 2-bromo-2-methylpropane reacted completely to form 2-methylpropene?

Design an Experiment

Imagine yourself in a research laboratory where you are going to investigate the factors that affect the outcome of a reaction. The compounds that you want to investigate are the haloalkanes and the competing substitution and elimination reactions they undergo. For each set of experiments that you devise, formulate a research question that the experiments may answer, and give a rationale for how your experiment may address that question. Variables in the experiment could include: the halide used, the structure of the haloalkane, the reagent employed, the concentrations of the components, the solvent used, and the temperature conditions of the reaction. Think also how you may determine the outcome of the reaction and what changes may be observed during the course of the reaction.

WHAT'S AHEAD

28.1 ▶ Aldehydes, Ketones, and the Carbonyl Group

28.2 ▶ Preparation of Aldehydes and Ketones

28.3 ▶ Reactions of Aldehydes and Ketones

28.4 ▶ Carbohydrates

28

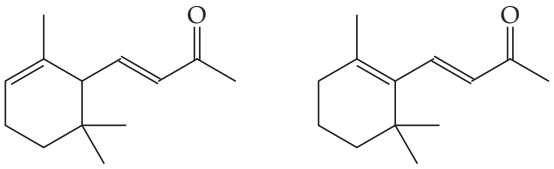
ALDEHYDES, KETONES, AND CARBOHYDRATES

28.1 | Aldehydes, Ketones, and the Carbonyl Group



The first written reference to a chemist occurred about 4000 years ago. The perfume maker Tapputi is mentioned on a cuneiform tablet from Mesopotamia. She is said to have distilled flowers and essential oils in order to extract their fragrant essence. Over the centuries, there have been many reports in documents right across the ancient world of similar activities. There are, of course, very many different substances that are used in the perfume industry however, the aldehyde and ketone functional groups are frequently encountered.

For example, a class of compounds called the ionones are central to the fragrance of roses and violets. They may be formed from α-carotene by an enzyme-mediated reaction. For example, a class of compounds called the ionones are central to the fragrance. A mixture of α-ionone and β-ionone results in the scent of violets, while β-ionone is a significant contributor to the scent of roses.



α-ionone β-ionone

By the end of this section, you should be able to:

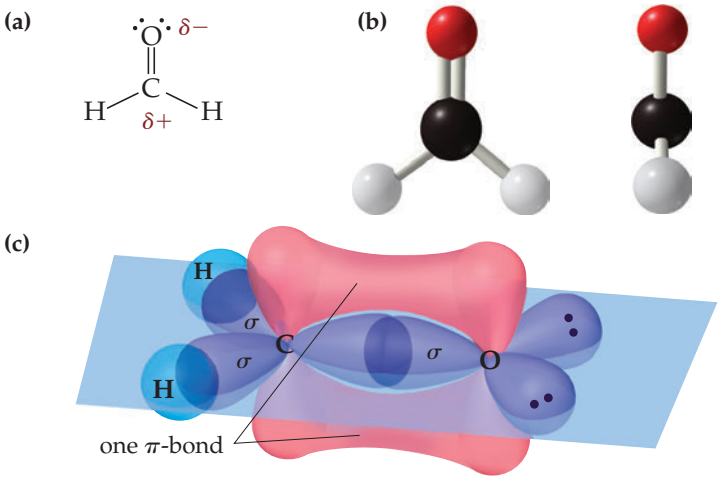
- Recognize and systematically name simple aldehydes and ketones.

Many important functional groups contain a double bond between carbon and oxygen—a combination of atoms called the **carbonyl group**. In Table 24.8, the carbonyl group appears in the aldehyde, ketone, carboxylic acid, ester and amide functional groups. The chemistry of the latter three functional groups differs from that of aldehydes and ketones and so will be dealt with in the next chapter. The geometry of the carbonyl group is similar to that of an alkene. The presence of the carbon–oxygen double bond (**Figure 28.1**) signifies that both the carbon and oxygen atoms are sp^2 hybridized. That is, a set of hybridized orbitals forms the σ-bond and a set of unhybridized *p* orbitals forms the π-bond of the carbon–oxygen double bond by direct overlap. Figure 28.1(c) illustrates the bonding in methanal (formaldehyde), the simplest of all the carbonyl-containing compounds. Because the oxygen in the carbonyl group is sp^2 hybridized, its lone pairs have a trigonal planar arrangement. Notice the polarity of the C—O group, which is due to the difference in electronegativity between the carbon atom and the more electron-rich oxygen atom. This polarity, and the nature of the π-bond, is very important for the reactivity of carbonyl compounds.

The carbonyl double bond is shorter, stronger and more polarized than a carbon–carbon double bond.

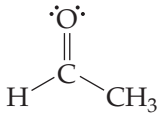
	Length	Bond enthalpy
C=O	123 pm	745 kJ/mol
C=C	134 pm	611 kJ/mol

Go Figure What does the structure of CO_2 look like?

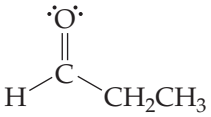


▲ **Figure 28.1 The carbonyl group of methanal.** (a) The structural formula; (b) a molecular model representation, in front-on and side-on views; (c) a molecular orbital view of the bonding, indicating σ- and π-bonds.

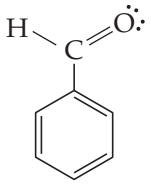
An **aldehyde** is characterized by the functional group CHO. The structures and systematic names of five simple aldehydes (with common names in blue) are:



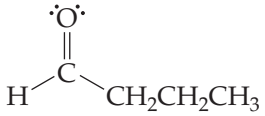
ethanal
(acetaldehyde)



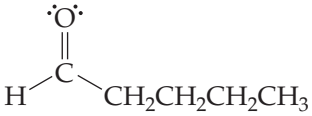
propanal
(propionaldehyde)



benzaldehyde



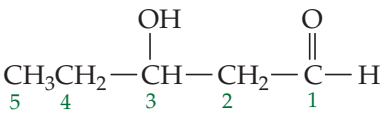
butanal
(butyraldehyde)



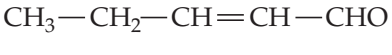
pentanal

Aldehyde nomenclature requires the selection of the parent alkane (longest alkyl chain) containing the carbonyl group. The carbon of the carbonyl group constitutes part of that parent alkane's name. The suffix *-ane* is partly retained, replacing the *e* with *al*. (Note the difference with benzaldehyde. Here the aldehyde group lies outside the ring system. Aromatic compounds such as this have their own unique nomenclature.) As you can see from these examples, an aldehyde group, by definition, must also occur at the beginning (or end) of a hydrocarbon chain. As a result, there is no need to number the position of the aldehyde—it is always assigned position 1.

In terms of hierarchy, the aldehyde group takes precedence over alkene and alkyne functionality. Two aliphatic aldehyde examples illustrate this:

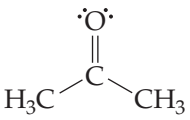


3-hydroxypentanal

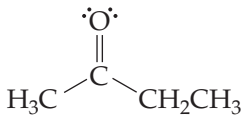


pent-2-enal

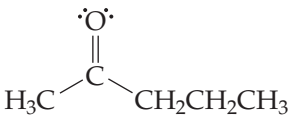
In **ketones** the carbonyl group occurs within the interior of a hydrocarbon chain and is therefore flanked on either side by carbon atoms:



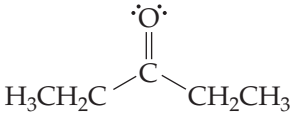
propanone
(acetone)



butanone



2-pentanone or pentan-2-one

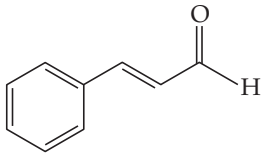


3-pentanone or pentan-3-one

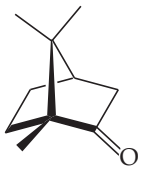
In naming ketones, the parent alkane is derived from the longest chain containing the carbonyl group. The suffix *-ane* is partly retained, replacing the *e* with *one*. Ketones containing parent alkanes greater than C4 can exist as constitu- tional isomers, so require numbering to define unambiguously the position of the carbonyl group. Two representations of the names to describe the compound are shown and are commonly interconverted.

Many compounds found in nature possess an aldehyde or ketone functional group. Vanilla and cinnamon flavorings are derived from the naturally occurring aldehydes, vanillin, and cinnamaldehyde. Citronellal is a naturally occurring insect repellent. Carvone

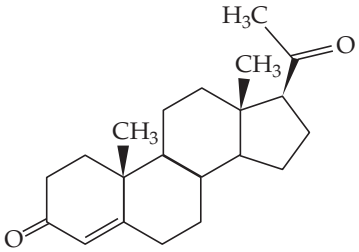
(see figure 27.7) and camphor are ketones that impart characteristic flavors and scents. Steroids, such as testosterone and progesterone, are also ketones. Testosterone is predominantly a male hormone; progesterone is predominantly a female hormone used by the body to stop further ovulation after an ovum has been fertilized.



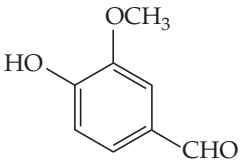
cinnamaldehyde (cinnamon)



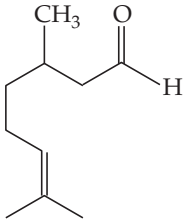
camphor



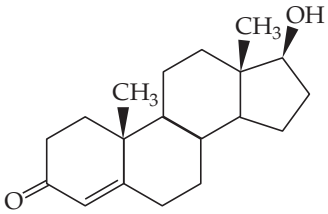
progesterone



4-hydroxy-3-methoxybenzaldehyde (vanillin)



citronellal



testosterone

Ketones are less reactive than aldehydes and are used extensively as solvents. Acetone, which boils at 56 °C, is the most widely used ketone. Acetone is completely miscible with water, yet it dissolves a wide range of organic substances. These features made it ideal for use as an early nail polish remover, among other domestic uses. Butanone ($CH_3COCH_2CH_3$), which boils at 80 °C, is used as an industrial solvent.

Sample Exercise 28.1

Naming Aldehydes and Ketones

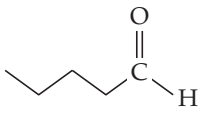
Write the structural formulas for all aldehydes and ketones of molecular formula $C_5H_{10}O$ and name each structure systematically.

SOLUTION

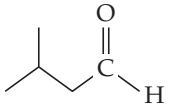
Analyze We are given a molecular formula and asked to generate as many different aldehydes and ketones as possible. We are given one oxygen atom in the molecular formula.

Plan Draw out the carbon skeleton, add the carbonyl group starting at one end (this will give an aldehyde) then progress this along the chain.

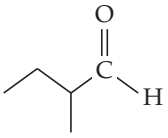
Solve



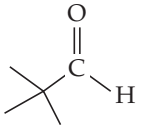
pentanal



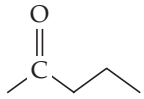
3-methylbutanal



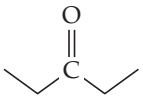
2-methylbutanal



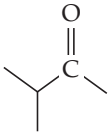
2,2-dimethylpropanal



2-pentanone



3-pentanone



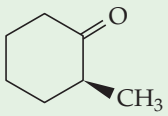
3-methyl-2-butanone

Continued

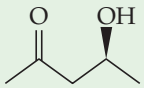
Practice Exercise

Name these compounds including stereochemistry:

(a)



(b)



Self-Assessment Exercise

28.1 What is the systematic name of citranellal?

(a) 3,7-dimethyloct-6-enal
(b) 3,7,7-trimethylhept-6-enal
(c) 2,6-dimethyloct-2-enal

Exercises

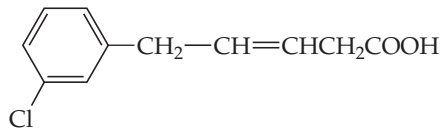
28.2 Why do propanone and butanone not require position numbers for the carbonyl group?

28.3 Identify the functional groups in each of the following compounds:

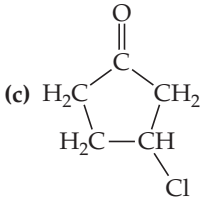
(a)



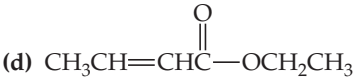
(b)



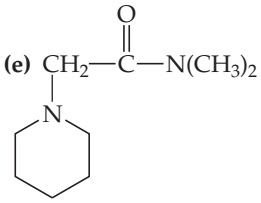
(c)



(d)



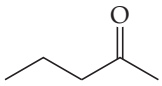
(e)



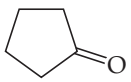
28.4 Give the structural formula for **(a)** an aldehyde that is an isomer of acetone, **(b)** an ether that is an isomer of propanone.

28.5 Name the following compounds:

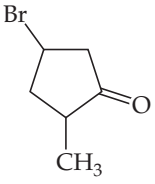
(a)



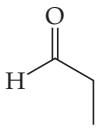
(b)



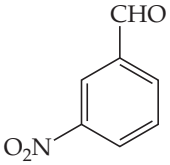
(c)



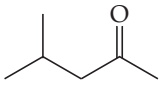
(d)



(e)



(f)



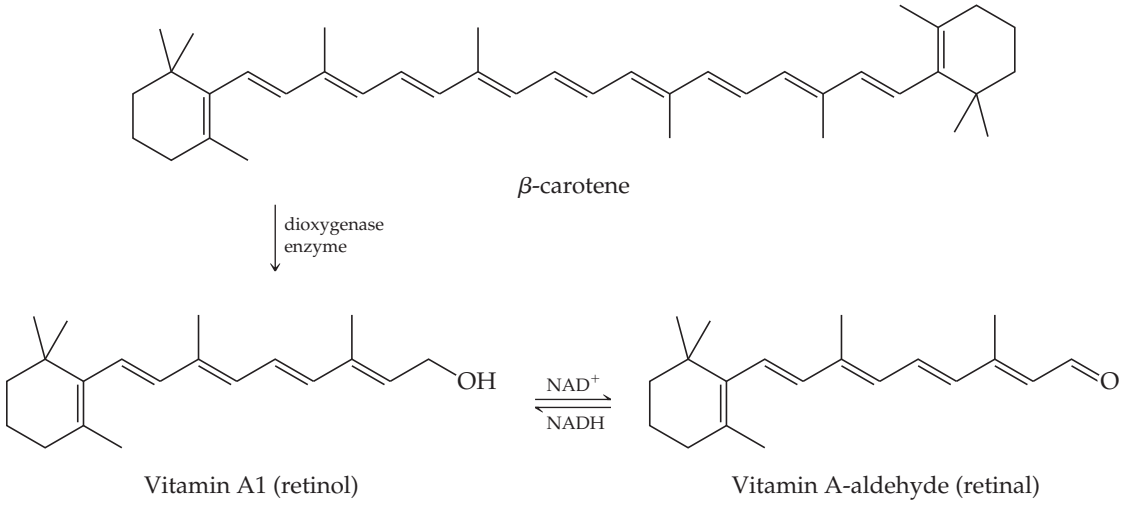
Answers to Self-Assessment Exercises

28.1 (a)

28.2 Preparation of Aldehydes and Ketones



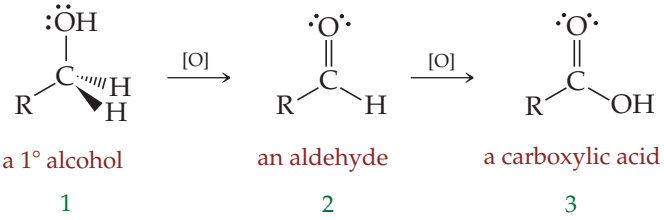
Vitamin A is essential for the function of vision as well as many other processes involving our immune system, gene transcription, and skin health. This group of vitamins may be obtained directly from animal sources, for example cod liver oil, or derived from the carotenes, which are present in many fruits and vegetables. The orange color of carrots is due to β-carotene, which is the principle vegetable source of retinol—Vitamin A1. Retinol is the form in which the vitamin is stored in the body and may be easily converted to retinal, which enters the visual cycle.



In this section, we look at the synthesis of aldehydes and ketones by two methods, the principal of which is the oxidation of an alcohol to the carbonyl compound. By the end of the section, you should be able to:

- Understand the preparation of aldehydes and ketones by an oxidation reaction.

Go Figure What is the major organic product formed by the oxidation of 1-propanol, 2-propanol?



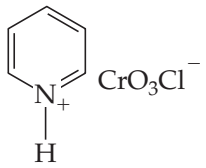
▲ **Figure 28.2 Oxidation of primary alcohols.** Primary alcohols are converted to carboxylic acids under standard experimental conditions. The symbol [O] represents an oxidation. To demonstrate the oxidation (that is, addition of oxygen) imagine C═O as being 2 × C—O.

Aldehydes and ketones are generally prepared by using similar reactions. Here, we concentrate on two sample types. The first involves the oxidation of alcohols, which is the standard technique for their preparation. The second involves the ozonolysis of alkenes.

Oxidation of 1° and 2° Alcohols

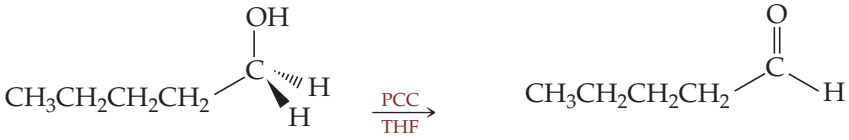
When primary alcohols are oxidized using strong oxidising agents such as potassium dichromate ($K_2Cr_2O_7$) in H_2SO_4 or chromic acid ($CrO_3/H_2O/H_2SO_4$), they are usually converted to the corresponding carboxylic acid, via the intermediary aldehyde (**Figure 28.2**).

Pyridinium chlorochromate (PCC), on the other hand, is a mild oxidizing agent capable of converting primary alcohols to aldehydes.



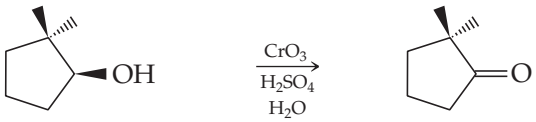
pyridinium chlorochromate

Unlike other oxidising agents, PCC is soluble in organic solvents such as tetrahydrofuran (THF) and dichloromethane. The oxidation of pentan-1-ol using this reagent yields the aldehyde as the major oxidation product.



pentan-1-ol pentanal [28.1]

Secondary alcohols are oxidized by PCC, chromic acid or potassium dichromate to yield the corresponding ketone. Further reaction is restricted because it would require the breaking of a C—C bond.



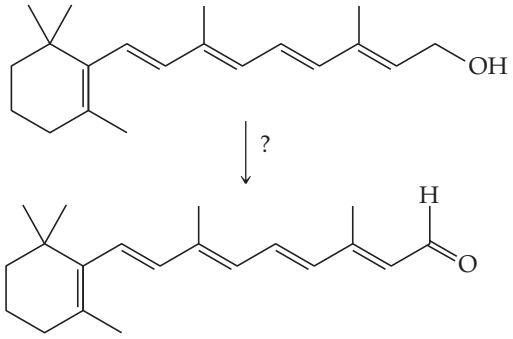
(*S*)-2,2-dimethylcyclopentanol 2,2-dimethylcyclopentanone [28.2]

Tertiary alcohols resist oxidation altogether, as a C—C bond would have to be broken for any oxidation to occur.

Sample Exercise 28.2

Oxidation of Alcohols

What reagent would you use to convert retinol (vitamin A) into retinal in the laboratory?



SOLUTION

Analyze We are asked how to convert an alcohol to an aldehyde.

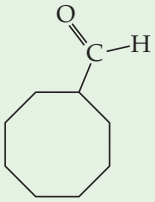
Plan Determine the type of alcohol, where the conversion takes place and what is retained from starting material to product.

Solve This conversion is the oxidation of a primary alcohol to an aldehyde. To achieve this, pyridinium chlorochromate in acetone is the best reagent. The mild reactivity of this reagent does not affect the alkene groups and produces the aldehyde in excellent yield. Note that the reaction is conducted in acetone solvent. This solvent is useful for oxidations because it cannot be further oxidized under the experimental conditions employed.

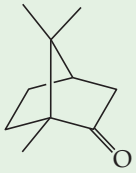
Practice Exercise

What starting alcohol would you use to prepare the following compounds?

(a)

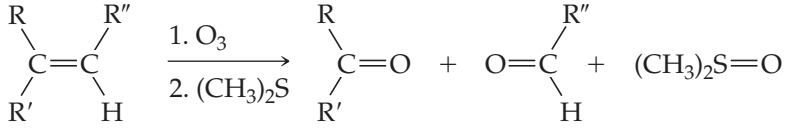


(b)



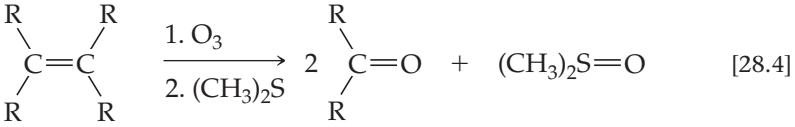
Ozonolysis

Aldehydes and ketones can be prepared in good yield by the reaction of alkenes with ozone, followed by a mild reduction using dimethylsulfide. This process, called **ozonolysis**, is a synthetically useful way of generating aldehydes and ketones.



an alkene a ketone an aldehyde dimethylsulfoxide [28.3]

Whether an aldehyde, ketone or a mixture of the two are formed depends solely on the substitution of the alkene. For symmetrical alkenes, only one product is formed.

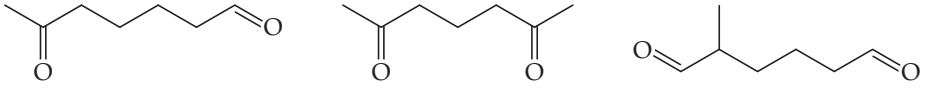


[28.4]

In some instances, ozonolysis leads to the formation of one high molecular weight and one low molecular weight product, which can easily be separated by distillation.

Self-Assessment Exercise

28.6 Which carbonyl compound is formed on treatment of 1-methylcyclohexene with ozone followed by dimethyl sulfide?

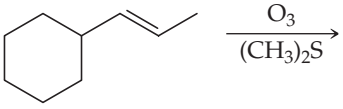


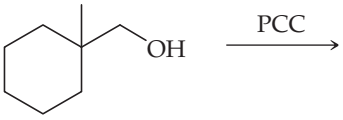
(a) **(b)** **(c)**

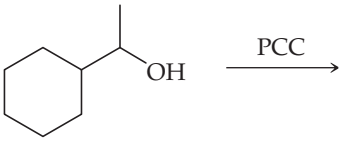
Exercises

28.7 Provide the structure of the major organic products in the following reactions:

(a) 

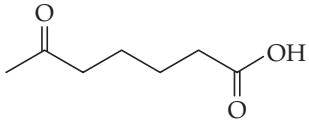
(b) 

(c) 

(d) 

(e) 

28.8 An unknown alkene was treated with ozone/dimethylsulfide and then with $K_2Cr_2O_7$, forming the following product. What was the alkene?

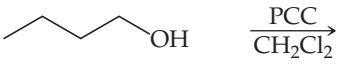


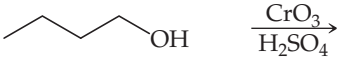
28.9 Suggest ways of conducting the following transformations.

(a) 

(b) 

28.10 Suggest a possible stable reaction product for each of the following reactions:

(a) 

(b) 

Answers to Self-Assessment Exercises

28.6 (a)

28.3 Reactions of Aldehydes and Ketones

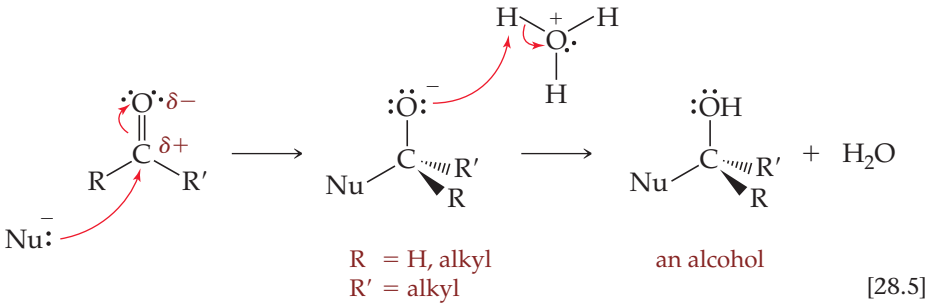


Throughout history, dyes have been used to color fabrics, as paints, and for skin coloring. The Picts of ancient Scotland were literally "The Painted People," who used the leaves of the woad plant (*Isatis tinctorial*) to produce a deep blue color. A more abundant source was provided by the plant *Indigofera tinctorial*, which grows in the tropics. As early as two thousand years ago, there was trade in the dye from India to the Mediterranean, where the highly prized dye became known as indigo. It was one of the few dyes that could color cotton in a process that involved soaking the cloth in a vat containing the water-soluble, reduced form of the dye and hanging the cloth to dry where aerial oxidation would produce the insoluble blue pigment familiar to us in denim jeans. The dye was very expensive, and, when Adolf von Baeyer discovered a synthetic route to indigo from 2-nitrobenzaldehyde and acetone, a new industry was born. He was awarded the Nobel Prize in chemistry in 1905 "in recognition of his services in the advancement of organic chemistry and the chemical industry, through his work on organic dyes and hydroaromatic compounds".

Carbonyl compounds form the basis of many important synthetic transformations, and, by the end of this section, you should be able to:

- Recognize a variety of nucleophilic addition reactions to carbonyl compounds
- Identify the structural factors that allow tautomerism
- Understand the mechanism of substitution α to a carbonyl group

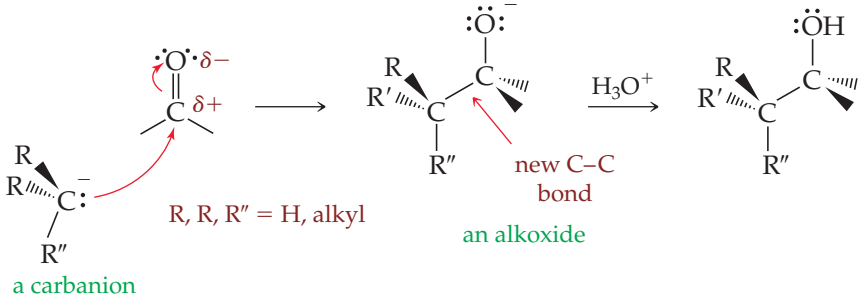
The carbon in a carbonyl group has a partial positive charge. Consequently it is susceptible to nucleophilic attack. Many important synthetic reactions depend on this fact. In this section we concentrate on reactions where the tetrahedral intermediate formed from the initial attack on an aldehyde or ketone by a nucleophile is reacted with acid to produce an alcohol. Generally, the reaction can be described as:



[28.5]

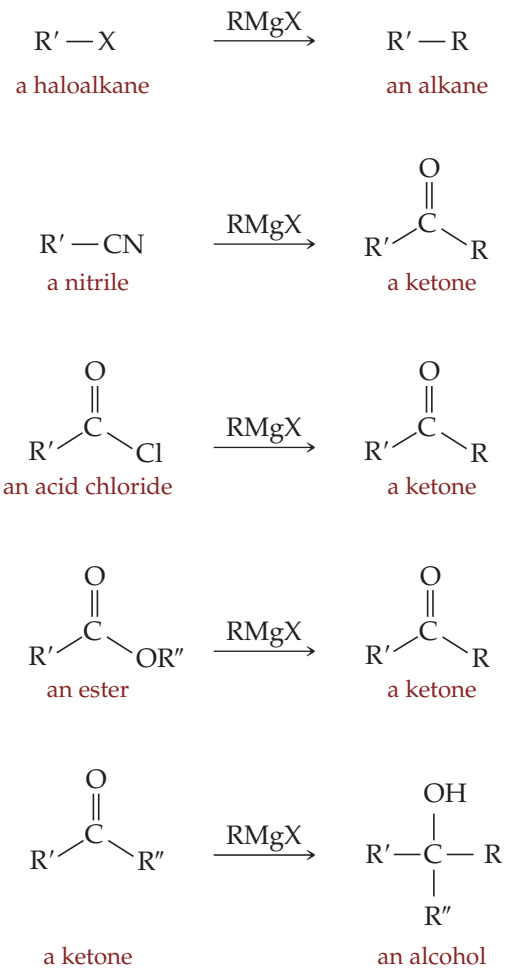
Addition of Carbon Nucleophiles—Grignard Reactions

Of the reaction types available to organic chemists, those that form new C—C bonds are especially useful. One example of C—C bond formation is the reaction of carbon nucleophiles, or **carbanions**, with carbonyl compounds:



[28.6]

Organometallic compounds such as Grignard reagents are a useful source of carbanions. An organometallic compound contains a bond between a carbon atom and a metal (designated C—M, where M = metal). The nature of the C—M bond can be ionic or covalent, depending on the choice of the metal. A **Grignard reagent** is one that uses magnesium as the metal, forming organomagnesium compounds of the general



▲ **Figure 28.3** **The versatility of Grignard reagents.**

type RMgX, where R = alkyl or aryl, and X = halide. For this discovery in 1902 and the general usefulness of these reagents in organic synthesis (**Figure 28.3**), Victor Grignard (1871–1935) shared the 1912 Nobel Prize for Chemistry with Paul Sabatier (1854–1941).

Many C—M bonds are covalent, but in bonds between carbon and more electropositive metals, the electrons that make up the bond reside closer to the carbon atom. Most C—M bonds, such as those formed between carbon and magnesium, are classed as polar covalent (**Figure 28.4**). Although an alkyl group bonded to a metal is not formally a carbanion, we can approximate it as such. Grignard reagents are formed by the addition of magnesium metal to a haloalkane in an ether solvent (for example, THF or diethyl ether). This exothermic reaction is sometimes called an oxidative metallation because the magnesium metal is oxidized to Mg^{2+}. The Grignard reagents are named as the alkyl magnesium halide.

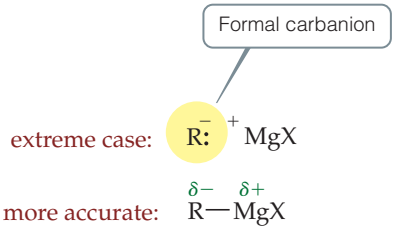
$$\underset{\text{1- bromobutane}}{CH_3CH_2CH_2\overset{\delta+}{C}H_2\overset{\delta-}{Br}} + Mg \xrightarrow{THF} \underset{\text{butyl magnesium bromide}}{CH_3CH_2CH_2\overset{\delta-}{C}H_2\overset{\delta+}{Mg}Br} \qquad [28.7]$$

The effect of magnesium insertion changes the polarity of the carbon that used to bear the halogen from positively polarized to negatively polarized. This change has a dramatic effect on reactivity.

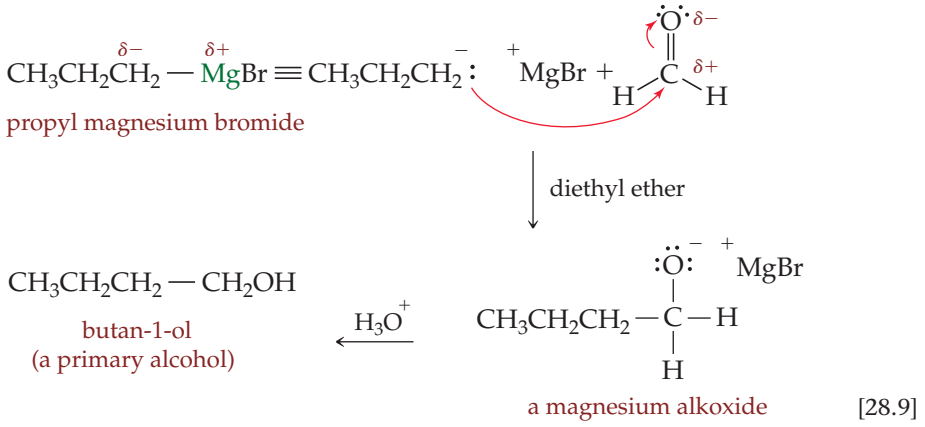
Grignard reagents are strong bases (as well as nucleophiles), so they are moisture-sensitive and tend to be prepared when needed rather than stored in a bottle. The presence of water will immediately protonate the Grignard reagent and generate the corresponding hydrocarbon.

$$\underset{\text{butyl magnesium bromide}}{CH_3CH_2CH_2\overset{\delta-}{C}H_2\overset{\delta+}{Mg}Br} \xrightarrow[THF]{H_2O} \underset{\text{butane}}{CH_3CH_2CH_2CH_3} \qquad [28.8]$$

The type of alcohol formed (1°, 2° or 3°) in a Grignard reaction is dictated by the nature of the carbonyl compound used. For example, addition of the Grignard reagent propyl magnesium bromide to formaldehyde yields butan-1-ol, a 1° alcohol, upon aqueous workup.

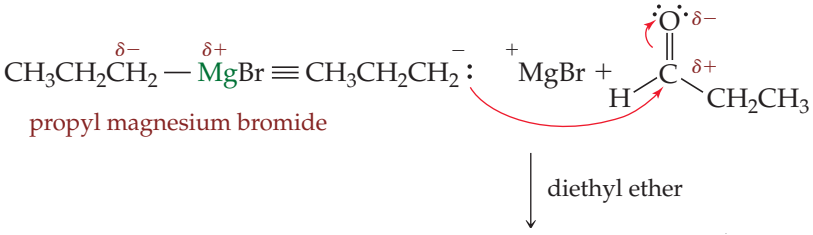


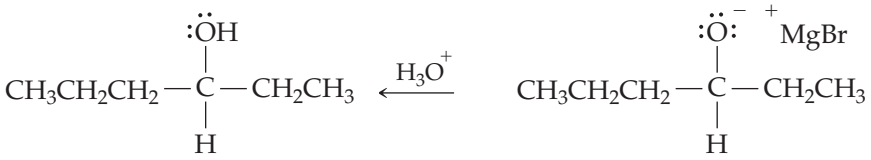
▲ **Figure 28.4** **Grignard reagents as carbanion equivalents.** The bonding between carbon and magnesium is best described as polar covalent. It is still useful to think of Grignard reagents as a form of carbanion.



[28.9]

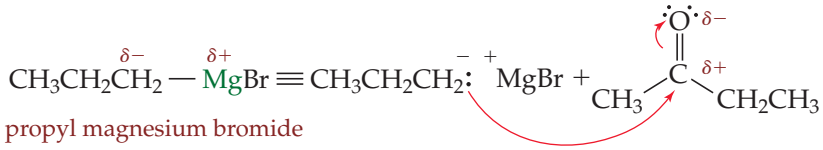
The addition of propyl magnesium bromide to any other aldehyde—for example, propanal—yields a 2° alcohol upon aqueous workup.



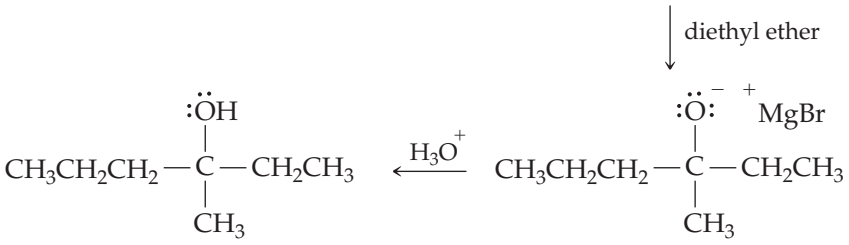


hexan-3-ol (a secondary alcohol) — a magnesium alkoxide [28.10]

The addition of propyl magnesium bromide to any ketone, such as 2-butanone, yields a 3° alcohol upon aqueous workup.



propyl magnesium bromide

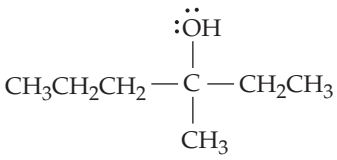


3-methylhexan-3-ol (a tertiary alcohol) — a magnesium alkoxide [28.11]

Sample Exercise 28.3

Addition of Grignard Reagents

The compound 3-methylhexan-3-ol can be prepared from three different combinations of ketones and Grignard reagents. Show each combination.



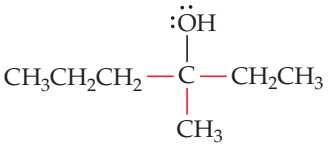
3-methylhexan-3-ol

SOLUTION

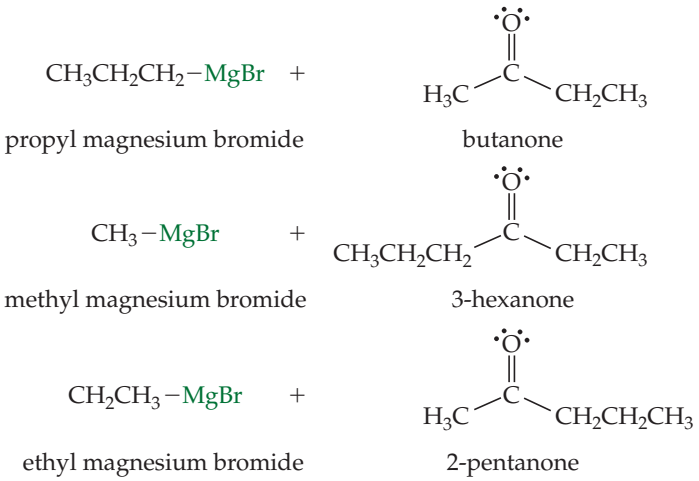
Analyze How can 3-methylhexan-3-ol be formed from three different ketones?

Plan Tertiary alcohols can be formed from ketones by reaction with carbanions and their equivalents. Since reaction about the C=O group leads to the formation of a C—C bond, we need to investigate the groups tethered off the C—OH group.

Solve First, let us identify in red the three C—C bonds that could be formed about the carbonyl carbon. This gives us a clue to the identification of ketones and Grignard reagents:



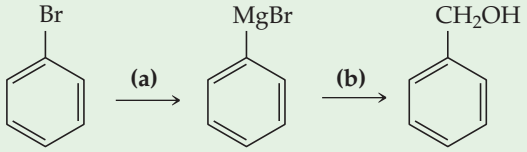
The C—OH grouping is derived from the carbonyl of the starting ketone. The substituents attached to this group could each be used to form the Grignard reagent. Hence, the three combinations are:



Continued

Practice Exercise

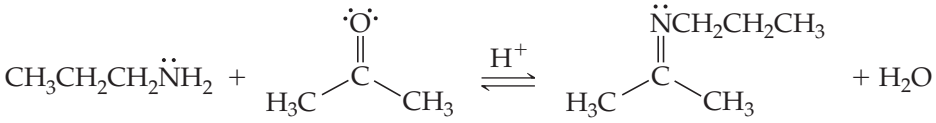
What reagents would you use to bring about the following transformations?



Addition of Nitrogen and Oxygen Nucleophiles: Formation of Imines and Acetals

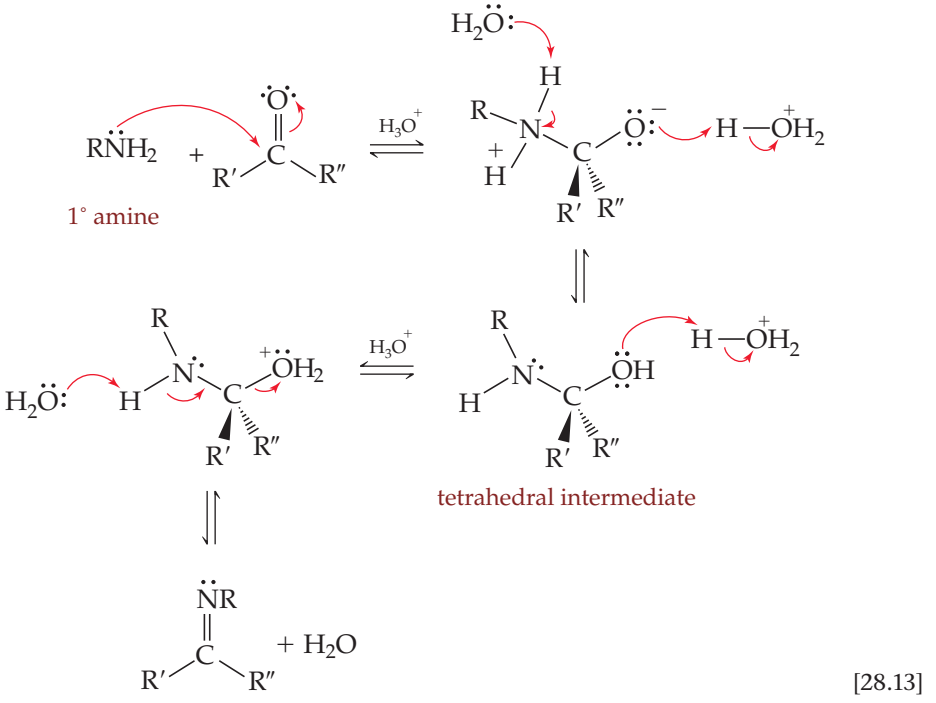
The formation of new C—C bonds through the reaction of a carbonyl compound with a Grignard reagent is not only high yielding, but also occurs only in the forward direction. This means that the reaction is not under the same level of equilibrium control we have discussed for the hydration of an alkene or the dehydration of an alcohol. However, other nucleophiles are able to react with carbonyl compounds, under equilibrium conditions, to form stable compounds. The two most important reactions are those of carbonyl compounds with amines (nitrogen-containing weak organic bases) to form *imines*, and those of carbonyl compounds with alcohols to form *acetals* and *hemiacetals*. Both reactions have biological significance.

Imines, also known as Schiff bases, are formed by the acid-catalyzed condensation of a *primary amine* (RNH_2, R = alkyl, aryl) an aldehyde or ketone. For example, the reaction of propanamine, an aliphatic 1° amine, with propanone is shown here. Imines are characterized by a C—N double bond. They have geometries similar to those of alkenes, with the lone pair occupying one of the trigonal planar positions.



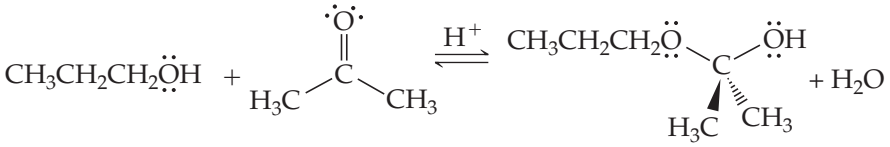
propanamine propanone an imine [28.12]

The mechanism of imine formation is shown in Equation 28.13. Attack of the nucleophilic amine on the electrophilic carbonyl carbon atom leads to a tetrahedral intermediate amino alcohol. The acid-catalyzed dehydration of this intermediate yields the imine. The reaction usually occurs at room temperature and in high yield. Removal of water as the reaction proceeds ensures near quantitative yields.

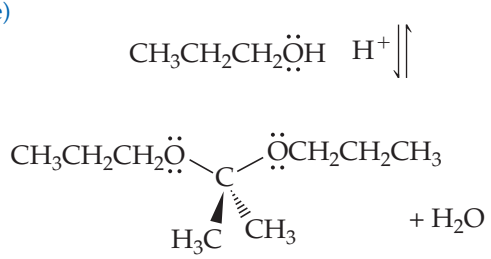


[28.13]

Acetals and **hemiacetals** are formed by the reaction of alcohols with aldehydes and ketones in the presence of an acid catalyst. In such reactions, the hemiacetal is formed in minor yield because it is relatively unstable. Further reaction with alcohol usually yields the acetal and water. Acetals are stable under basic and nucleophilic conditions, so provide a common way to protect aldehydes and ketones during complex reaction sequences in organic synthesis. Because the reaction is in equilibrium, acetal formation can be reversed by the addition of H_3O^+.

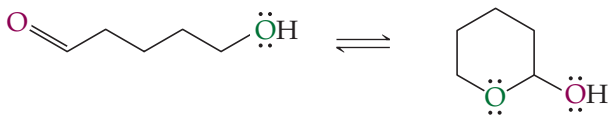


propan-1-ol propanone (acetone) a hemiacetal



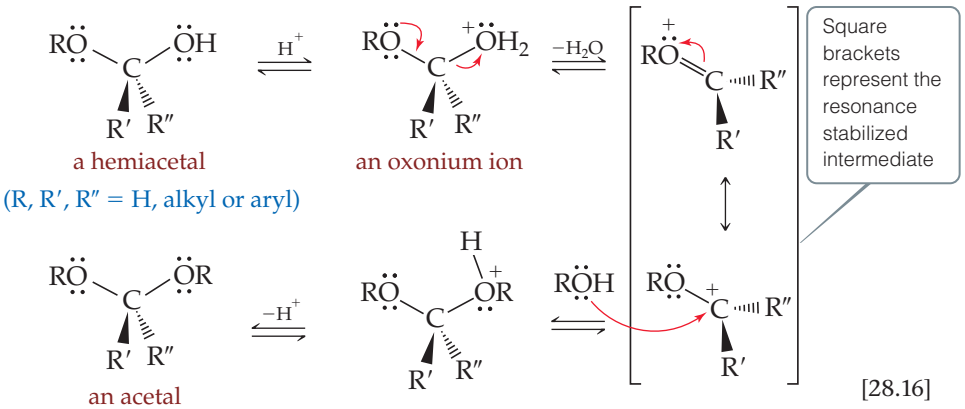
an acetal [28.14]

Hemiacetals are important in the function of *carbohydrates*, a class of biologically active molecules, of which sugars and cellulose are members. Carbohydrates gain their stability by undergoing *intramolecular* hemiacetal formation. To do this, carbohydrates must have aldehyde and alcohol functionality within the same molecule and at a distance apart that allows for cyclization. Typically, cyclic hemiacetals are five-membered (furanose) or six-membered (pyranose) systems. The equilibrium between cyclic and acyclic compounds is heavily favored towards the cyclic hemiacetal. The cyclization of 5-hydroxypentanal demonstrates the principle.



5-hydroxypentanal a cyclic hemiacetal [28.15]

The mechanism of acetal formation can be divided into two steps. The first, formation of the hemiacetal, follows a mechanism similar to that described for the reaction of amines with carbonyl compounds (without loss of water, Equation 28.13). Formation of the acetal from the hemiacetal is an acid-catalyzed process involving the generation of an oxonium ion. Loss of water leads to a resonance-stabilized carbocation. This carbocation reacts with another molecule of alcohol, which, after proton transfer, yields the acetal.



a hemiacetal (R, R′, R″ = H, alkyl or aryl) an oxonium ion

an acetal [28.16]

Sample Exercise 28.4

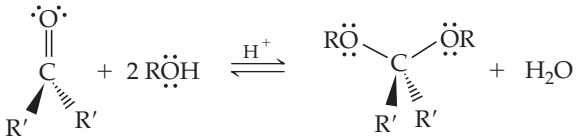
Acetals

Diols such as ethene glycol (1,2-ethanediol) are useful reagents with which to protect aldehydes and ketones in chemical syntheses. Give the product of the acid-catalyzed reaction of ethene glycol and cyclohexanone.

SOLUTION

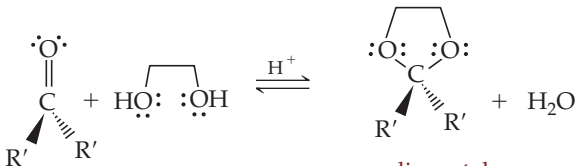
Analyze We are asked for the outcome of a reaction between an alcohol functional group and a ketone.

Plan Acetals require the acid-catalyzed addition of two alcohols to a ketone:



an acetal

Solve Ethene glycol acts to satisfy this need because it is a diol. Hence the product of this reaction is



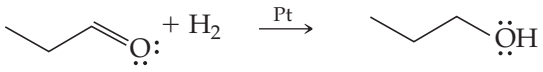
a cyclic acetal

Practice Exercise

What product would you expect from the acid-catalyzed reaction of benzaldehyde and ethanol?

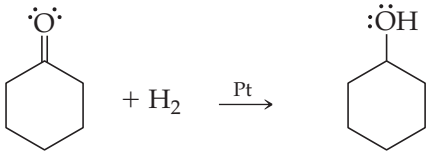
Reduction Reactions

Aldehydes and ketones are easily reduced to the corresponding primary and secondary alcohols, respectively. Catalytic hydrogenation, using Pd, Pt, Ni or Rh metal catalysts, is typically a high-yielding reaction and the product is easily isolated and purified.



aldehyde 1° alcohol

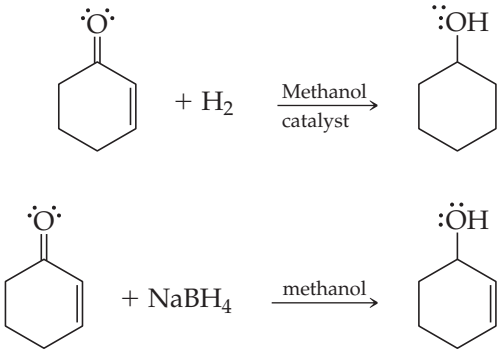
[28.17]



ketone 2° alcohol

[28.18]

In a laboratory situation, the reduction of aldehydes and ketones using **metal hydrides** is preferred over catalytic hydrogenation because it selectively reduces the carbonyl group rather than any alkene double bonds present and no gas-handling equipment is required.



[28.19]

The two most common metal hydride reagents are sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$). These compounds behave as a source of **hydride ion** (H^-),

Go Figure How soluble would sodium borohydride be in typical organic solvents? Why?



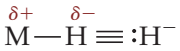
sodium borohydride
Non-reactive in water or methanol
Mild reductant
Selective for aldehydes and ketones

lithium aluminum hydride
Highly reactive in water or methanol
Powerful reductant
Reduces aldehydes, ketones, carboxylic acids and esters

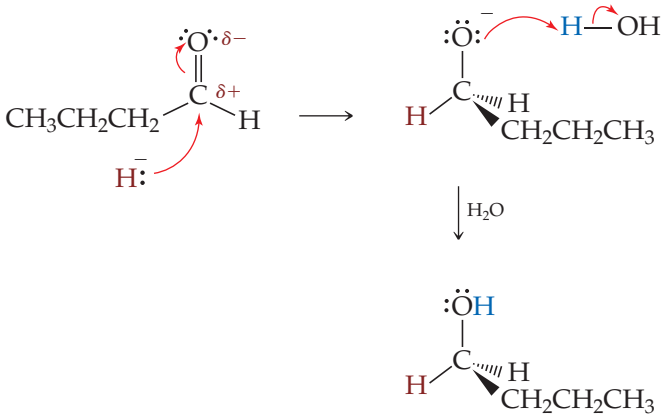
▲ **Figure 28.5 Metal hydrides.** The two most common metal hydrides for reduction are sodium borohydride and lithium aluminum hydride.

which is a powerful nucleophile. **Figure 28.5** shows the structural formula of both metal hydrides and compares their chemical reductive properties.

Metal hydrides act as a source of hydride ion (H^-) because they contain polar metal–hydrogen bonds, which place a partial negative charge on hydrogen in the same way as a negative charge is placed on carbon within a Grignard reagent:



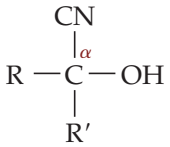
In fact, the mechanism for the reduction of an aldehyde or ketone by a metal hydride, which involves nucleophilic attack on the carbonyl group by hydride, followed by protonation, follows a similar pathway to that demonstrated for the Grignard reaction in Equation 28.10. A typical mechanism, showing the reduction of butanal using hydride, is



[28.20]

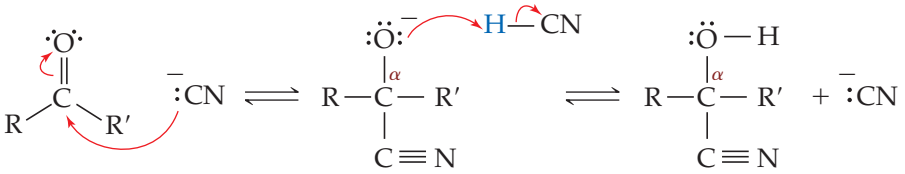
Cyanohydrins

Cyanohydrins are a class of compounds containing a hydroxy (—OH) and nitrile (—CN) group, both directly bonded to an α-carbon. Organic compounds containing the CN group are called **nitriles**. A cyanohydrin is therefore an *α-hydroxynitrile*.



a cyanohydrin

Cyanohydrins are formed by the addition of the cyanide ion ($^-$CN) to an aldehyde or ketone. Cyanide ion is the conjugate base of hydrogen cyanide (HCN), which is itself a weak acid ($pK_a \sim 9.2$). The cyanide ion is small, and because it is both a base and a strong nucleophile, it can add to the carbonyl group by a **nucleophilic addition** mechanism.



R, R′ = H, alkyl — a tetrahedral intermediate — a cyanohydrin [28.21]

In the first step, the strong $^-$CN nucleophile adds to the electropositive carbonyl carbon to give a tetrahedral alkoxide intermediate. Protonation of the alkoxide yields the cyanohydrin. Note that in the example here, the protonation step regenerates cyanide ion. Thus the process is truly catalytic in the addition of cyanide ion and this reaction is classed as a *base-catalyzed reaction*.

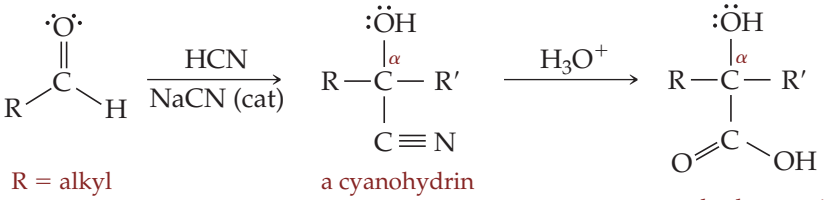
As shown by the mechanism in Equation 28.21, cyanohydrin formation is reversible. The formation of cyanohydrins is best with aldehydes, with formaldehyde being quantitative. Ketones are slower to react, though for simple ketones the yields are still greater than 90%. Bulky ketones do not react well, being slow and poor yielding. Note that the reversibility of cyanohydrin formation is put to use by the millipede *Apheloria corrugata,* which releases the cyanohydrin mandelonitrile from a storage gland to an outer chamber (**Figure 28.6**). There it is enzymatically degraded to benzaldehyde and hydrogen cyanide before being sprayed at an enemy as a defense mechanism. Cyanohydrins can be formed by using HCN with a catalytic amount of sodium or potassium cyanide to initiate reaction. Hydrogen cyanide, however, is highly toxic and volatile. A more practical method is to use sodium or potassium cyanide in a stoichiometric quantity dissolved in a protic solvent such as ethanol.

Nitriles such as those found in cyanohydrins are readily hydrolyzed to carboxylic acids under acidic conditions. In this case, cyanohydrins hydrolyze to give *α-hydroxy acids*.

Go Figure Suggest the structure of the organic compound produced by the generation of HCN from mandelonitrile.



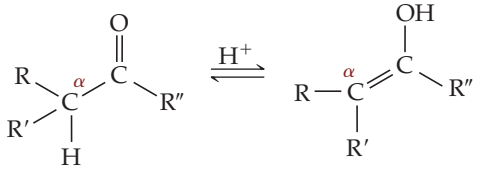
▲ **Figure 28.6 Millipede defense.** *Apheloria corrugata* releases mandelonitrile as part of its defense strategy. The nitrile is degraded to hydrogen cyanide which is deadly to predators.



[28.22]

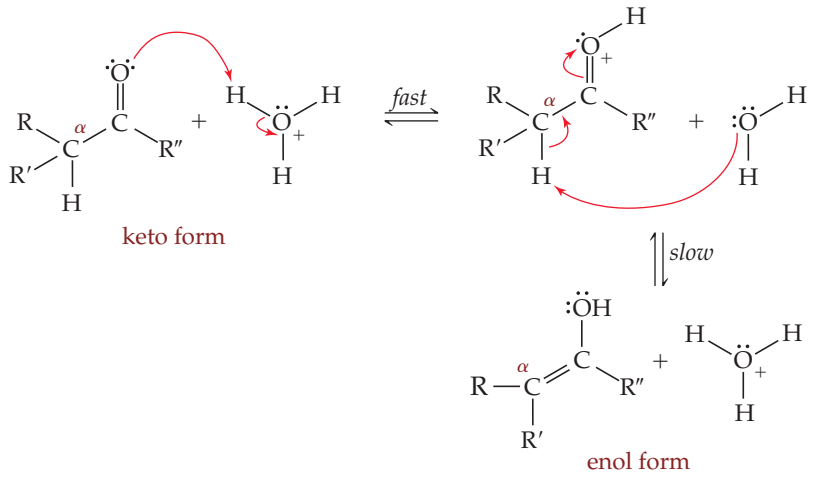
Tautomerism in Aldehydes and Ketones

Aldehydes and ketones bearing an α-hydrogen (that is, a hydrogen on a carbon atom next to the carbonyl carbon) are able to undergo tautomerism to form enols ("ene ols", or a compound bearing a double bond (alkene) and a hydroxyl group (alcohol)). Enols are constitutional isomers of their respective *keto* form (that is, an aldehyde or ketone). **Tautomerism** is the process by which two isomers, in this case the aldehyde or ketone and the enol, are interconverted by a formal movement of an atom or group, following normal valency rules. Hence an enol and its keto form are *tautomers* of the same structure.



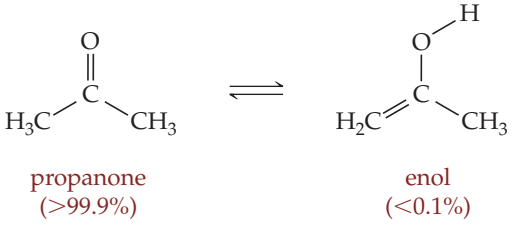
[28.23]

Aldehydes and ketones are in equilibrium with their enol forms and this equilibrium is acid catalyzed. The process involves two separate proton transfers rather than a single proton jump, as might be expected just by looking at Equation 28.23. What tautomerism exploits is essentially the relative acidity of the α-hydrogen (pK_a ~9–13).

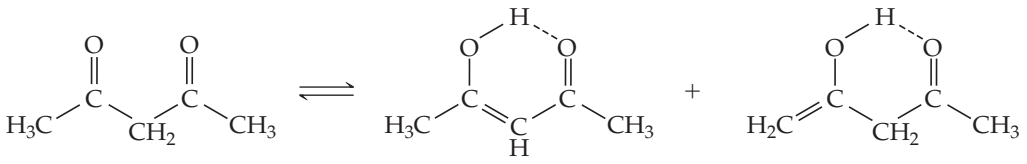


[28.24]

The extent of tautomerization depends very much on the aldehyde or ketone. For example, propanone (acetone) exists >99.9% in the ketone form, whereas 2,4-pentanedione exists preferentially as the enol (~80%) by virtue of stabilising hydrogen bonding.



[28.25]



2, 4-pentanedione (20%) | major enol formed | minor enol formed

(80%)

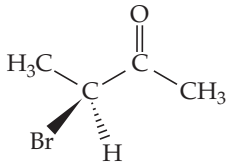
[28.26]

Though many aldehydes and ketones do not exist in the enol form to a large extent, enols do play a significant part in the reactivity of aldehydes and ketones. One example, that of halogenation, is the next topic of discussion.

Sample Exercise 28.5

Keto–enol Tautomerism

Some ketones, such as the one shown here, are chiral. In solution, such compounds are quite stable and retain their optical activity. However, the addition of a small amount of acid causes the optical rotation to tend to 0° over time. Comment on why this is so.

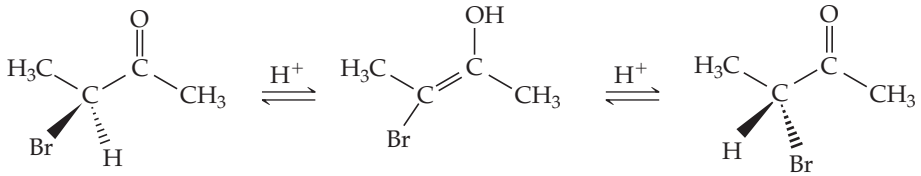


SOLUTION

Analyze We are asked about the acid-catalyzed stereoisomerization of ketones bearing a stereocenter on the α-carbon.

Plan Ketones undergo tautomerism to the enol form if they possess a hydrogen atom alpha to the carbonyl group. We need to explain the loss of optical activity.

Solve There are two possible causes. Since this ketone has an α-hydrogen, and optical activity is lost under acidic conditions, there is a high chance that tautomerism is occurring, leading to the achiral enol. However, we know that tautomerism is an equilibrium, so the enol is able to reconvert to the keto form. In this case, the proton could add from behind the page (leading to the original structure) or it could add from in front of the page, leading to the enantiomer. Since there is nothing to favour the addition from one face or the other, both are equally likely, leading to a racemic mix. This can be summarized as the following:



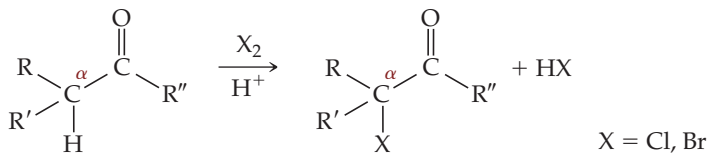
keto form | enol form | keto form

Practice Exercise

Draw the enol forms of **(a)** cyclohexanone, **(b)** 3-pentanone and **(c)** propanal.

Halogenation of Aldehydes and Ketones

Aldehydes and ketones undergo a substitution reaction at the α-carbon in the presence of molecular chlorine or bromine in good yield.

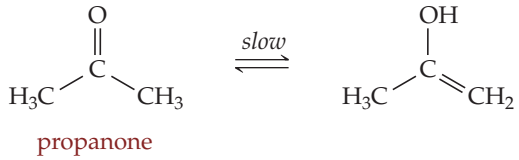


aldehyde or ketone | α-halo aldehyde or ketone

X = Cl, Br

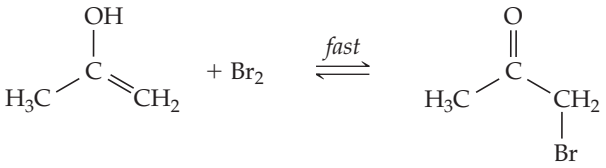
[28.27]

This reaction is *regiospecific* in that *only* the α-hydrogen is substituted under these conditions. Interestingly, when the reaction was first studied mechanistically by Arthur Lapworth (1872–1941) in 1904, he discovered that the rates of chlorination, bromination and iodination were all the same. This meant that halogenation occurred after the rate-determining step. We now know that the rate-determining step is the conversion of the ketone to its enol isomer. Let us look at this reaction in more detail, using the bromination of propanone (acetone) as the example.



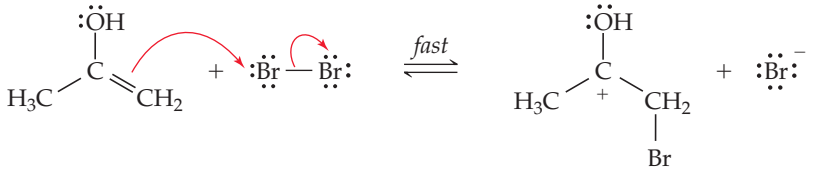
propanone

[28.28]



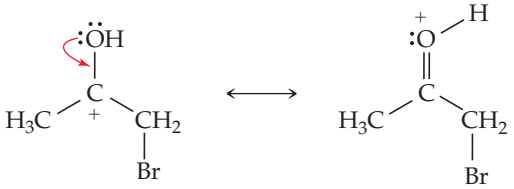
[28.29]

We can understand the enol halogenation by comparing it to the halogenation of an alkene. The first step involves attack of the double bond of the enol on bromine.



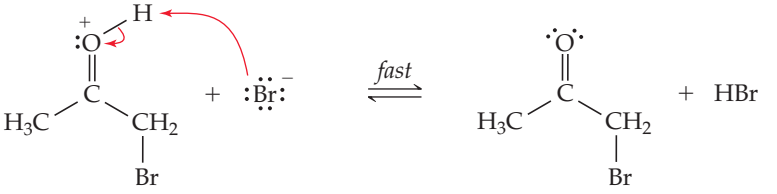
[28.30]

If the reaction followed the bromination of an alkene, then the next phase of the mechanism would be the formation of the second C—Br bond by attack of the bromide ion on the carbocation intermediate in an *intermolecular* reaction. However, in this case, the lone pair on the oxygen can stabilize the carbocation by resonance with the major resonance contributor being the oxonium ion.



[28.31]

The final stage is loss of a proton to yield the desired α-haloketone.



[28.32]

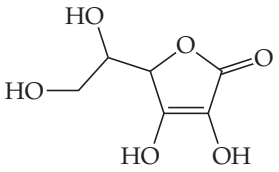
Self-Assessment Exercises

28.11 What reagent is used in the following transformation?

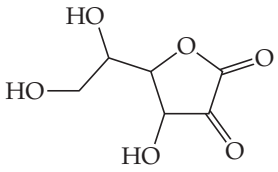


(a) $NaBH_4$ followed by H_3O^+
(b) CH_3MgI followed by H_3O^+
(c) HCN

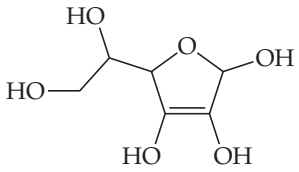
28.12 Which of the following structures is a tautomer of vitamin C?



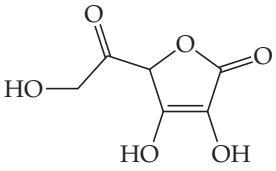
vitamin C



(a)

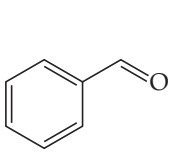


(b)

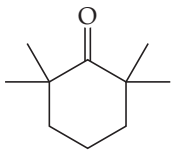


(c)

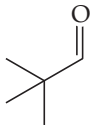
28.13 Which of the following molecules will react with iodine?



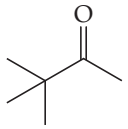
(a)



(b)



(c)



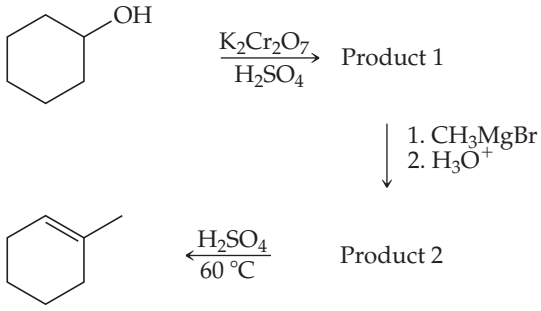
(d)

Exercises

28.14 Which reducing agent is best used in this reaction?

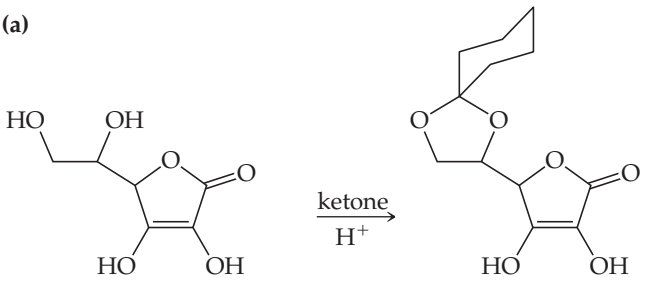


28.15 Draw the likely product for each transformation.



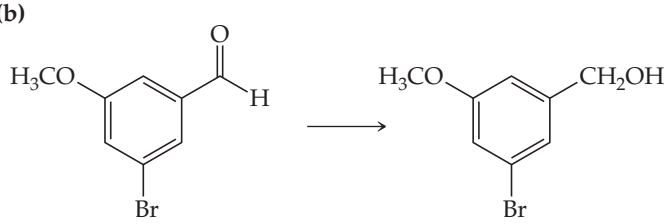
28.16 Write down the reagents necessary to make the following conversions:

(a)

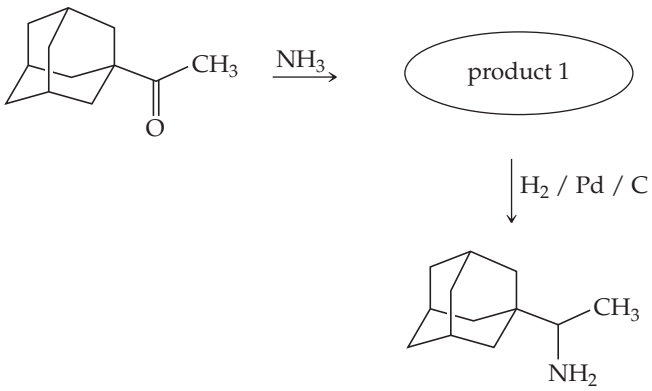


ascorbic acid

(b)

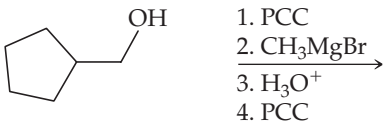


28.17 Rimantadine is effective in preventing infections caused by the influenza A virus. The final steps in the synthesis of this compound are shown. Complete the reaction sequence by placing in the missing structure.



rimantadine

28.18 Provide the major organic product for the following set of reactions.

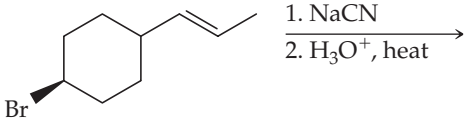


28.19 Provide the major organic product for the following set of reactions.

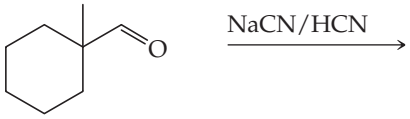
(a)



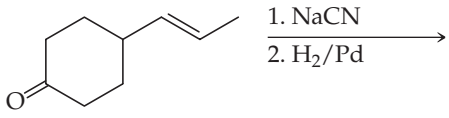
(b)



(c)



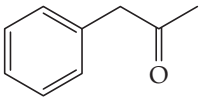
(d)



(e)



28.20 Draw the most stable enol tautomer of the ketone shown here. Explain your choice.



28.21 What is the carbon nucleophile that attacks molecular bromine in the acid-catalyzed α-bromination of a ketone?

Answers to Self-Assessment Exercises

28.11 (b) **28.12** (a) **28.13** (d)

28.4 Carbohydrates



Sugar is one of the oldest and best documented of all commodities. The crystallinity of the popular sugars—mainly sucrose, lactose, and fructose—as well as their sweet flavor has made them popular for over two millennia.

Sugar is classified as a member of the carbohydrate food group, and its main natural sources are sugar cane (*Saccharum* spp.) and sugar beets (*Beta vulgaris*), in which sugar can account for 12% to 20% of the plant's dry weight. During the times of Alexander the Great,

sugar cane arose as a popular alternative to honey, with people chewing on the raw cane to extract its sweetness.

Today, most sugar cane comes from countries with warm climates, such as Brazil, India, China, Thailand, Mexico, and Australia, the top sugar-producing countries in the world. From a regional perspective, Asia produces more sugar cane than any other region.

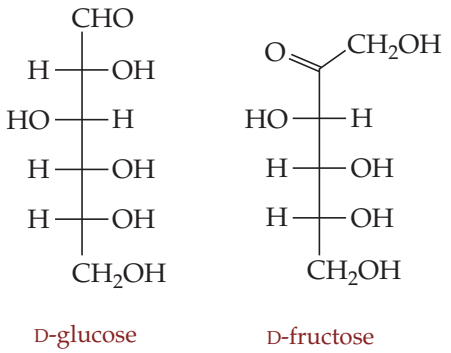
Refined sugar can be made by dissolving raw sugar and purifying it using phosphoric acid. Alternative methods of purification include a carbonation process involving calcium hydroxide and carbon dioxide, or various filtration strategies. The sugar is then further purified by filtration through a bed of activated carbon or bone char, depending on where the processing takes place. White refined sugar is typically sold as granulated sugar, which has been dried to prevent clumping.

Understanding the chemistry of sugars and appreciating their structure requires a grounding in the chemistry of the carbonyl (C═O) group from which aldehydes and ketones are formed. By the end of this section, you should be able to:

- Understand the components that make up a carbohydrate
- Be able to identify an anomeric carbon atom
- Recognize the meaning of the different parts that make up a name of a carbohydrate molecule

Carbohydrates are an important class of naturally occurring substances, found in both plant and animal matter. They perform a variety of vital functions, such as energy storage; they act as structural components in plants; and they are an essential component of the nucleic acids, DNA and RNA, which store genetic information. The name **carbohydrate** (hydrate of carbon) comes from the empirical formulas for most substances in this class, which can be written as $C_x(H_2O)_y$ (x, y integers). For example, **glucose**, the most abundant carbohydrate, has the molecular formula $C_6H_{12}O_6$, which could also be written as $C_6(H_2O)_6$. Carbohydrates are not really hydrates of carbon; rather, they are polyhydroxyaldehydes and ketones. Glucose, for example, is a six-carbon aldehyde sugar; *fructose*, the sugar that occurs widely in fruit, is a six-carbon ketone sugar (Figure 28.7).

Go Figure How many chiral centers are there in the open-chain form of glucose?



D-glucose D-fructose

▲ **Figure 28.7 Linear structure of glucose and fructose.** Together with galactose, glucose and fructose are the most common carbohydrates found in nature.

Monosaccharides

Both glucose and fructose are examples of **monosaccharides**—simple sugars that can't be broken into smaller molecules by hydrolysis with aqueous acids. Monosaccharides have the general formula $C_nH_{2n}O_n$ (where the integer $n = 3$ to 8). They are classified by their functionality as well as by the number of carbon atoms they contain.

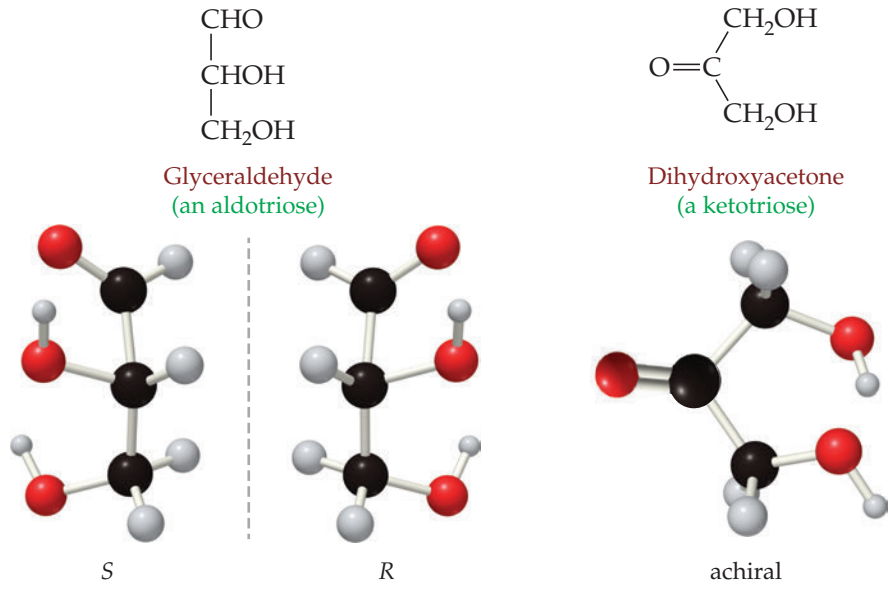
Polyhydroxyaldehydes are known as **aldoses** to signify the aldehyde functional group, while polyhydroxyketones are classified as **ketoses** to signify the ketone group within the molecule. For example, *glucose* is an *aldose* and *fructose* is a *ketose* (see Figure 28.7). Table 28.1 lists the names of different monosaccharide classes based on the number of carbon atoms within that molecule. Based on this table, glucose can be further classified as an *aldohexose*, and fructose as a *ketohexose*. The simplest monosaccharides are the trioses: glyceraldehyde and 1,3-dihydroxyacetone (Figure 28.8). These two molecules are constitutional isomers. Glyceraldehyde, an aldotriose, is chiral because the central carbon atom is a stereocenter. The achiral dihydroxyacetone is classified as a ketotriose.

TABLE 28.1 Classifying monosaccharides

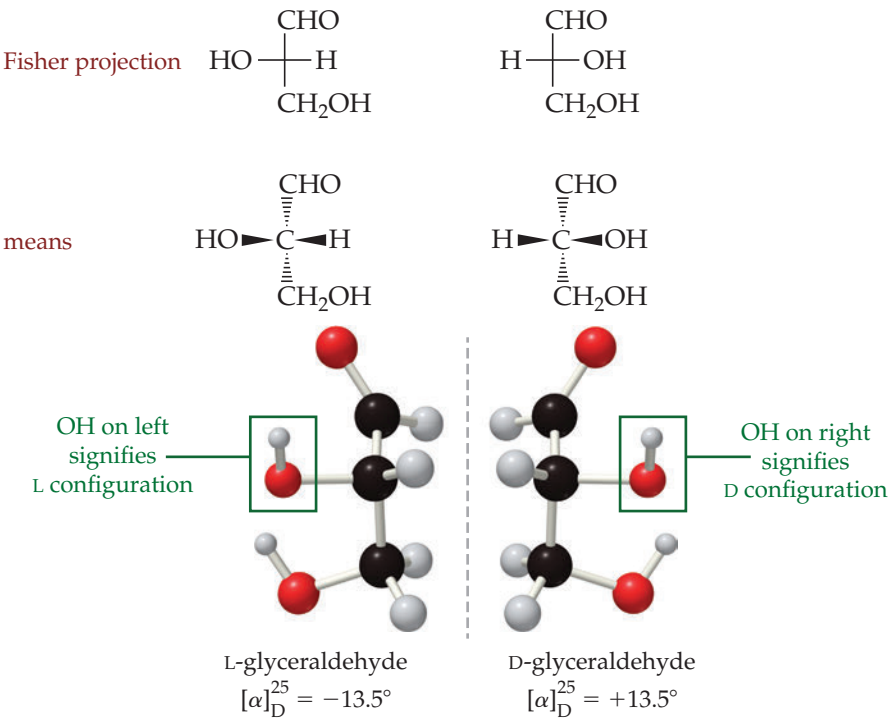
Name	Formula
Triose	$C_3H_6O_3$
Tetrose	$C_4H_8O_4$
Pentose	$C_5H_{10}O_5$
Hexose	$C_6H_{12}O_6$
Heptose	$C_7H_{14}O_7$
Octose	$C_8H_{16}O_8$

Let's return to Figure 28.7. Notice that the structures have been named D-glucose and D-fructose, yet there is no indication of stereochemistry using the now customary bold and dashed wedges. In fact, these two molecules do infer stereochemistry and are being shown as **Fischer projections**. This representation, which is most common among carbohydrates, is a two-dimensional representation of chiral centers. The carbon stereocenters are not shown, which is an indication that Fischer projections are being used. Figure 28.9 illustrates how the Fischer projections for glyceraldehyde relate to the types of structures you have become familiar with. Fischer projections are drawn so that the most oxidized carbon (usually the aldehyde or ketone) is positioned at the top of the drawing. The vertical lines

Go Figure Why is dihydroxyacetone achiral?



▲ **Figure 28.8 Glyceraldehyde and dihydroxyacetone.** A structural formula and ball-and-stick representations of the two trioses are shown. Glyceraldehyde, which contains a stereocenter, is chiral and can exist as an *S*- or *R*-enantiomer.

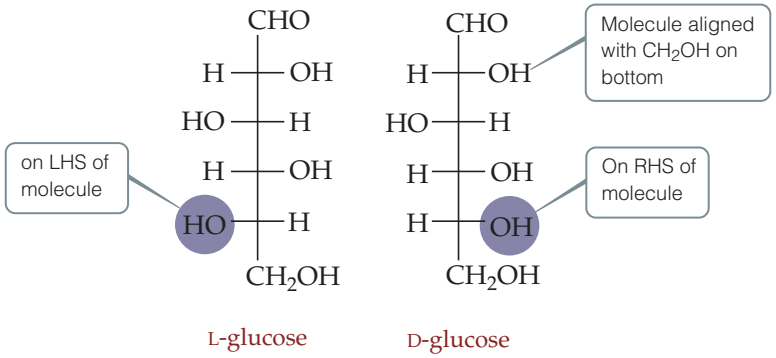


◀ **Figure 28.9 Fischer projections.** The D and L nomenclature for monosaccharides is referenced from D- and L-glyceraldehyde. The reference point is the position of the carbon stereocenter furthest away from the carbonyl group (aldehyde or ketone).

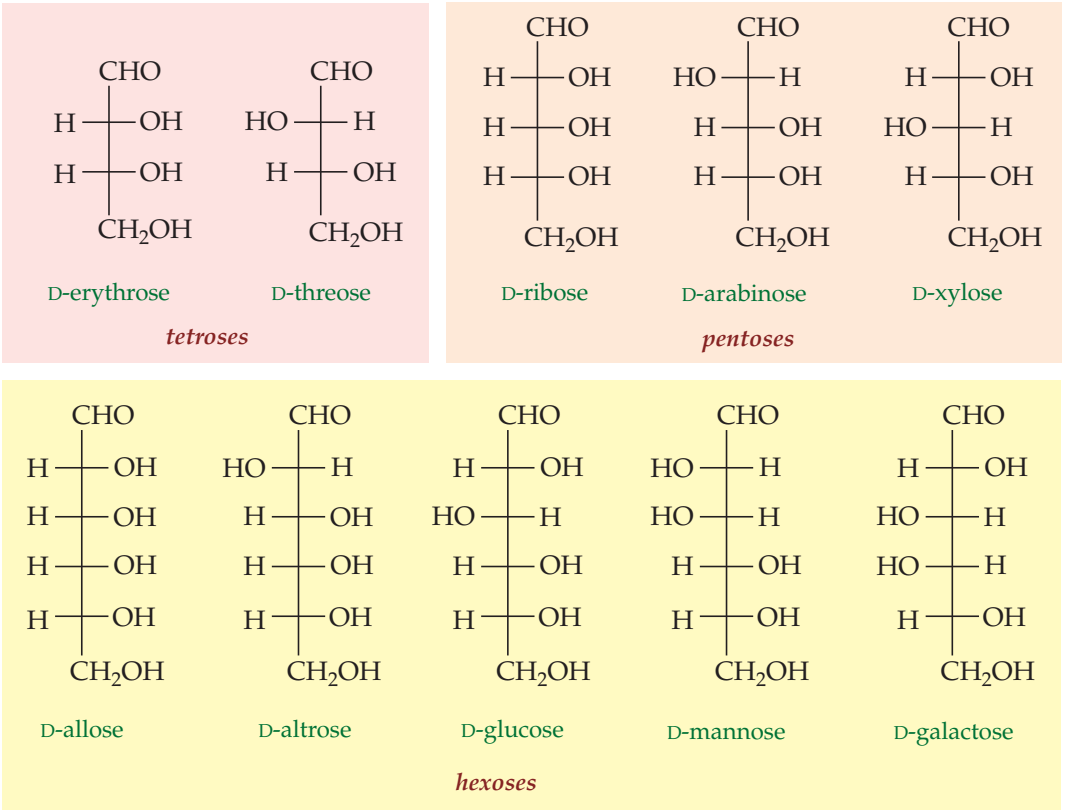
represent bonds oriented back into the page, while the horizontal lines represent bonds coming out of the page. The point at which they cross indicates a stereocenter.

The trioses D- and L-glyceraldehyde serve as the reference for determining whether a carbohydrate has the D or L configuration. According to the conventions proposed by Fischer, the D form of a carbohydrate implies that the OH group on the carbon stereocenter furthest away from the aldehyde (or ketone) is positioned on the right-hand side of the molecule, as is the case for D-glyceraldehyde (**Figure 28.10**). Conversely, a carbohydrate is in

▶ **Figure 28.10** **Fischer projections of D- and L-glucose.**



▶ **Figure 28.11** **Configurational relationships between selected naturally occurring aldoses.**

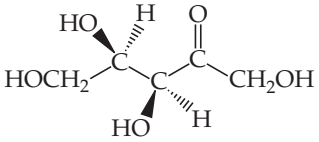


the L form when the OH group on the furthest stereocenter from the aldehyde (or ketone) is positioned on the left-hand side of the molecule. Almost all biological carbohydrates are of the D form. Several of the more common naturally occurring carbohydrates are shown in **Figure 28.11**.

Sample Exercise 28.6

Fischer Projections

Draw the Fischer projection of the following carbohydrate. By what name would you classify this molecule? Is this molecule in the D or L configuration?

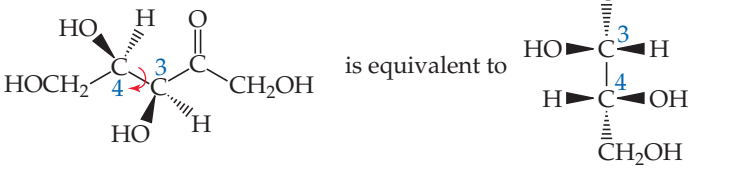


SOLUTION

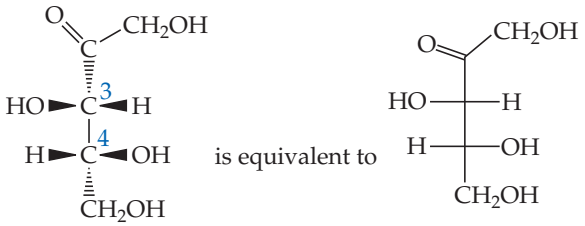
Analyze We are asked to convert the open-chain form of a carbohydrate into its Fischer projection, class it as aldose or ketose, and determine its configuration using the D, L nomenclature.

Plan To begin, we need to arrange the molecule in such a way that the OH groups and H atoms point out of the page and convert this to a Fischer projection. The Fischer projection will also help determine D, L configuration based on glyceraldehyde. We can classify this carbohydrate based on the number of carbon atoms present and the carbonyl functional group contained—whether aldehyde or ketone.

Solve Arranging the structure in such a way that the OH groups and H atoms point out of the page is achieved by rotating about the C3–C4 bond:



Position the structure in such a way that the ketone group is at the top of the molecule. From this point, the conversion from a stereoview to the Fischer projection is:

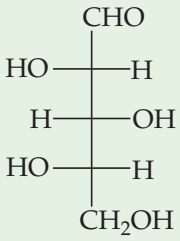


This molecule is classified as a *ketopentose*. It has the D configuration because the OH group on the stereocenter furthest from the ketone is positioned on the RHS, comparable with D-glyceraldehyde.

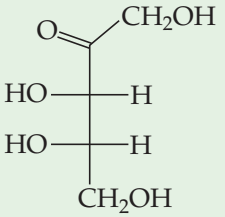
Practice Exercise

Which molecules are D-monosaccharides and which are L-monosaccharides? What are their classifications?

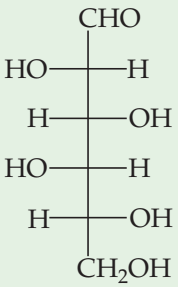
(a)



(b)

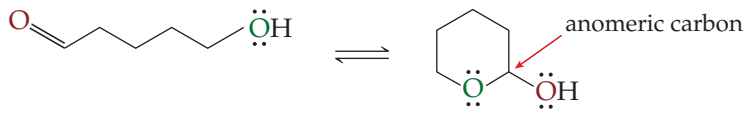


(c)



Cyclic versus Open-Chain Structures

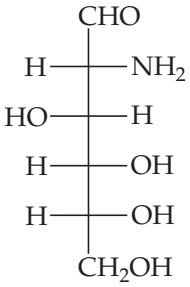
In Section 28.3 we discussed the reaction of aldehydes and ketones with alcohols to form hemiacetals and acetals. We also discussed the formation of cyclic hemiacetals by an intramolecular reaction between a hydroxyl group and an aldehyde or ketone. For example, 5-hydroxypentanal forms a cyclic six-membered hemiacetal. Notice that this reaction converts an acyclic, achiral molecule into a cyclic, chiral molecule. The new stereocenter created in forming the cyclic structure is called the **anomeric carbon**.



5-hydroxypentanal a cyclic hemiacetal [28.33]

CHEMISTRY AND LIFE Glucosamine

Amino sugars such as glucosamine contain an NH_2 group in place of one of the OH groups (Figure 28.12). Only three amino sugars are commonly found in nature: D-glucosamine, D-mannosamine and D-galactosamine. D-Glucosamine is an amino derivative of glucose that is found especially in the polysaccharides contained within chitin, shellfish and cell membranes. Its use in the formation and repair of cartilage has more recently seen its popularity increase as a *nutraceutic*—a natural product with the capacity to prevent or heal disease.



D-glucosamine



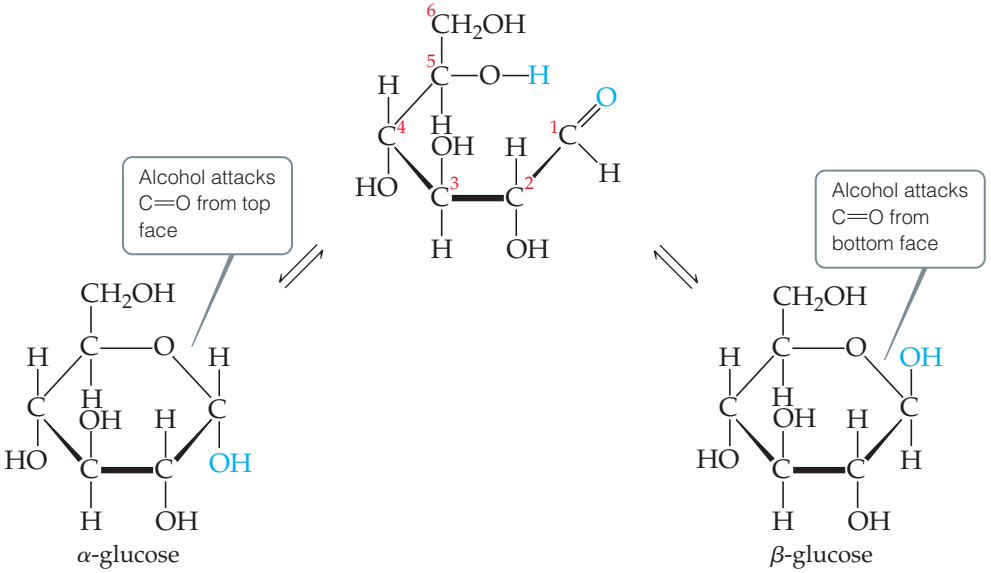
▲ **Figure 28.12 Glucosamine is sold as a dietary supplement.**

Glucosamine and its salts, most commonly the hydrochloride or sulfate salts, have been included in recent guidelines as therapy options for people with symptomatic osteoarthritis, especially in the knees. Osteoarthritis is a condition that involves damage to the cartilage in the joints of humans and animals, causing pain and stiffness. Glucosamine can be isolated in quantity from shellfish or shark cartilage or prepared synthetically.

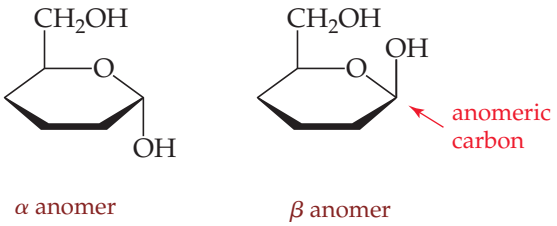
Glucosamine and its salts are widely available as licensed products or health supplements, and may also be combined with chondroitin, vitamins and various herbs. In Australia, glucosamine is classified as a complementary medicine and is available as over-the-counter supplements. It is thought that supplementing glucosamine levels in the body will replace the deficit and restore the proper glucosamine balance.

Glucose, having both hydroxyl and carbonyl groups, and a reasonably long and flexible backbone so as to form an unstrained ring structure, can also react intramolecularly to form a six-membered ring structure, as shown in Figure 28.13. In fact, only a small percentage of glucose molecules are in the open-chain form in aqueous solution. Of the two cyclic forms for D-glucose, the β form is present in greater proportion in glucose solutions. Although the ring is often drawn as if it were planar, the molecules are actually non-planar because of the tetrahedral bond angles around the C and O atoms of the ring. This planar way of representing the cyclic structures of monosaccharides is known as a **Haworth projection**. Named after W. Norman Haworth (1883–1950), recipient of the 1937 Nobel Prize for Chemistry for research in carbohydrate chemistry, this representation is a simplified way to visualize the complexities of cyclic saccharides. Convention is to write the structure with the anomeric carbon on the right side and the hemiacetal ring oxygen in the back right position.

Go Figure How many hydroxyl groups are in an equatorial position in β-glucose?



▲ **Figure 28.13 Cyclic glucose.** The carbonyl group of a glucose molecule can react with one of the hydroxyl groups to form either of two six-membered ring structures, designated α and β.



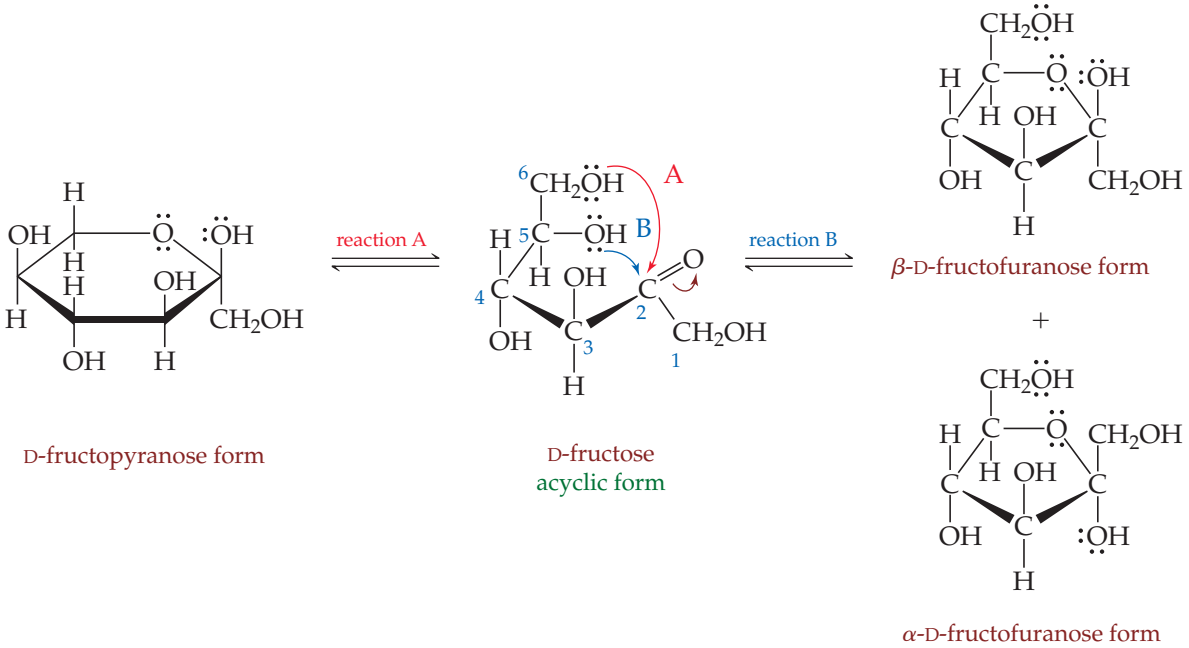
◀ **Figure 28.14 Anomers.** The α and β anomers differ by their orientation to the CH_2OH group outside the ring.

Figure 28.13 indicates that the ring structure of glucose can have two relative orientations at the anomeric carbon. In the α form, the OH group on the anomeric carbon (C1) and the CH_2OH group on C5 point in opposite directions. In the more stable β form, the OH group on the anomeric carbon and the CH_2OH group on C5 point in the same direction. The α and β forms are called **anomers** (Figure 28.14). Although the difference between the α and β forms might seem small, it has enormous biological consequences. As we will soon see, this one small change in structure accounts for the vast difference in properties between the biopolymers starch and cellulose.

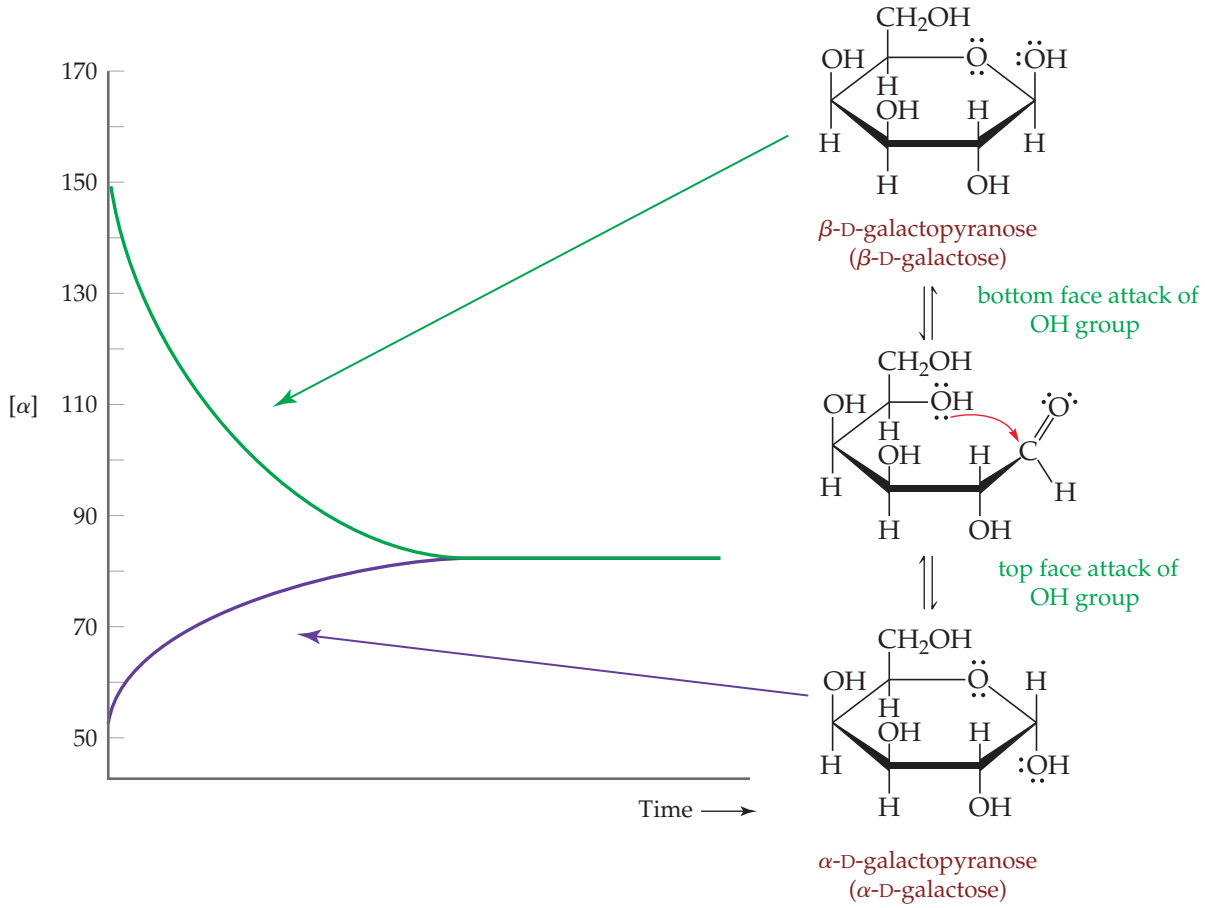
Fructose can cyclize to form either five- or six-membered rings (Figure 28.15). The five-membered ring forms when the OH group on C5 reacts with the carbonyl group on C2 (reaction B in Figure 28.15). The six-membered ring results from the reaction between the OH group on C6 and the carbonyl group on C2 (reaction A in Figure 28.15). Monosaccharides that exist as six-membered rings are named as derivatives of the oxygen-containing heterocycle, pyran. Hence, a cyclic monosaccharide that forms a six-membered ring is named a *pyranose*. Five-membered ringed monosaccharides are named as derivatives of the oxygen-containing heterocycle, furan. Hence, a cyclic monosaccharide that forms a five-membered ring is named a *furanose*.



We are now armed with enough information to name a cyclic monosaccharide unambiguously. For example, the top right-hand structure shown in Figure 28.15 has the name



▲ **Figure 28.15 Fructofuranose and fructopyranose.** Fructose is just one of many monosaccharides that are able to exist in furanose and pyranose forms.



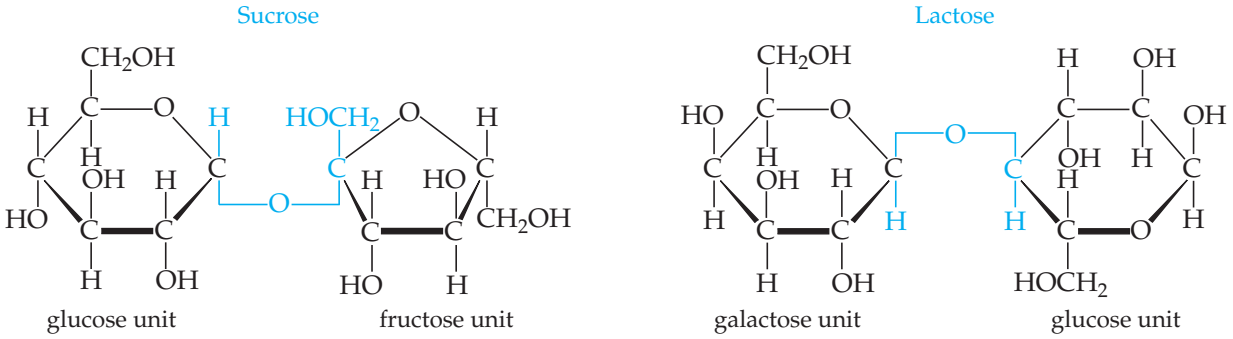
▲ **Figure 28.16 Mutarotation of D-galactose.** At equilibrium, D-galactose exists as a 72 : 28 mixture of α : β anomers. The mutarotation process is easily followed by changes in the specific rotation of pure samples of both anomers.

β-D-fructofuranose. This name indicates that the five-membered cyclic monosaccharide is derived from D-fructose. The β anomer has the OH and CH_2OH group found on C5 of the furanose form on the same side, which allows us to put in place the only unanswered variable from the open-chain form. As a point of completion, the two structures in Figure 28.13 are fully named α-D-glucopyranose and β-D-glucopyranose, although α-D-glucose and β-D-glucose are also acceptable.

The inference that the α and β anomers are interconvertible through an acyclic intermediate, as shown in Figure 28.15, is entirely true. This process, called **mutarotation**, is common to all carbohydrates that exist in a cyclic hemiacetal form. Mutarotation is easily observable by monitoring the specific rotation of an aqueous solution of either anomer over time. For example, a solution prepared by dissolving crystalline β-D-galactose in water shows an initial rotation of +151°. Over time, this value decreases until, at equilibrium, a rotation value of +80° is observed (**Figure 28.16**). The value of the rotation corresponds to a 72 : 28 ratio of α : β anomers in solution. A similar experiment can be performed using crystalline α-D-galactose. Initially, the rotation of a solution of α-D-galactose in water is +53°. Over time, this value rises as a result of the mutarotation, forming larger quantities of β-D-galactose. At equilibrium, a rotation value of +80° is also achieved (Figure 28.16). The value of the rotation still corresponds to a 72 : 28 ratio of α : β anomers in solution at equilibrium.

Oligosaccharides and Polysaccharides

Two monosaccharide units can be linked together by a condensation reaction to form a *disaccharide*. The structures of two common disaccharides, *sucrose* (table sugar) and *lactose* (milk sugar), are shown in **Figure 28.17**. The word *sugar* makes us think of sweetness. All



▲ **Figure 28.17 Two disaccharides.** The structures of sucrose (left) and lactose (right). Note that the glycosidic bond (blue) is often shown with a 90°-kink in it. This is for ease of representation and does *not* indicate an extra carbon atom.

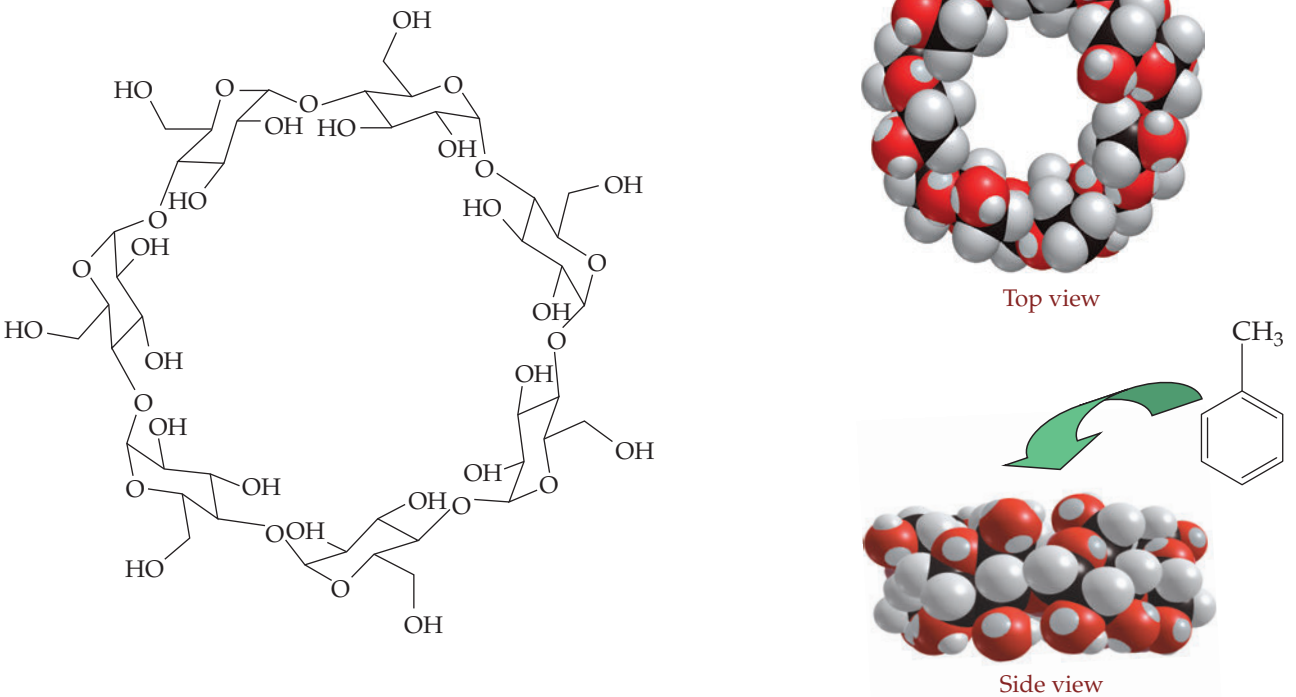
sugars are sweet, but they differ in the degree of sweetness we perceive when we taste them. Sucrose is about six times sweeter than lactose, slightly sweeter than glucose, but only about half as sweet as fructose. Disaccharides can react with water (hydrolysis) in the presence of an acid catalyst to form two monosaccharides. When sucrose is hydrolyzed, the

CHEMISTRY AND LIFE Cyclodextrins

Cyclodextrins, such as the one shown in **Figure 28.18**, are *macrocyclic* compounds with the ability to include small organic molecules within their cavity. These cyclic molecules, which are composed of glucose units, have a *hydrophobic* (water-hating) interior and a *hydrophilic* (water-loving) exterior, due to the fact that the OH groups radiate out from the macrocycle rather than in towards the center. This feature causes cyclodextrins to be water soluble. Molecules that are hydrophobic (that is, do not mix with water) are easily included within the cyclodextrin cavity, provided they are not too large.

Cyclodextrins have found uses recently as solubilising agents. For example, toluene is immiscible with water, forming a separate layer when added to water. The addition of cyclodextrin to the aqueous layer causes the two layers to mix by providing a way of optimising the interactions between cyclodextrin, water and toluene. The use of cyclodextrins in the pharmaceutical industry is ever-increasing as scientists realize their benefits as both a non-toxic solubilising agent at physiological pH and as a chiral "reaction vessel" with which to carry out enantioselective reactions.

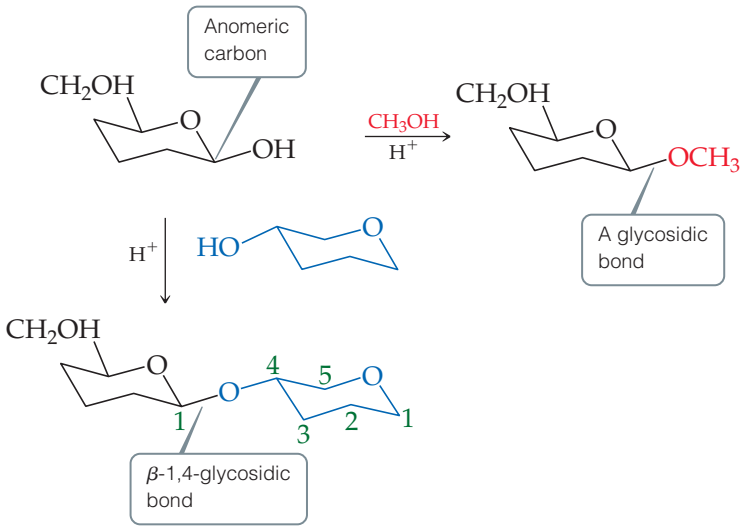
Cyclodextrins are formed by the enzymatic action of cyclodextrin glucanotransferase (CGTase) on glucose. Using this green process, tonnes of cyclodextrin can be prepared industrially.



▲ **Figure 28.18 Cyclodextrins as solubilising agents.**

mixture of glucose and fructose that forms, called *invert sugar*, is sweeter to the taste than the original sucrose. The sweet syrup present in canned fruits and lollies is largely invert sugar formed from the hydrolysis of added sucrose.

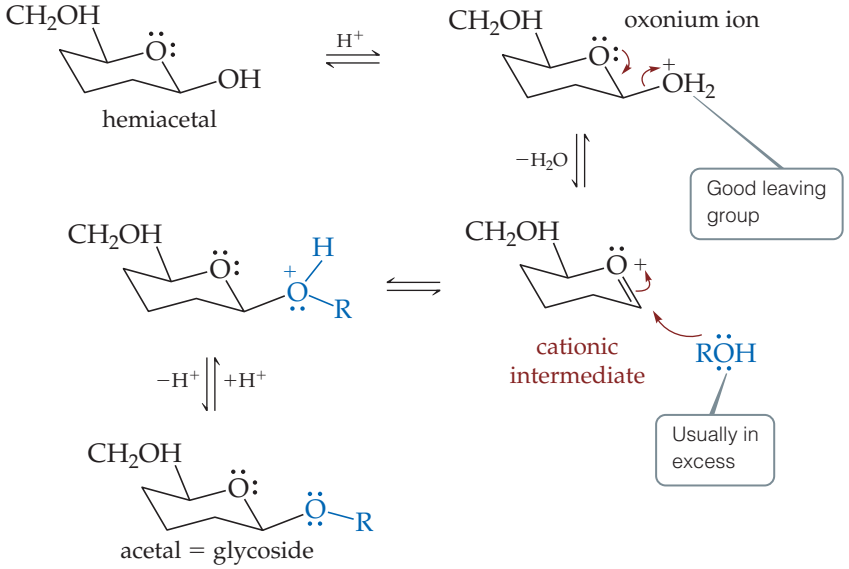
You might recall from our discussion on the formation of acetals in Section 28.3 that, provided there is an excess of alcohol present, the major product of the acid-catalyzed reaction of an aldehyde or ketone with an alcohol is the acetal and not the intermediate hemiacetal. The same can be stated for cyclic monosaccharides, which in the presence of excess alcohol form acetals, as illustrated by the following reactions:



[28.34]

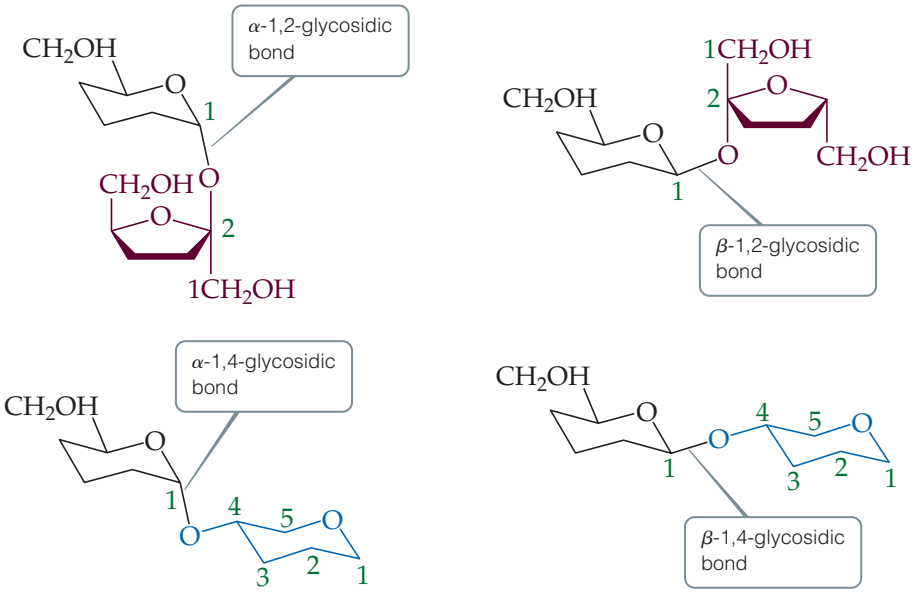
A cyclic acetal formed from a monosaccharide is called a **glycoside**. Both sucrose and lactose are *glycosides*. The bond between the anomeric carbon and the exocyclic alkoxy group of the acetal is called a **glycosidic bond**. Glycosides are stable in water, unlike simple acetals, and *do not* undergo mutarotation since, unlike the hemiacetal, the glycoside is not in equilibrium with its open-chain form in neutral solution. Hydrolysis of the glycoside is possible in aqueous acid, as is shown by the example of invert sugar.

The mechanism for the formation of the glycoside from the cyclic hemiacetal is illustrated in the set of equilibria given in Equation 28.35 for a simplified β-monosaccharide and the general alcohol, ROH. The acid-catalysed reaction occurs mainly by an elimination pathway. Elimination of H_2O by use of one of the lone pairs on the endocyclic oxygen yields the cationic intermediate (Equation 28.35). Attack at what used to be the anomeric carbon by ROH leads to an intermediate oxonium ion, which on proton loss yields the glycoside. This reaction pathway is unique to carbohydrate chemistry.



[28.35]

The position of the glycosidic bond in a carbohydrate is important for the properties it exhibits. Glycosidic bonds are classified by their orientation—that is, whether they are α or β bonds (equating to axial and equatorial bonds in the chair conformation, respectively), as well as on which carbons link the two monosaccharide subunits. Some examples of naming glycosidic bonds are:

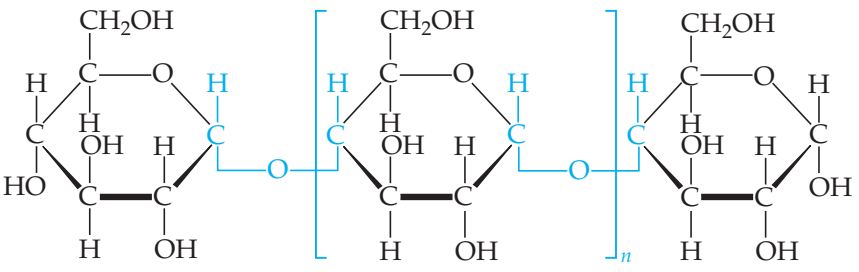


Polysaccharides are made up of many monosaccharide units, joined together by a bonding arrangement similar to those shown for the disaccharides in Figure 28.17. The most important polysaccharides are starch, glycogen and cellulose, which are formed from repeating glucose units.

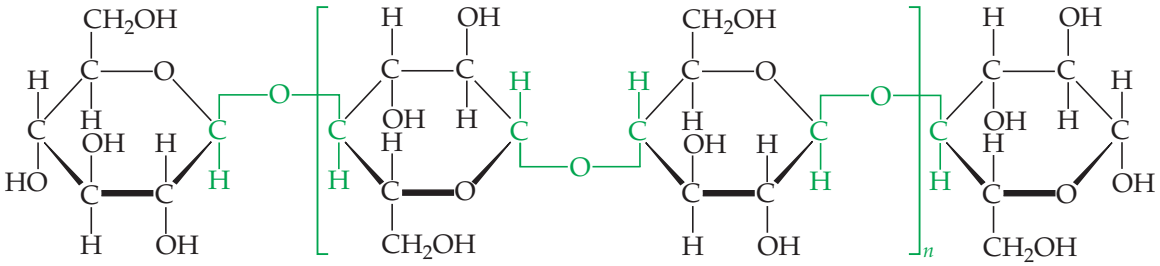
Starch is not a pure substance. The term refers to a group of polysaccharides found in plants, composed of glucose units bound by α-1,4-glycosidic bonds. Starches serve as a major method of food storage in plant seeds and tubers. Corn, potatoes, wheat and rice all contain substantial amounts of starch. These plant products serve as major sources of food energy for humans. Enzymes within the digestive system called *amylases* catalyze the hydrolysis of starch to glucose. Starch molecules that form unbranched chains are called **amyloses**, whereas those that are branched are called **amylopectins**. Figure 28.19 illustrates an unbranched structure of starch. In this structure, the glucose units are in the α form.

Glycogen is a starch-like substance synthesized in animals, consisting of glucose units connected by α-1,4- and α-1,6-glycosidic bonds. Glycogen molecules vary in molecular weight from about 5000 u to more than 5 million u. Glycogen acts as a kind of energy bank in the body and is concentrated in the muscles and liver. In muscles it serves as an immediate source of energy; in the liver it serves as a storage place for glucose and helps to maintain a constant glucose level in the blood.

Cellulose forms the major structural unit of land plants. Wood is about 50% cellulose; cotton fibres are almost entirely cellulose. Cellulose consists of unbranched chains of glucose units linked by β-1,4-glycosidic bonds, with molecular weights averaging more than 500 000 u. The structure of cellulose is shown in Figure 28.20. At first glance



◀ **Figure 28.19 Structure of a starch molecule.** The molecule consists of many glucose units of the kind enclosed in brackets, joined by linkages of the α form. Note the glycosidic bond (blue) is often shown with a 90°-kink in it. This is for ease of representation and does *not* indicate an extra carbon atom.



▲ **Figure 28.20 Structure of cellulose.** Like starch, cellulose is a polymer. The repeating unit is shown between brackets. The linkage in cellulose is of the β form, different from that in starch (see Figure 28.19).

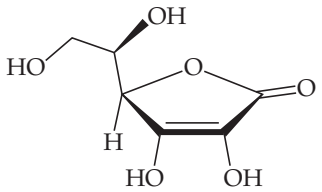
this structure looks very similar to that of starch. In cellulose, however, the glucose units are in the β form.

The distinction between starch and cellulose is made clearer when we examine their structures in a more realistic three-dimensional representation, as shown in **Figure 28.21**. The individual glucose units have different relationships to one another in the two structures. Because of this fundamental difference, enzymes that readily hydrolyze starches do not hydrolyze cellulose.

CHEMISTRY AND LIFE Vitamin C

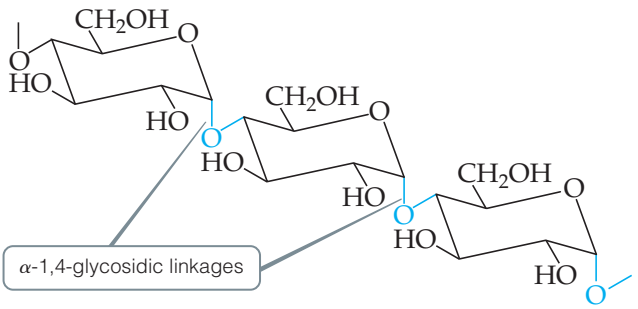
L-Ascorbic acid, more commonly known as vitamin C, is derived from D-glucose via the uronic acid pathway. Although many animals synthesize vitamin C, primates (and guinea pigs) cannot. The structural formula of L-ascorbic acid resembles the furanose form of a cyclic monosaccharide.

The most important reaction requiring ascorbate as a cofactor is the hydroxylation of proline residues in collagen. This reaction is required for the maintenance of normal connective tissue, as well as for healing wounds. The best-known functions of vitamin C are its use as a reducing agent and antioxidant. Deficiency in vitamin C leads to the disease *scurvy*. Scurvy is characterized by easily bruised skin, muscle fatigue, soft swollen gums, decreased wound healing, haemorrhaging, osteoporosis and anaemia.

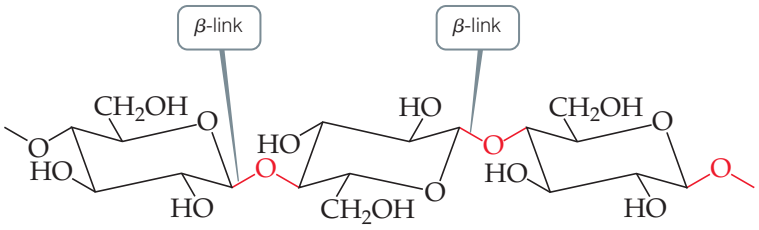


vitamin C

▶ **Figure 28.21 Structural differences in starch and cellulose.** These representations show the geometrical arrangements of bonds about each carbon atom. The glucose rings are orientated differently with respect to one another in the two structures.



(a) starch

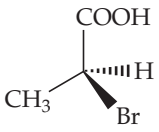


(b) cellulose

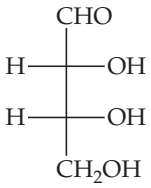
You might eat a kilogram of cellulose and receive no caloric value from it whatsoever, even though the heat of combustion per unit weight is essentially the same for both cellulose and starch. A kilogram of starch, in contrast, would represent a substantial caloric intake. The difference is that the starch is hydrolyzed to glucose, which is eventually oxidized with release of energy. Cellulose, however, is not readily hydrolyzed by enzymes present in the body, so it passes through the digestive system relatively unchanged. Many bacteria contain enzymes, called *cellulases*, that hydrolyze cellulose. These bacteria are present in the digestive systems of grazing animals, such as cattle, which use cellulose for food.

Self-Assessment Exercises

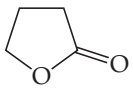
28.22 Which of the following structures represent a carbohydrate molecule?



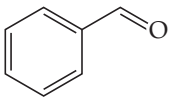
(a)



(b)

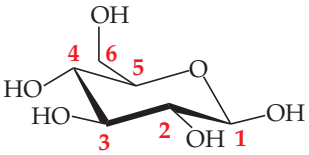


(c)



(d)

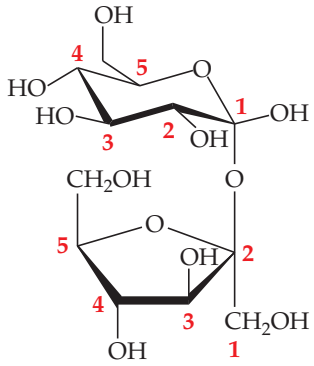
28.23 One representation of D-glucose looks like this:



The carbon atoms are numbered as shown in red. Which atom is the anomeric carbon?

(a) 1 **(b)** 2 **(c)** 3
(d) 4 **(e)** 5 **(f)** 6

28.24 Sucrose is a disaccharide composed of glucose and fructose, shown here with some of the carbon atoms numbered:



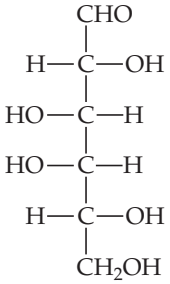
How is the linkage between the two sugars described?

(a) α-1,1-glycosidic bond
(b) β-1,1-glycosidic bond
(c) α-1,2-glycosidic bond
(d) β-1,2-glycosidic bond

Exercises

28.25 **(a)** What is the difference between α-glucose and β-glucose? **(b)** Show the condensation of two glucose molecules to form a disaccharide with a 1,4-α-linkage; **(c)** with a 1,4-β-linkage.

28.26 The structural formula for the linear form of galactose is:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the pyranose ring form of this sugar.

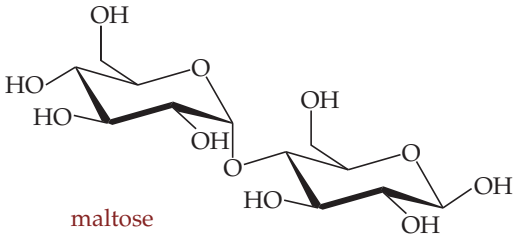
28.27 **(a)** What is the empirical formula of cellulose? **(b)** What is the unit that forms the basis of the cellulose polymer? **(c)** What form of linkage joins these monomeric units?

28.28 Monosaccharides can be categorized in terms of the number of carbon atoms (pentoses have five carbons and hexoses have six carbons) and according to whether they contain an aldehyde (prefix *aldo-*, as in aldopentose) or ketone group (prefix *keto-*, as in ketopentose). Classify galactose and ribose in this way.

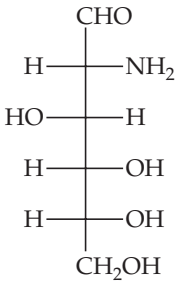
28.29 Aqueous solutions of pure α-D-galactose and β-D-galactose have specific rotations of +52.8° and +150.7°, respectively. After standing for several hours, a solution of α-D-galactose is found to have a new specific rotation of +80°. **(a)** Name the process observed. **(b)** Calculate the percentage of the α-anomer in the solution.

28.30 The structure of maltose is drawn here. **(a)** Is this a monosaccharide, disaccharide and/or a glycoside? **(b)** Identify the anomeric carbon/s. **(c)** Highlight the glycosidic bond and determine its connectivity—for example, 1,2-, 1,3-, 1,4-. **(d)** The identity of the anomer of maltose drawn below can

be determined by the orientation of the OH group on the non-glycosidic anomeric carbon. Which anomer is it?

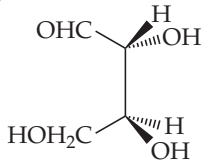


28.31 The open-chain structure of glucosamine is drawn here. **(a)** Determine whether the structure drawn is D- or L-glucosamine. **(b)** Draw glucosamine in its β-pyranose form.

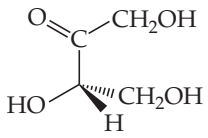


28.32 Convert each compound to a Fischer projection and hence class it as having D or L configuration.

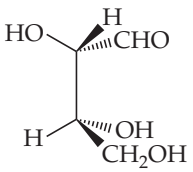
(a)



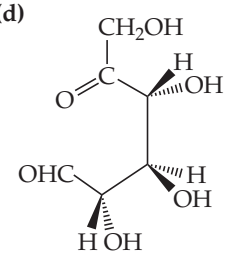
(b)



(c)



(d)



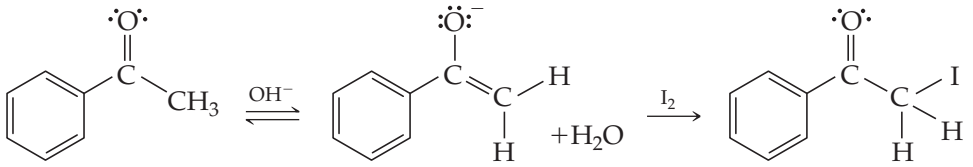
Answers to Self-Assessment Exercises

28.22 (b) **28.23** (a) **28.24** (c)

Sample Integrative Exercise

Putting Concepts Together

The halogenation of an aldehyde or ketone is promoted by the presence of a base, for example:



A hydrogen attached to a carbon atom is not normally acidic. **(a)** Suggest a reason why the hydrogen atom α to the carbonyl group may be lost as H^+. The equilibrium between the ketone and the enolate ion lies heavily on the left-hand side. **(b)** Explain what happens to the equilibrium when iodination takes place. **(c)** Predict whether the remaining α hydrogen atoms of the iodomethyl ketone are more or less acidic than those of the starting material. If excess hydroxide solution and iodine are used in this reaction, formation of iodoform, CHI_3, occurs rapidly. **(d)** Predict the structure of the other product formed.

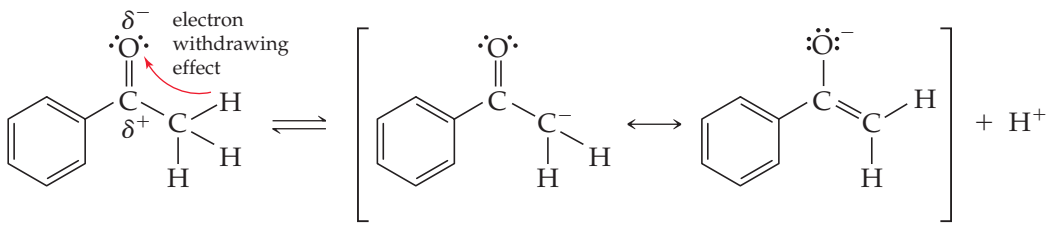
SOLUTION

Analyze This question focuses on factors that affect an acid–base equilibrium.

Plan Examine the structure or equilibrium involved and determine the relative stability of the species involved.

Solve

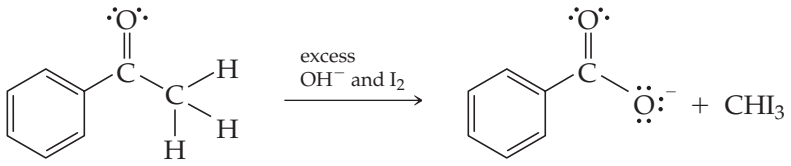
(a) There are two factors at work here. The carbonyl group has an electron withdrawing influence on the adjacent atoms which increases the ease with which H^+ is lost from the α carbon atom and the resulting anion is resonance stabilized.



(b) Reaction of iodine with the enolate ion lowers the concentration of the enolate ion, which shifts the equilibrium to the right-hand side. Even though there is a very small amount of enolate present at any time, the reaction can go almost to completion as more enolate ion is generated as the iodination reaction proceeds.

(c) Substitution of a hydrogen atom with a more electronegative halogen atom increases the electron withdrawing effect on the remaining hydrogen atoms and consequently makes them more acidic.

(d) A carboxylic acid is the other product from this reaction which, under the basic conditions present, will exist as the carboxylate ion.



Chapter Summary and Key Terms

SECTIONS 28.1 AND 28.2 **Aldehydes** and **ketones** are compounds containing a **carbonyl group** (C═O). Aldehydes contain the functional group CHO, whereas ketones contain a carbonyl group within a hydrocarbon chain. The polarity of the carbonyl group makes it susceptible to nucleophilic attack on carbon. Aldehydes and ketones can be prepared by the oxidation of 1° or 2° alcohols, respectively. Another approach to their preparation is through the **ozonolysis** of alkenes.

SECTION 28.3 The conversion of ketones and aldehydes to alcohols can occur by attack of an **organometallic compound** such as a **Grignard reagent** (RMgX) that acts as the nucleophile. Grignard reagents are equivalent to **carbanions** in reactivity. Reaction of aldehydes and ketones with amines yield **imines** and with alcohols yield **hemiacetals** and **acetals**. Imines can be catalytically hydrogenated to yield amines. **Metal hydrides** such as sodium borohydride act as a source of **hydride ion**, which can reduce ketones and aldehydes to alcohols. The **nucleophilic addition** reaction of aldehydes and ketones with cyanide ion ($^-$CN) leads to the formation of **cyanohydrins**, which can be converted to α-hydroxy acids by hydrolysis of the nitrile group. Compounds containing the CN functional group are often called **nitriles**. **Tautomerism** occurs in carbonyl compounds bearing an **α-hydrogen**.

SECTION 28.4 **Carbohydrates**, which are polyhydroxyaldehydes and ketones, are the major structural constituents of plants and are a source of energy in both plants and animals.

Glucose is the most common **monosaccharide**, or simple sugar. Monosaccharides are classed as **aldoses** or **ketoses** depending on what functional group is present in its open-chain form. The open-chain form of a monosaccharide is often drawn as a **Fischer projection**, which is an easy way to determine whether the monosaccharide is of the D- or L-form.

Monosaccharides are usually drawn as a **Haworth projection** in their cyclic form. Two cyclic forms are common: the pyranose (six-membered ring) and furanose (five-membered ring) forms. Monosaccharides are classed as one of two **anomers** according to the stereochemistry of the groups on the **anomeric carbon**. **Mutarotation** occurs when the two anomeric forms come to equilibrium in solution. A **glycoside** is formed when some group other than OH is bonded to the anomeric carbon. Glycosides do not interconvert between anomeric forms and do not exist in open chain and cyclic forms. The link between two monosaccharide units via the anomeric carbon is termed the **glycosidic bond**.

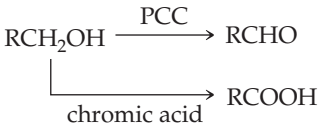
Two monosaccharides can be linked together by means of a condensation reaction to form a disaccharide. **Polysaccharides** are complex carbohydrates made up of many monosaccharide units joined together. The three most important polysaccharides are **starch**, which is found in plants; **glycogen**, which is found in animals; and **cellulose**, which is also found in plants. Starch molecules that form largely unbranched chains are called **amylose**, whereas those that are highly branched are called **amylopectins**.

Key Skills

- Understand how to identify aldehyde and ketone functional groups and use systematic approaches to naming. (Section 28.1)
- Be able to predict that the oxidation of primary alcohols gives aldehydes and oxidation of secondary alcohols give ketones and be able to quote the reagents necessary to undertake these interconversions. (Section 28.2)
- Understand the generality of nucleophilic addition to carbonyl compounds in the context of acetals, hemiacetals, imines and cyanohydrins. (Section 28.3)
- Be able to form and use Grignard reagents for nucleophilic addition. (Section 28.3)
- Be able to identify the major carbohydrates and identify whether a sugar is a mono-, di- or polysaccharide. (Section 28.4)
- Understand the stereochemistry of carbohydrates, the difference between α- and β-anomers, D and L and how it relates to carbohydrates. (Section 28.4)
- Be able to draw and interpret Fischer projections. (Section 28.4)

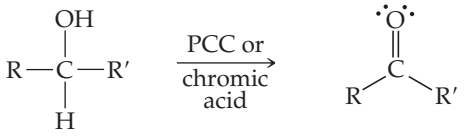
Key Equations

- Oxidation of 1° alcohols



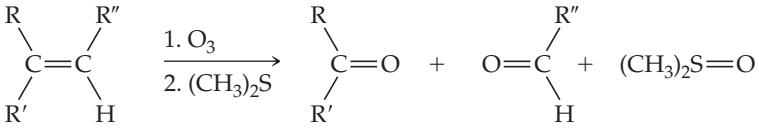
[28.1]

- Oxidation of 2° alcohols



[28.2]

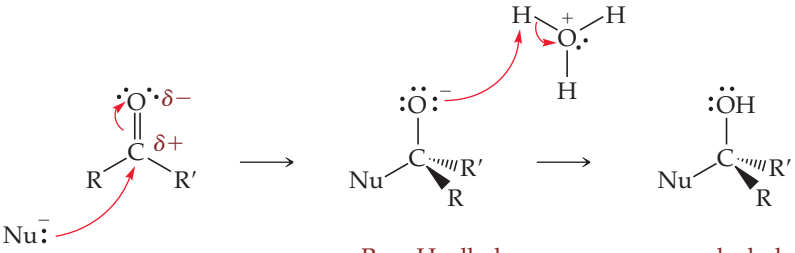
- Ozonolysis



an alkene — a ketone — an aldehyde — dimethylsulfoxide

[28.3]

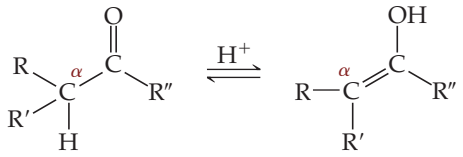
- Nucleophilic addition reaction



R = H, alkyl
R′ = alkyl

[28.5]

- Tautomerization



keto form
aldehyde or ketone

enol form

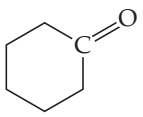
[28.23]

Exercises

Visualizing concepts

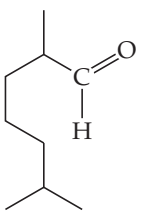
28.33 Draw the structure of the alcohol precursor, its systematic name and the reaction conditions you might use to obtain the following compounds by oxidation. [Section 28.2]

(a)

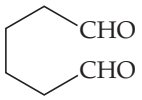


(b) $CH_3CH_2CH_2CH_2CH_2CHO$

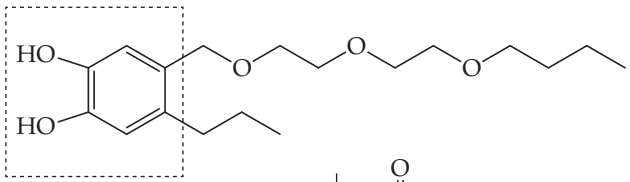
(c)



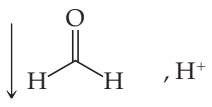
(d)

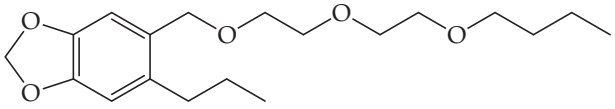


28.34 Piperonyl butoxide is used commercially as an additive to pyrethrum-based insecticides to enhance their effect. In this case, the cyclic ether is prepared by the action of formaldehyde on a catechol derivative. By what other functional group might this cyclic ether be named? [Section 28.3]



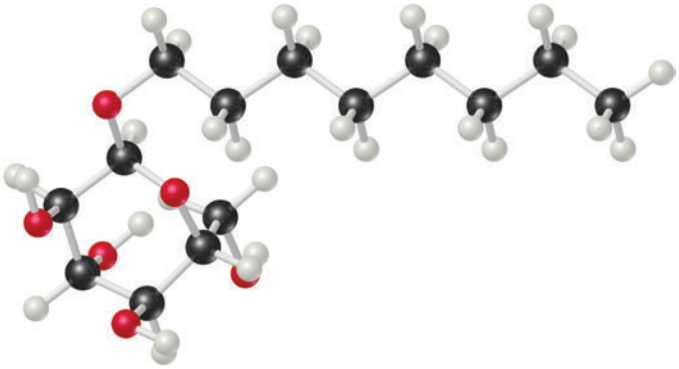
a catechol



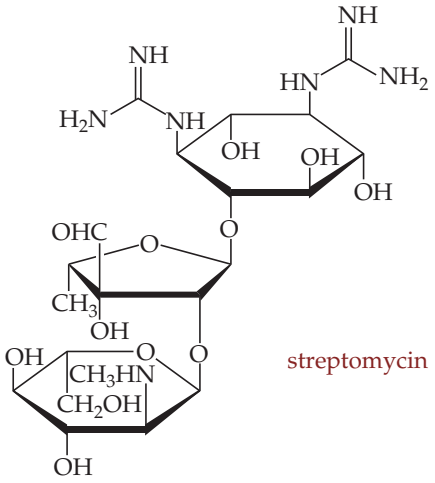


piperonyl butoxide

28.35 The molecule *n*-octylglucoside is widely used in biochemical research as a non-ionic detergent for "solubilizing" large hydrophobic protein molecules. What characteristics of this molecule are important for its use in this way? [Section 28.4]



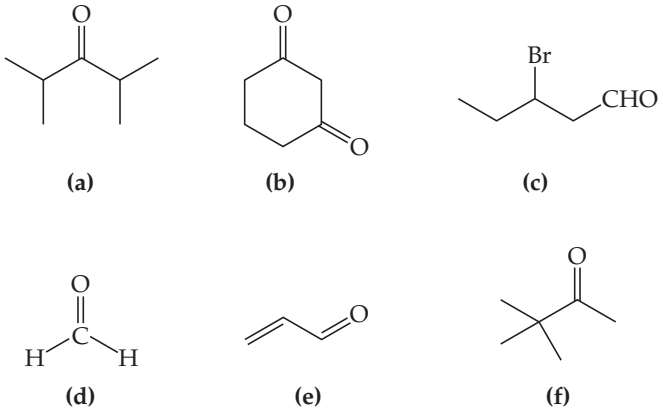
28.36 Streptomycin is a potent antibiotic produced by certain soil types. Its structure is shown here. Highlight the furanose and pyranose rings in streptomycin. [Section 28.4]



streptomycin

Aldehydes, Ketones and the Carbonyl Group (Section 28.1)

28.37 Name the following compounds:



(a) (b) (c) (d) (e) (f)

28.38 Draw the structural formula for the following aldehydes or ketones: **(a)** propanal, **(b)** 2-pentanone, **(c)** 3-methylbutanone, **(d)** 2-methylbutanal.

28.39 Draw the condensed structural formulas for two molecules containing a carbonyl group with the formula C_3H_4O.

28.40 Identify the functional groups in each of the following compounds:

(a) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$ **(b)** $CH_3C(=O)OH$

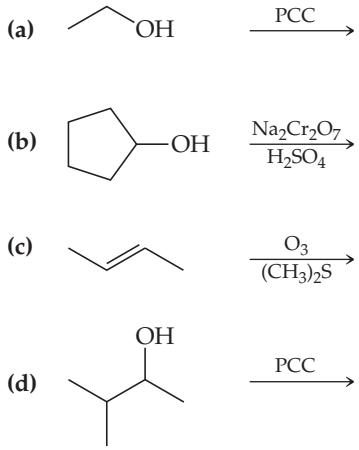
(c) $CH_2CH_2CH_3$ (OH) **(d)** $CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_3$

(e) $H_2N\overset{\overset{O}{\|}}{C}CH_3$ **(f)** $CH_3CH_2NHCH_3$

Preparation of Aldehydes and Ketones (Section 28.2)

28.41 A chemical oxidation requires the species being oxidized to lose electrons. Write the half-equation for the oxidation of 2-propanol to propanone

28.42 Provide the structure for the major organic product in the following reactions:



(a) OH —PCC→

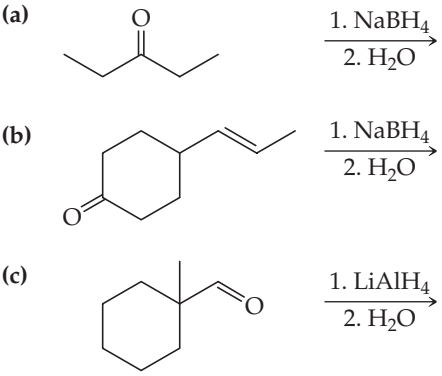
(b) OH —$Na_2Cr_2O_7$, H_2SO_4→

(c) —O_3, $(CH_3)_2S$→

(d) OH —PCC→

Reactions of Aldehydes and Ketones (Section 28.3)

28.43 Provide the major organic product(s) of the following reactions:

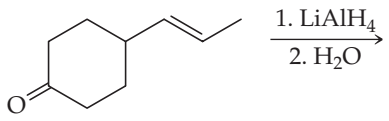


(a) —1. $NaBH_4$, 2. H_2O→

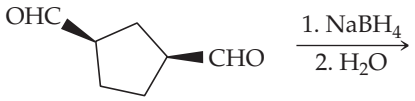
(b) —1. $NaBH_4$, 2. H_2O→

(c) —1. $LiAlH_4$, 2. H_2O→

(d)



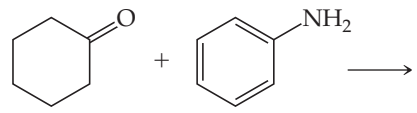
(e)



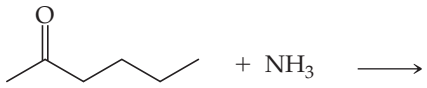
28.44 Why is it only possible to from imines with primary amines?

28.45 Draw the major product expected under the following conditions:

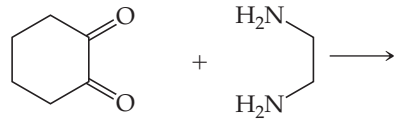
(a)



(b)



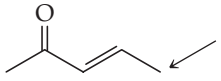
(c)



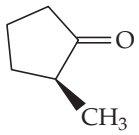
28.46 Write a mechanism for the acid-catalyzed reaction of methanol with propanal to form an acetal. What solvent would you choose to maximize the conversion of propanal to its acetal?

28.47 **(a)** Draw the product formed when acid is added to a solution of 5-hydroxypentanal. **(b)** What general class of compound is this?

28.48 **(a)** Draw the resonance contributors for the structure you would form by deprotonating at the methyl group indicated with the arrow. **(b)** Identify the keto and enolate forms. **(c)** What might you say about the acidity of these methyl protons compared to pentane? **(d)** What other tautomer is possible?



28.49 How many Hs in this compound are replaced by Ds when it is shaken in D_2O containing trace acid?

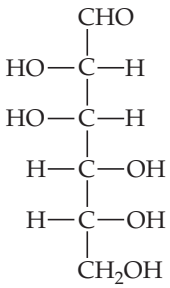


28.50 How would you prepare 2-cyanocyclohexanone from cyclohexanone?

Carbohydrates (Section 28.4)

28.51 In your own words, define the following terms: **(a)** carbohydrate, **(b)** monosaccharide, **(c)** disaccharide, **(d)** anomer, **(e)** glycoside.

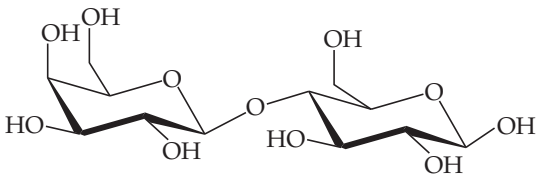
28.52 The structural formula for the linear form of D-mannose is as follows:



(a) How many chiral carbons are present in the molecule? **(b)** Draw the structure of the pyranose ring form of this sugar.

28.53 Starch, glycogen, and cellulose are all polymers of glucose. **(a)** What are the structural differences between them? **(b)** Explain the structural differences that cause the difference in water solubility between these polymers.

28.54 The structure of lactose is shown. **(a)** Is this a monosaccharide, disaccharide and/or a glycoside? **(b)** Identify the anomeric carbon/s. **(c)** Highlight the glycosidic bond and determine whether it is a 1,2-, 1,3- or 1,4-glycosidic bond.

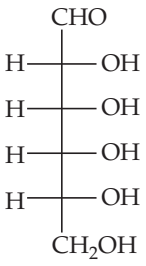


lactose

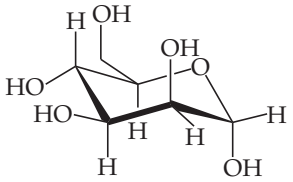
28.55 *Arbutin* is the principal antibacterial agent of the traditional herbal medicine called *uva-ursi*. Its systematic name is 4-hydroxyphenyl-β-D-glucopyranoside. Draw the structure of arbutin.

28.56 Convert each into a Haworth projection.

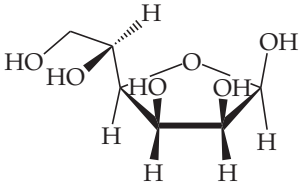
(a) Convert into an α-pyranose form



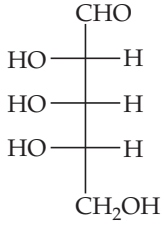
(b) Convert into an α-pyranose form



(c) Convert into an α-pyranose form



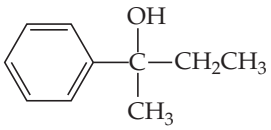
(d) Convert into a β-furanose form



28.57 Give the structure of the alkene that would yield propanone and propanal upon ozonolysis.

Integrative Exercises

28.58 2-Phenyl-2-butanol can be synthesized by three different combinations of a Grignard reagent and a ketone. Show each combination.



28.59 Acetone, $(CH_3)_2CO$, is widely used as an industrial solvent. **(a)** Draw the Lewis structure for the acetone molecule, and predict the geometry around each carbon atom. **(b)** Is the acetone molecule polar or non-polar? **(c)** What kinds of intermolecular attractive forces exist between acetone molecules? **(d)** 1-Propanol, $CH_3CH_2CH_2OH$, has a molecular weight that is very similar to that of acetone, yet acetone boils at 56.5 °C and 1-propanol boils at 97.2 °C. Explain the difference.

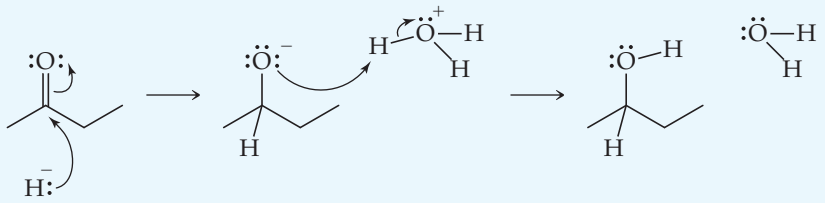
28.60 **(a)** How many stereocenters are present in 3-methylpentan-2-ol? List the configuration of the stereocenters for each possible isomer and indicate the relationship (enantiomers or diastereoisomers) that exists between the isomers. **(b)** Write the equation for the reaction of 3-methylpentan-2-ol with acidified dichromate solution. **(c)** How many stereoisomers are there in the product of this reaction? **(d)** Draw two structures representing the enol forms of this product. **(e)** Describe the change in optical rotation that you might expect if you performed this reaction on a single stereoisomer of starting material.

28.61 Use Figure 8.8 on page 283 to determine the difference in electronegativity of the following pairs of atoms and classify the bond between them as ionic, polar covalent or non-polar covalent: Na—Cl; Mg—Cl; H—Cl; C—Cl; C—Mg; C—C.

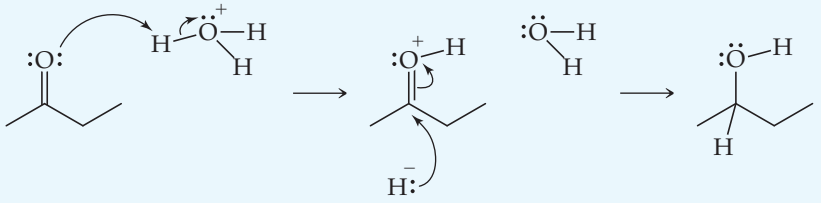
28.62 Use the following data to determine whether glucose ($C_6H_{12}O_6$) or sucrose ($C_{12}H_{22}O_{11}$) provides the greatest energy per gram. $\Delta_{combustion}H°$ (glucose) = −2803 kJ mol^{-1}; $\Delta_{combustion}H°$ (sucrose) = −5640 kJ mol^{-1}.

Design an Experiment

A nucleophilic addition reaction, the reduction of a ketone for example, is a two-step process in which the nucleophile adds to the carbon of the carbonyl followed by protonation of the oxygen. The mechanism may be written as follows:



But what if protonation of oxygen was the first step? This is shown in this mechanism:



How are you going to distinguish the two possibilities? Assuming that the first step in each case is the slow step of the reaction, describe the kinetic experiments you might conduct to determine which mechanism is the likely one. What precautions do you need to take if you were to add a water-sensitive compound such as lithium aluminum hydride to a substrate that had been treated with aqueous acid? The intermediate drawn in the second mechanism is resonance stabilized. Draw the other resonance contributor. From your knowledge of Lewis structures, is the contributor you have just drawn or the intermediate in the first mechanism likely to be more stable? Why?

WHAT'S AHEAD

29.1 ▶ Carboxylic Acids

29.2 ▶ Preparation of Carboxylic Acids

29.3 ▶ Esters and Esterification

29.4 ▶ Fats, Oils, and Waxes

29.5 ▶ Acid Chlorides, Anhydrides, and Nucleophilic Acyl Substitution

29.6 ▶ Condensation Polymerization

29

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

29.1 | Carboxylic Acids





Carboxylic acids are weak acids that are widely distributed in nature and are commonly used in consumer products.

One of the most common carboxylic acids is acetic acid, which is the primary ingredient of vinegar. The acetyl group is central to the metabolism of carbohydrates and fats through its role in the enzyme acetyl CoA. Acetic acid is also an important industrial chemical with a global production of approximately 6.5 million metric tons each year. For example, aspirin (acetylsalicylic acid) is formed by the reaction of acetic acid with salicylic acid. Vinyl acetate is just one polymer precursor that is also derived from acetic acid. When vinyl acetate is polymerized, the product is poly(vinyl acetate), which is used in water-based latex paints and in glues for paper and wood.

By the end of this section, you should be able to:

- Recognize the carboxylic acid functional group and name simple molecules containing it
- Understand the connection between acid–base chemistry and solubility

Carboxylic acids contain the *carboxyl* functional group (a combination of *carbo*nyl and hydr*oxyl* groups), which is often written as COOH or CO_2H.

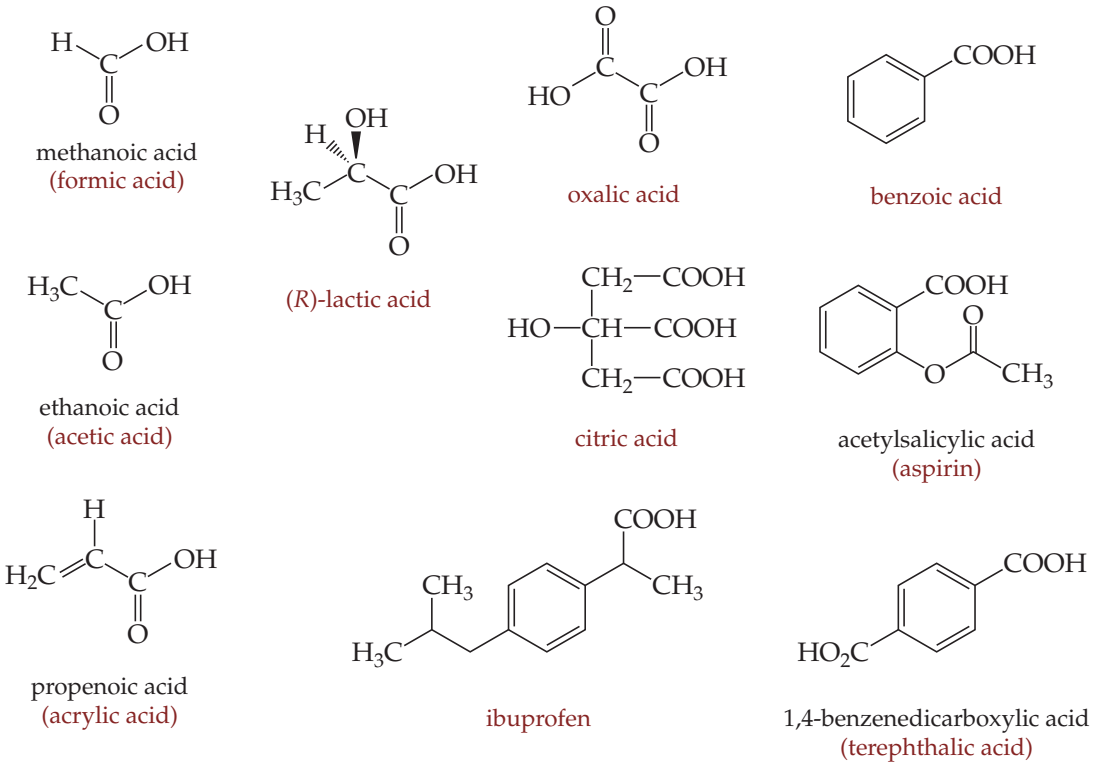
Figure 29.1 shows the structural formulas of several carboxylic acids. Notice that oxalic acid and citric acid contain two and three carboxyl groups, respectively. Oxalic acid, which is found in high concentration in rhubarb leaves, is poisonous if ingested. Terephthalic acid is a key component of PET, a durable polymer used in packaging. Lactic acid is generated in muscle cells and tissue during the synthesis of adenosine triphosphate (ATP) from carbohydrates during sustained exercise. Ibuprofen is an analgesic, used to treat pain and inflammation. Benzoic acid is often used as a fungicide.

Structure, Properties, and Nomenclature

The carboxyl functional group (COOH) that characterizes carboxylic acids is constituted by a sp^2 hybridized carbon atom bonded to two oxygen atoms. One oxygen is sp^2 hybridized, leading to the formation of σ- and π-bonds with carbon (leading to a C—O double bond). The other oxygen is sp^3 hybridized, leading to a C—O single bond.

In Chapter 11, we studied the phenomenon of hydrogen bonding. We have already described the need for two components: a hydrogen bond donor (such as O—H, N—H) and a hydrogen bond acceptor, which is usually an electronegative atom containing a lone

Go Figure Which of these substances have both a carboxylic acid functional group and an alcohol functional group?

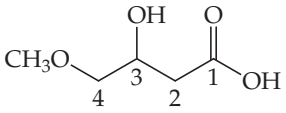


▲ **Figure 29.1 Structural formulas of some common carboxylic acids.** The IUPAC names are given in black type for the monocarboxylic acids, but they are generally referred to by their common names.

pair of electrons such as O, N or F. In the case of carboxylic acids, both hydrogen bond donor and acceptor are present in the same functional group in a favourable geometry. As a result, carboxylic acids are able to dimerize (**Figure 29.2**) in concentrated solutions or as neat (without solvent) liquids. Dimerization is as a result of the intermolecular hydrogen bonding between the carbonyl oxygen and the OH group. Consequently, carboxylic acids have relatively high boiling points (**Table 29.1**).

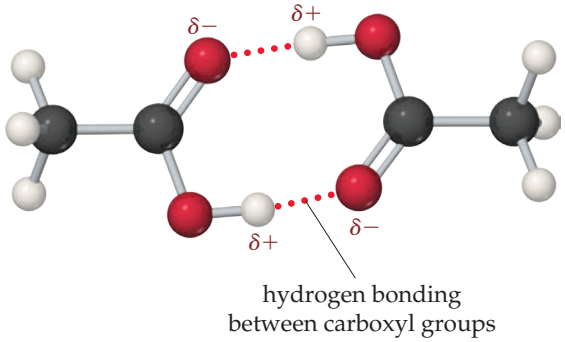
Alkane-derived carboxylic acids have the general formula $C_nH_{2n}O_2$, and are named based on the longest carbon chain (parent alkane) bearing the carboxyl group, although sometimes common names are still employed (**Figure 29.6**). The *e* of the alkane is replaced by *oic acid* to signify the carboxylic acid. Table 29.1 gives the names of the first 10 straight-chain carboxylic acids, their condensed formulas and their melting points.

In terms of the nomenclature hierarchy we have been developing for organic chemistry, the carboxylic acids sit at the pinnacle. All other functional groups we have come across are named as substituents if a carboxylic acid group is present. For example, 3-hydroxy-4-methoxybutanoic acid is *not* named as the alcohol, but rather the carboxylic acid.



3-hydroxy-4-methoxybutanoic acid

Go Figure Would dimerization be aided by polar or non-polar solvents?



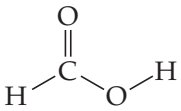
▲ **Figure 29.2 Carboxylic acid dimerization.** In concentrated solution or as neat liquids, carboxylic acids are able to dimerize through intermolecular hydrogen bonding.

TABLE 29.1 First 10 members of the aliphatic carboxylic acid series

Molecular formula	Condensed structural formula	IUPAC name (common name)	Melting point (°C)*	Boiling point (°C)*
CH_2O_2	HCOOH	Methanoic (formic) acid	8	101
$C_2H_4O_2$	CH_3COOH	Ethanoic (acetic) acid	17	118
$C_3H_6O_2$	CH_3CH_2COOH	Propanoic (propionic) acid	−24	141
$C_4H_8O_2$	$CH_3CH_2CH_2COOH$	Butanoic (butyric) acid	−6	163
$C_5H_{10}O_2$	$CH_3CH_2CH_2CH_2COOH$	Pentanoic (valeric) acid	−20	186
$C_6H_{12}O_2$	$CH_3CH_2CH_2CH_2CH_2COOH$	Hexanoic (caproic) acid	−4	205
$C_7H_{14}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2COOH$	Heptanoic (enanthylic) acid	−10	223
$C_8H_{16}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Octanoic (caprylic) acid	16	239
$C_9H_{18}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Nonanoic (pelargonic) acid	9	253
$C_{10}H_{20}O_2$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COOH$	Decanoic (capric) acid	29	219

* Rounded to the nearest degree.

Carboxylic acids have higher melting and boiling points than their corresponding alkanes, alcohols, aldehydes or ketones because of their added polarity and ability to hydrogen bond (Table 29.1). Although the boiling points of carboxylic acids increase with molecular size in a regular manner, their melting points do not. Unbranched acids made up of an even number of carbon atoms have melting points higher than their odd-numbered homologues, having one more or one less carbon. This difference reflects subtle changes in intermolecular attractive forces in the solid state. The even-numbered carboxylic acids are able to interact more strongly than their odd-numbered homologues, which increases the amount of energy needed to break the interactions in order to melt, thus increasing the melting point. For example, decanoic acid is a waxy solid at room temperature. Formic acid and acetic acid are special in that their melting points seem appropriate for much higher molecular weight species. The reason is that the properties of formic acid and acetic acid are dominated by the hydrogen bonding interactions of the carboxyl group with other molecules. These interactions occur more often because the COOH group makes up a large proportion of the molecule.



formic acid

The number of carbon atoms in the carboxylic acid chain not only affects its melting point, but also its solubility in water. Typically, a carboxylic acid is more water soluble than its alcohol analogue because of more extensive hydrogen bonding capacity. For example, formic, acetic, propanoic and butanoic acids are all infinitely soluble in water. As the length of the carbon chain increases, however, the polar COOH group becomes an ever decreasing proportion of the molecule, and the molecule behaves more like a hydrocarbon in terms of its solubility. The solubility of the carboxylic acids in water decreases correspondingly. In contrast, the solubility of carboxylic acids in non-polar solvents increases as the non-polar hydrocarbon chain length increases. Hence decanoic acid is more "alkane-like" than acetic acid.

Acidity

We have already mentioned that carboxylic acids are weak acids. **Table 29.2** compares the pK_a values for several organic and inorganic acids. Being a weak acid, carboxylic acids dissociate by the following equation:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+ \qquad [29.1]$$

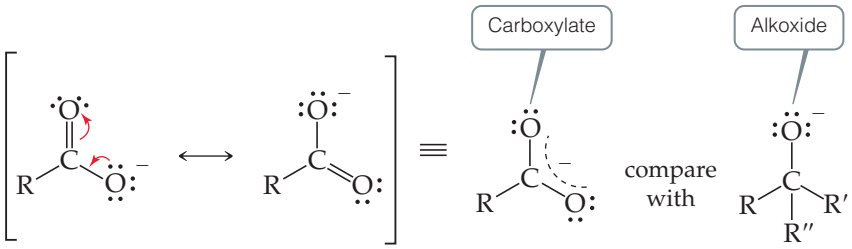
One of the main contributing factors that allows the pK_a of a carboxylic acid to be lower than that of the corresponding alcohol—for example, acetic acid (pK_a 4.8) compared with ethanol (pK_a 16)—is the relative stability of the two conjugate bases, that is, the **carboxylate anion** versus the alkoxide anion. The carboxylate anion is resonance stabilized (**Figure 29.3**), having two contributors to the overall structure, whereas the alkoxide

TABLE 29.2 Relative pK_a values for selected carboxylic acids*

Compound	Structural formula	pK_a	
Hydrogen chloride	HCl	−7	**Strong acid**
Sulfuric acid	H_2SO_4	−5	
Trichloroacetic acid	Cl_3CCOOH	0.7	
Dichloroacetic acid	$Cl_2CHCOOH$	1.5	
Chloroacetic acid	$ClCH_2COOH$	2.8	
Acetic acid	CH_3COOH	4.8	
Water	H_2O	15.7	**Weak acid**

* Error in measurement ± 0.2.

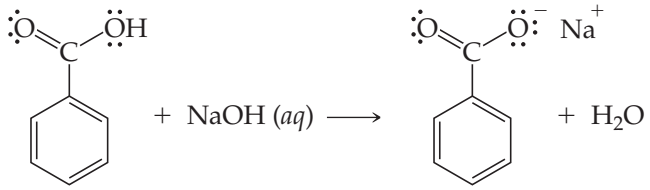
▶ **Figure 29.3** **The carboxylate anion is resonance stablilized.**



is not resonance stabilized. As a result, the carboxylate anion is not as reactive as the alkoxide.

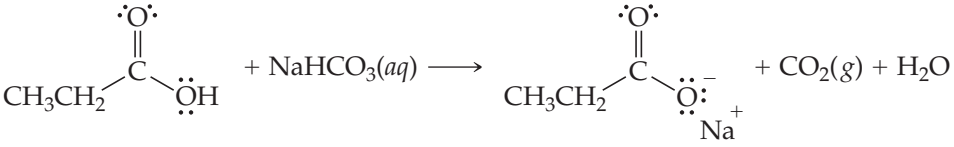
The pK_a of a carboxylic acid can be influenced inductively by substituents (Table 29.2). The addition of an electron-withdrawing substituent such as a halide adjacent to the COOH group reduces the pK_a by weakening the carboxyl O—H bond (**Figure 29.4**). For example, the pK_a of acetic acid is 4.8 whereas the pK_a of chloroacetic acid is 2.8. The addition of more chlorine atoms reduces the pK_a further (for example, pK_a of trichloroacetic acid is 0.7). The inductive effect is reduced dramatically as the number of intervening bonds between the electron-withdrawing substituent and the COOH group increases. Such an effect is seen in amino acids.

Carboxylic acids react with bases such as NaOH, $NaHCO_3$ or Na_2CO_3 to form the corresponding sodium carboxylate salt. For example, when benzoic acid reacts with an aqueous solution of NaOH, sodium benzoate and water are formed. The conversion of the acid form to the carboxylate salt enhances aqueous solubility. Note that the salts of carboxylic acids are named in the same order as other salts: first cation, then anion. The name of the anion is derived from the carboxylic acid by replacing *-oic acid* with *-oate*.



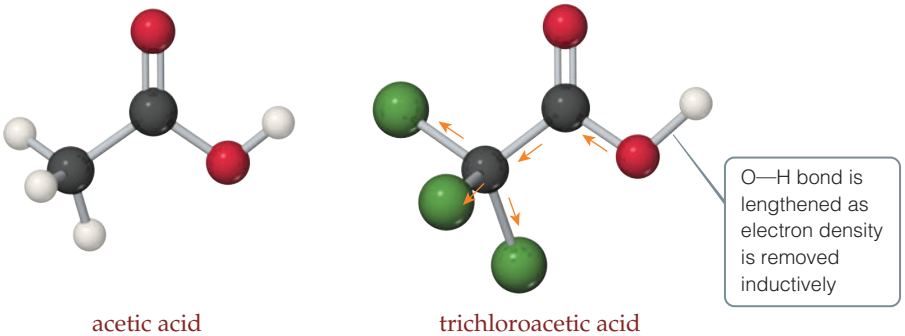
benzoic acid sodium benzoate [29.2]

When propanoic acid is reacted with a solution of sodium hydrogen carbonate ($NaHCO_3$), the products are sodium propanoate, carbon dioxide and water. The reaction of carboxylic acids with carbonates such as $NaHCO_3$, Na_2CO_3, K_2CO_3 and $CaCO_3$ has special significance. Oral tablets such as Berocca™ and Aspro Clear™ combine carbonates with vitamin acids or citric acid to dissolve the tablet contents in water. The fizz associated with their dissolution is caused by the release of CO_2.



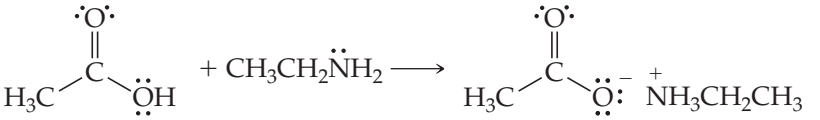
propanoic acid sodium propanoate [29.3]

▶ **Figure 29.4** **Inductive effect on pK_a.** Electron-withdrawing substituents (for example, Cl, NO_2) adjacent to the carboxyl group are able to weaken the carboxyl O—H bond relative to acetic acid, making the compound a stronger acid. Any effect of a substituent that acts "through bonds" rather than by providing an alternative resonance structure, is called an **inductive effect**.



acetic acid trichloroacetic acid

Carboxylic acids react with amines to form ammonium salts. For example, the reaction of acetic acid with ethanamine yields the ammonium salt, ethyl ammonium acetate:



[29.4]

The reaction types demonstrated in Equations 29.2–29.4 are extremely useful in the preparation of water-soluble compounds, particularly for the pharmaceutical industry. The salt products are highly soluble in aqueous solutions and can be achieved under mild conditions or formed *in situ*, as in the case of soluble aspirin. Water solubility aids in absorption of the therapeutic agent. This reaction is also useful in the *resolution* of chiral carboxylic acids.

Sample Exercise 29.1

Properties of Carboxylic Acids

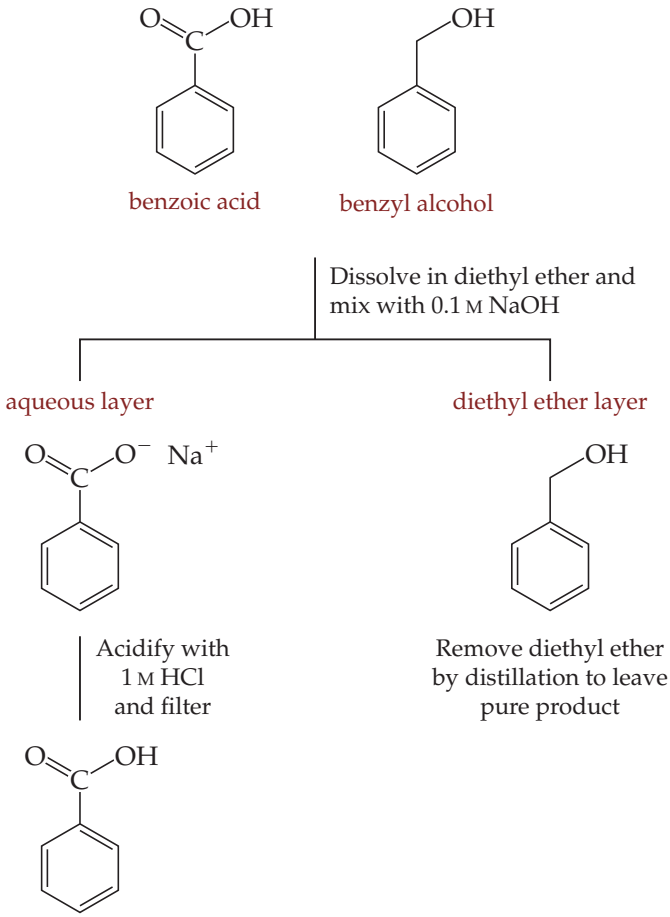
Describe a way of separating benzoic acid from benzyl alcohol.

SOLUTION

Analyze We are asked how to separate an alcohol from a carboxylic acid containing a similar structure.

Plan The carboxylic acid and alcohol functional group have a different reactivity and so can be separated using chemical reactions.

Solve In this case, we can use the differences in acidity between the two compounds and the aqueous solubility of the benzoate anion to separate them.

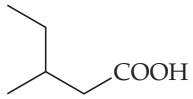


Practice Exercise

List the following set of carboxylic acids in order of acidity (lowest first): **(a)** butanoic acid, **(b)** 2-iodobutanoic acid, **(c)** 2-fluorobutanoic acid, **(d)** trifluoroacetic acid, **(e)** 3-iodobutanoic acid.

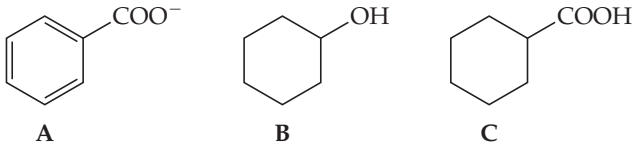
Self-Assessment Exercises

29.1 Name:



(a) 2-ethylbutanoic acid
(b) 3-ethylbutanoic acid
(c) 3-methylpentanoic acid

29.2 Order the following species in terms of increasing solubility in water.



(a) A < B < C
(b) A < C < B
(c) B < C < A
(d) B < A < C

Exercises

29.3 Give the IUPAC name for each of the following acids:

(a) HCOH (O double-bonded)

(b) $CH_3CH_2CH_2COH$ (O double-bonded)

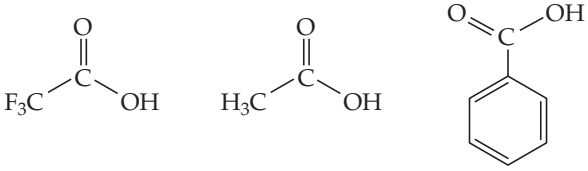
(c) $CH_3CH_2CHCH_2COH$ (O double-bonded; CH_3 branch)

29.4 Draw the structure for 2-bromobutanoic acid and indicate any stereogenic center within the molecule. How many stereoisomers are possible?

29.5 **(a)** Would you expect pure acetic acid to be a strongly hydrogen bonded substance? **(b)** How do the melting and boiling points of the substance support your answer? (See Table 29.1.)

29.6 Describe how you would distinguish between a carboxylic acid and its ester, using nothing more than an aqueous solution of sodium hydrogencarbonate ($NaHCO_3$, sodium bicarbonate).

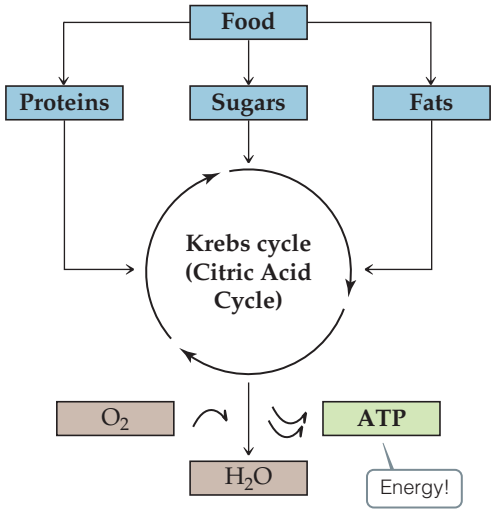
29.7 Which of the following carboxylic acids is the most acidic? Why?



Answers to Self-Assessment Exercises

29.1 (c) **29.2** (c)

29.2 | Preparation of Carboxylic Acids



Citric acid is a tricarboxylic acid with the structure shown in Figure 29.1. It is used in the food industry as a flavoring agent and acidifier and naturally occurs in fruits, particularly citrus fruits, where it may by up to 8% of the dry weight of lemons and limes. It plays a central role in the metabolism of all animals, plants, and bacteria as part of the Citric Acid Cycle, which is also called the Tricarboxylic Acid Cycle (TCA cycle) or Krebs Cycle. While the cycle has a number of important functions, it is responsible for converting the fats and carbohydrates we eat, together with oxygen, into a usable source of energy. Not surprisingly, it is one of the most studied biochemical pathways. The 1953 Nobel prize in Physiology and Medicine was awarded to Hans Adolf Krebs for his pioneering work on the cycle.

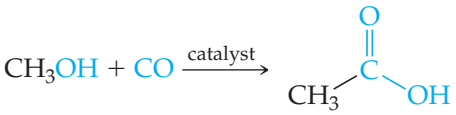
By the end of this section, you should be able to:

- Identify a number of preparation routes to simple carboxylic acids

Carboxylic acids can be synthesized through the oxidation of 1° alcohols, such as ethanol or propan-1-ol. Under appropriate conditions, the corresponding aldehyde may also be isolated as the first product of oxidation.

The oxidation of ethanol to acetic acid in air (with help from enzymes within wine) is responsible for causing wines to turn sour, producing vinegar.

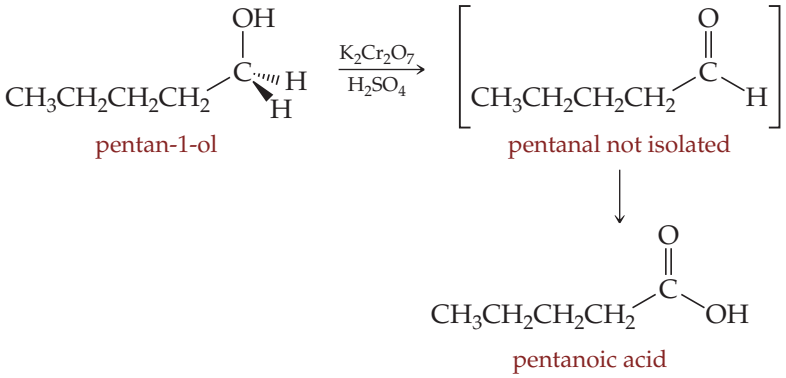
Acetic acid is produced industrially by the reaction of methanol with carbon monoxide in the presence of a rhodium catalyst:



[29.5]

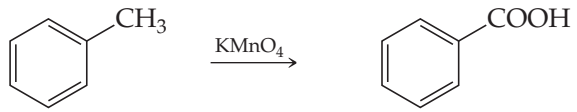
This reaction involves, in effect, the insertion of a carbon monoxide molecule between the CH_3 and OH groups. A reaction of this kind is called *carbonylation*.

When primary alcohols are oxidized using strong oxidising agents such as potassium dichromate ($K_2Cr_2O_7$) in H_2SO_4 or chromic acid ($CrO_3/H_2O/H_2SO_4$), they are converted to the corresponding carboxylic acid via the intermediary aldehyde. Aldehydes are more prone to oxidation than alcohols. In fact, left to stand, aldehydes are oxidized readily by the oxygen within air, also forming carboxylic acids. Hence, when the oxidation reaction of a primary alcohol proceeds, any aldehyde formed within the reaction is quickly converted to the carboxylic acid. For example, the oxidation of pentan-1-ol in the presence of acidic $K_2Cr_2O_7$ gives pentanoic acid as the major product:

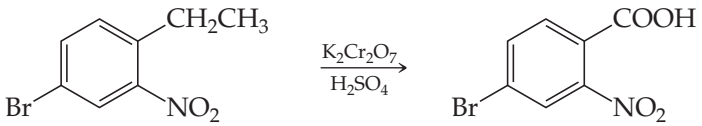


[29.6]

Toluene and other aromatics containing a benzylic CH group are easily oxidized to the corresponding benzoic acid on boiling with solutions of potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$). This occurs even if the benzylic carbon contains one, two or three C—C bonds.

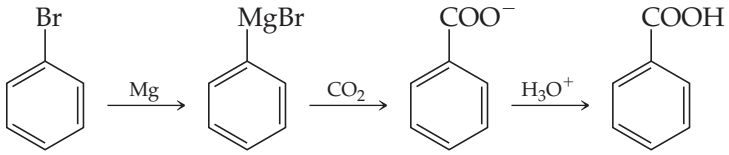


toluene benzoic acid [29.7]



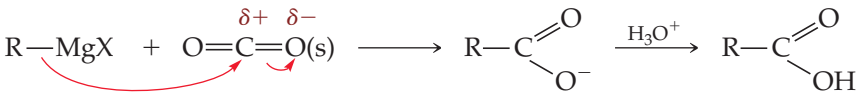
4-bromo-1-ethyl-2-nitrobenzene 4-bromo-2-nitrobenzoic acid [29.8]

Benzoic acids can also be prepared by the reaction of phenylmagnesium bromide with carbon dioxide (in the form of dry ice), followed by protonation.



[29.9]

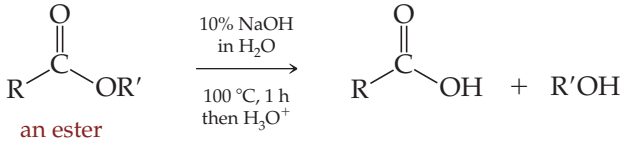
Recall from Chapter 28 that Grignard reagents make excellent nucleophiles, capable of reacting with carbonyl-containing compounds such as aldehydes and ketones. Generally speaking, the action of Grignard reagents (RMgX) on solid carbon dioxide to form carboxylic acids occurs by the following mechanism:



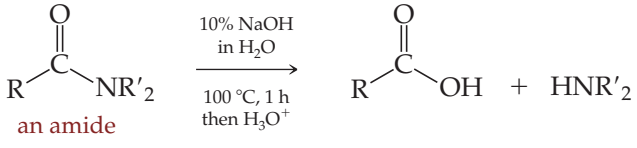
[29.10]

Carboxylic acids are also formed by the hydrolysis of certain functional groups. In the next section we discuss the reaction of carboxylic acids with alcohols to give an ester and with amines to give amides. We will also discuss the hydrolysis of esters to give carboxylic acids, using both acidic and basic conditions.

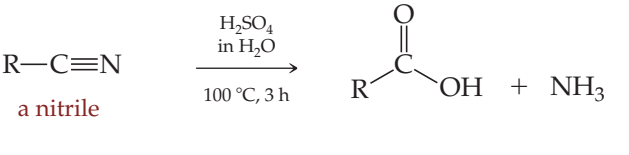
Carboxylic acids can be prepared by the hydrolysis of amides. It is fair to say that secondary and tertiary amides hydrolyse more slowly than primary amides under the conditions shown here. Finally, carboxylic acids can be formed readily by the hydrolysis of nitriles (RCN) under acidic conditions.



an ester [29.11]



an amide [29.12]



a nitrile [29.13]

Sample Exercise 29.2

Preparation of Carboxylic Acids

Describe a way of preparing pentanoic acid from 1-bromobutane.

SOLUTION

Analyze We are asked to propose a synthesis of a carboxylic acid from a specific starting material and note that the target compound contains one more carbon atom than the reactant.

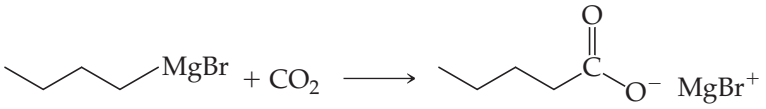
Plan There are two common methods of extending the number of carbon atoms in a chain: either a nucleophilic substitution by the cyanide ion or the addition of a Grignard reagent to a compound containing a C=O bond. Both could be extended to form a carboxylic acid. In the first case, hydrolysis of a nitrile under acid conditions will yield a carboxylic acid. In the second case, reaction of a Grignard reagent with carbon dioxide followed by dilute acid will furnish a carboxylic acid. We will choose the second route.

Solve Grignard reagents are very sensitive to moisture so are usually formed at the time they will be used in a "one pot" reaction. First, 1-bromobutane is treated with magnesium in diethyl ether solvent.

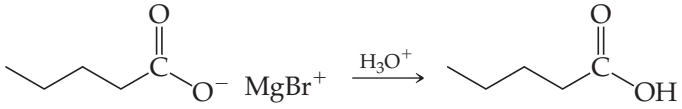


butyl magnesium bromide

Next, carbon dioxide in the form of dry ice is added to the reaction vessel.

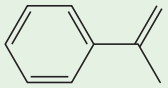


Finally, dilute acid is added to give the desired carboxylic acid.



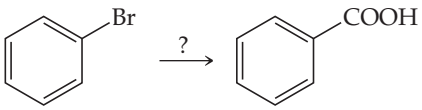
Practice Exercise

Write the structural formula of the carboxylic acid formed by treatment of chlorobenzene with magnesium, followed by carbon dioxide and finally aqueous acid.



Self-Assessment Exercise

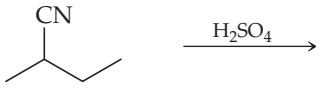
29.8 What reagents are used to synthesize benzoic acid from bromobenzene?

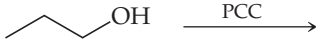


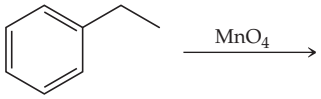
(a) 1) Mg 2) CO_2 3) H_3O^+
(b) 1) OH^- 2) K_2CrO_7/H_2SO_4
(c) 1) O_3 2) $(CH_3)_2S$
(d) $KMnO_4$

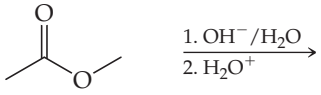
Exercises

29.9 What is the major organic product in the following reactions?

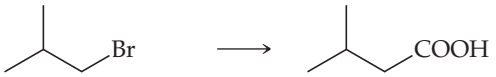
(a)


(b)


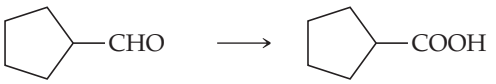
(c)


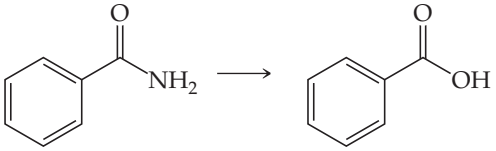
(d)


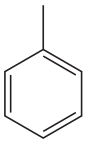
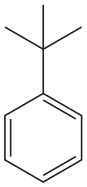
29.10 What reagent(s) are used in the following transformations?

(a)


(b)


(c)


(d)


29.11 Toluene,  is converted to benzoic acid by $KMnO_4$ but *tert*-butylbenzene,  is not. Explain.

Answers to Self-Assessment Exercise

29.8 (a)

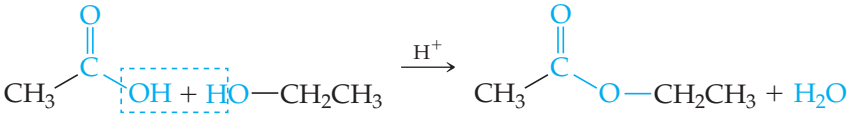
29.3 Esters and Esterification



The smell of ripe fruit results from a mixture of volatile compounds. Many of these are esters and, quite often, a single ester dominates the aroma of a particular fruit. In general, esters are sweet smelling and have a lower boiling point than carboxylic acids of similar molecular mass. By the end of this section, you should be able to:

- Understand the synthesis and hydrolysis of the ester functional group.

Carboxylic acids can undergo acid-catalyzed condensation reactions with alcohols to form **esters**:



acetic acid ethanol ethyl acetate [29.14]

The reaction is termed a *condensation reaction* due to the loss of one mole of water per mole of acid and alcohol. This reaction is commonly known as the **Fischer esterification**, named after the German chemist Emil Fischer (1852–1919), who was awarded the Nobel Prize for Chemistry in 1902.

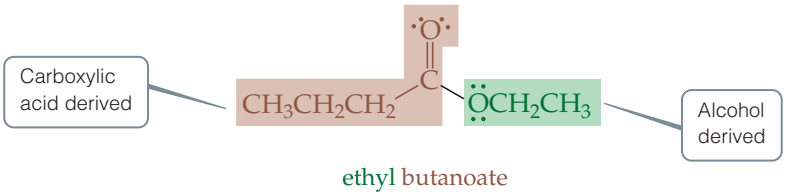
Esters are compounds in which the OH group of a carboxylic acid is replaced by an OR group:





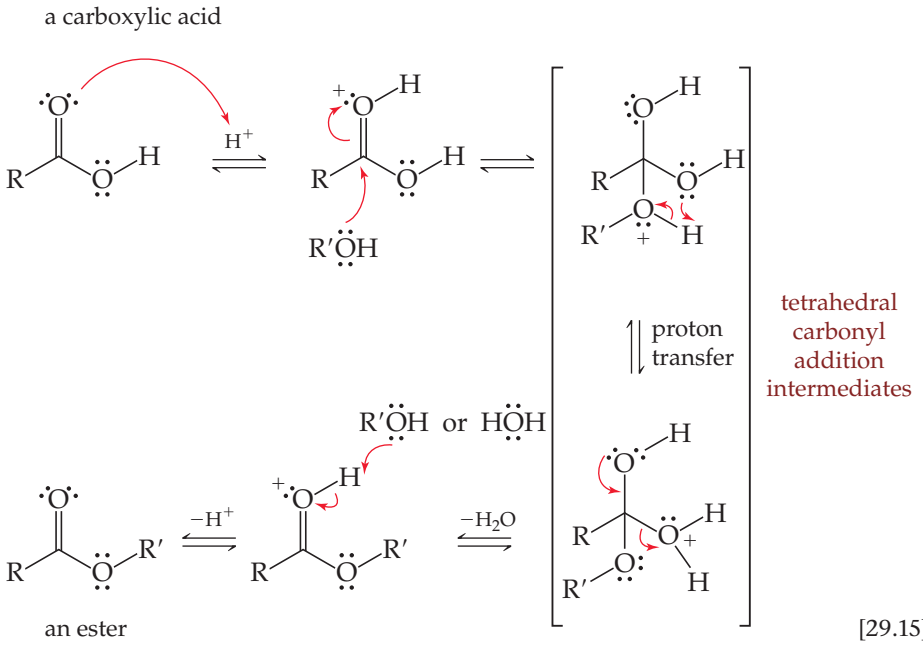
▲ **Figure 29.5 Everyday carboxylic acids and esters.** Many sunburn lotions contain the ester benzocaine; some nail polish remover is ethyl acetate; vegetable oils are also esters.

Figure 29.5 shows some common esters, which are named by using first the group from which the alcohol is derived and then the group from which the acid is derived. For example, ethyl butanoate is derived from ethanol and butanoic acid:



Esters generally have pleasant odours and are largely responsible for the pleasant aromas of fruit. **Table 29.4** lists some common esters and the structures, fragrances and flavors associated with them.

The mechanism of formation of an ester by the acid-catalyzed condensation of an alcohol and a carboxylic acid can be shown as follows:

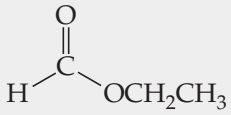
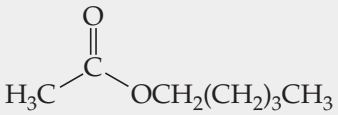
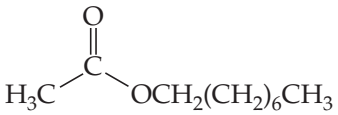
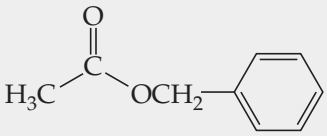
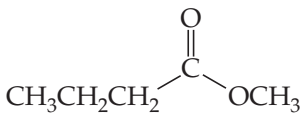
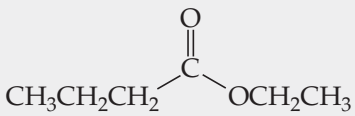
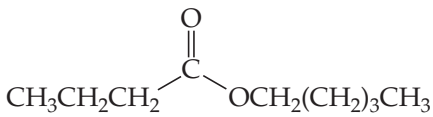
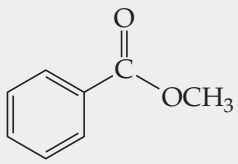
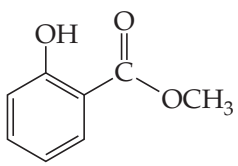
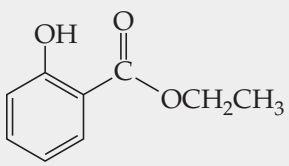
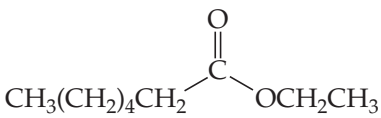


[29.15]

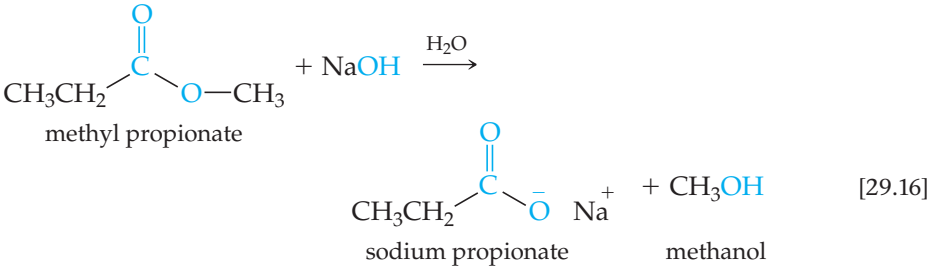
As with aldehydes and ketones, the basis of reactivity of the carboxylic acid occurs at the carbonyl group. The electronegativity of two oxygen atoms on the carbonyl carbon makes this carbon more electropositive than the corresponding carbon of either an aldehyde or ketone. Note from Equation 29.15 that the esterification reaction is fully reversible at each step and that formation of the ester from the carboxylic acid requires an excess of alcohol to drive the reaction in the direction that favors ester formation.

From the mechanism shown in Equation 29.15, it should become apparent that carboxylic acids can be formed from esters by the addition of excess water in the presence of an acid catalyst. This reaction, called hydrolysis, is the reverse of that described and is an important reaction in organic synthesis, as esters are often prepared to protect carboxylic acids.

TABLE 29.4 Simple esters as flavors and fragrances

Ester	Formula	Flavor/fragrance
Ethyl methanoate		rum
Butyl acetate		raspberry
Pentyl acetate		banana
Octyl acetate		orange
Benzyl acetate		jasmine
Methyl butanoate		apple
Ethyl butanoate		pineapple
Pentyl butanoate		pear or apricot
Methyl benzoate		almond
Methyl salicylate		oil of wintergreen
Ethyl salicylate		mint
Ethyl heptanoate		grape

The hydrolysis of esters is also possible in a basic aqueous medium, such as sodium hydroxide solution:



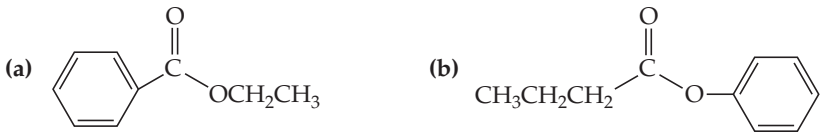
[29.16]

The products of the reaction are the sodium salt of the carboxylic acid and the alcohol. Distillation of the methanol and acidification of the aqueous solution of the sodium carboxylate yields the carboxylic acid. The hydrolysis of an ester in the presence of a base is called **saponification**, a term that comes from the Latin word for soap (*sapon*). The traditional synthesis of soap from animal fat is an example of this reaction.

Sample Exercise 29.3

Naming Esters and Predicting Hydrolysis Products

Name each of the following esters and indicate the products of their reaction with aqueous base.



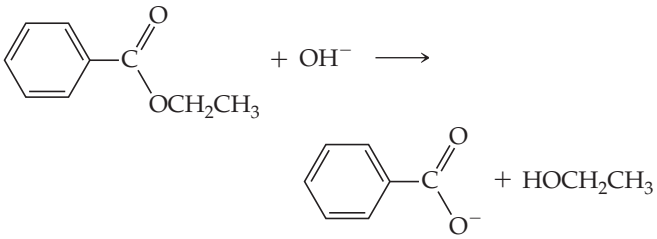
SOLUTION

Analyze We are asked to name each ester and to determine their saponification products.

Plan To name an ester, we must analyze its structure and determine the identities of the alcohol and acid from which it is formed. Identifying these two components will also allow us to determine the products of the saponification.

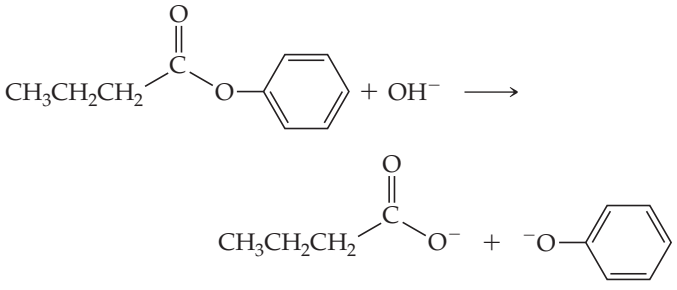
Solve Esters are formed by the condensation reaction between an alcohol and a carboxylic acid. We can identify the alcohol by adding an OH to the alkyl group attached to the O atom of the carboxyl (COO) group. We can identify the acid by adding an H group to the O atom of the carboxyl group. We've learned that the first part of an ester name indicates the alcohol portion and the second part indicates the acid portion. The name conforms to how the ester undergoes hydrolysis, reacting with base to form an alcohol and a carboxylate anion.

(a) This ester is derived from ethanol (CH_3CH_2OH) and benzoic acid (C_6H_5COOH).Its name is therefore ethyl benzoate. The net ionic equation for reaction of ethyl benzoate with hydroxide ion is:



The products are benzoate ion and ethanol.

(b) This ester is derived from phenol (C_6H_5OH) and butanoic acid ($CH_3CH_2CH_2COOH$). The residue from the phenol is called the phenyl group. The ester is therefore named phenyl butanoate. The net ionic equation for the reaction of phenyl butanoate with hydroxide ion is



The products are butanoate ion and phenoxide ion.

Practice Exercise

Write the structural formula for the ester formed from propanol and propionic acid.

Self-Assessment Exercise

29.12 What are the products of base hydrolysis of ethyl propanoate?

(a) CH_3COOH and $CH_3CH_2CH_2OH$

(b) CH_3CH_2COOH and CH_3CH_2OH

(c) $CH_3CH_2COO^-$ and CH_3CH_2OH

(d) CH_3CH_2COOH and $CH_3CH_2O^-$

Exercises

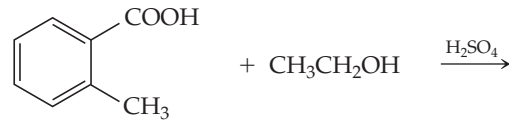
29.13 Identify the functional groups in each of the following compounds:

(a) $CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$ **(b)** $CH_3\overset{\overset{O}{\|}}{C}H$ (OH)

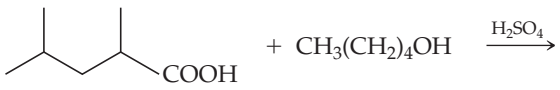
(c) $CH_2CH_2CH_3$ (OH) **(d)** $CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_3$

29.14 Draw the products of the following reactions. In each case, the sulfuric acid acts as a catalyst.

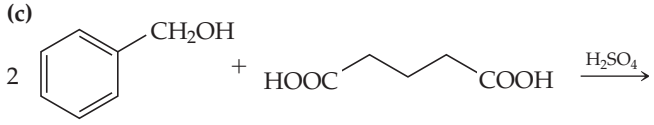
(a)



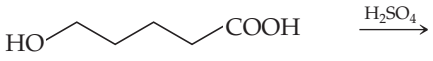
(b)



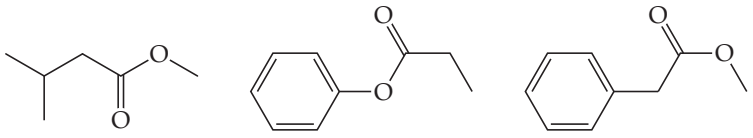
(c)



(d)



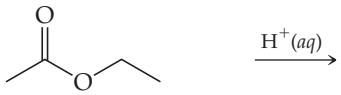
29.15 Give the condensed formulas for the carboxylic acid and alcohol from which each of the following esters may be formed.



(a) **(b)** **(c)**

29.16 Draw the products of the following reactions.

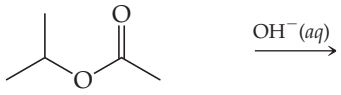
(a)



(b)



(c)



(d)



Answers to Self-Assessment Exercise

29.12 (c)

29.4 | Fats, Oils, and Waxes



Obesity is an increasing issue in modern society and is considered the main preventable cause of death in the western world. It significantly increases the risk of cardiovascular disease and type 2 diabetes as well as a range of other conditions. Typically, obesity results from a combination of eating too many sweet or fatty foods, which are high in energy-rich carbohydrates or lipids, respectively, while not getting enough exercise but other factors such as depression and genetic susceptibility may contribute. A change of diet and increase in physical activity is used to combat obesity but may require considerable willpower to implement. Obesity is defined by a body mass index (BMI) greater than 30 kg/m^2. BMI is calculated by dividing a person's weight in kg by the square of their height in m.

"Lipid" is a term that covers a range of molecules, all of which are hydrophobic. Fats, oils, and waxes are examples of lipids that we will now examine. By the end of this section, you should be able to:

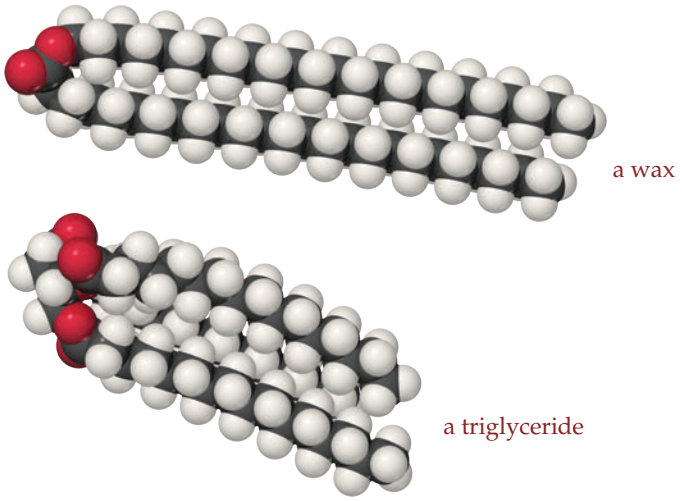
- Recognize the common structural unit of a lipid

Lipids are naturally occurring substances that can be extracted from cells and tissues by non-polar organic solvents. Common examples of lipids include cholesterol (a steroid), turpentine (a terpene), beeswax and olive oil. Even from this very limited group of compounds, it is quite clear that although lipids can contain a variety of functional groups, their overriding feature is the large proportion of hydrocarbon within the structure. The name "lipid" is derived from a property rather than from any functional group class (the Greek *lipos* means fat). **Complex lipids** are those that can be broken down into smaller constituents, usually by hydrolysis. **Simple lipids** are those that are not easily hydrolysed.

In this section we discuss a group of complex lipids that are esters of long-chain carboxylic acids called **fatty acids**. Two major groups of esters are derived from fatty acids: the waxes and triglycerides. **Waxes**, such as beeswax, are single esters made from fatty acids and long-chain alcohols. **Triglycerides** (more correctly known as triacyl glycerols) are triesters of glycerol and include common fats and oils. **Figure 29.6** shows two general examples of complex lipids. As you can see, even without investigating the type of functional group, both these molecules have alkyl chains of significant length. Their properties are derived from this feature. Waxes are typically greasy solids or semi-solids, while triglycerides can be solid or liquid at room temperature.

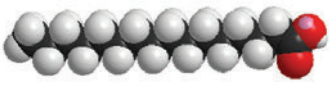
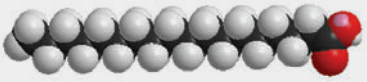
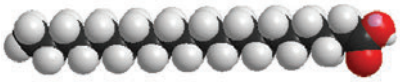
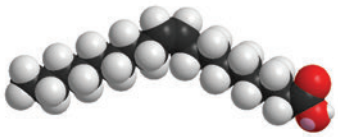
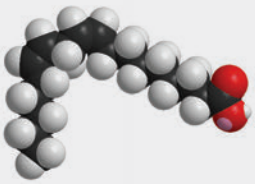
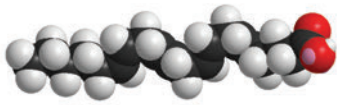
The most common triglycerides are those in which each fatty acid component is unbranched and has an alkyl chain more than 12 carbon atoms long. **Table 29.5** shows some of the more common saturated and unsaturated fatty acids found naturally.

Go Figure What structural features of a triglyceride molecule cause it to be insoluble in water?



▲ **Figure 29.6 Complex lipids.** A general example of the structure of a wax ($C_{25}H_{51}COOC_{24}H_{49}$) and a triglyceride using the C_{16} fatty acid, palmitic acid.

TABLE 29.5 Structure and names of some common fatty acids

Name	Chain length	Structure	Melting point (°C)
		Saturated acids	
Lauric acid	C12		45
Myristic acid	C14		53
Palmitic acid	C16		62
Stearic acid	C18		70
Arachidic acid	C20		75
		Unsaturated acids	
Oleic acid	C18 (1 × *cis* double bond)		13
Linoleic acid	C18 (2 × *cis* double bonds)		−5
Arachidonic acid	C20 (4 × *cis* double bonds)		−50

Note the difference in overall shape between saturated and unsaturated fatty acids. This shape difference is responsible for the different physical properties exhibited by the fatty acids and their corresponding triglycerides and waxes. For example, the melting point of stearic acid (mp = 70 °C), a saturated fatty acid, is 57 °C higher than oleic acid (mp = 13 °C) and 75 °C higher than linoleic acid (mp = −5 °C), despite the fact they all contain 18 carbon atoms. The reason is that "kinked" fatty acids—that is, fatty acids that contain one or more double bonds—cannot pack as closely or efficiently as the saturated fatty acids.

Most saturated triglycerides are **fats** because they are solid at room temperature. Most triglycerides containing double bonds do not pack as well as their saturated analogues and so are classed as **oils**. Oils are triglycerides that are liquid at room temperature. The term *polyunsaturated* simply means there is more than one double bond contained within the triglyceride.

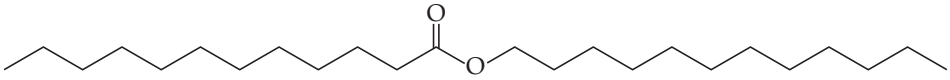
Consumers have come to realise that polyunsaturated vegetable oils are more easily digested than saturated ones. However, this has not always been the case. For many decades, the use of *lard*—a soft, white solid obtained by rendering pig fat—for cooking and baking meant that consumers wanted solid fats instead of liquid oils. Vegetable oils, cheaper to produce and polyunsaturated, are still converted to fats through a process called **hardening**. As chemists, we know this process as catalytic hydrogenation. The basic principle is not to reduce all the double bonds within an unsaturated triglyceride, but to reduce enough of them to yield the required properties and consistency. Needless to say, the process is carefully controlled. Margarine obtained from canola oil is a classic example.

Sample Exercise 29.4

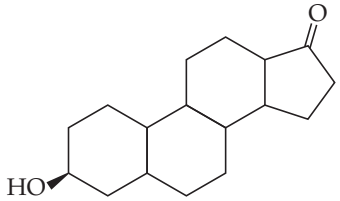
Lipids

Which of the following compounds is *not* classified as a lipid?

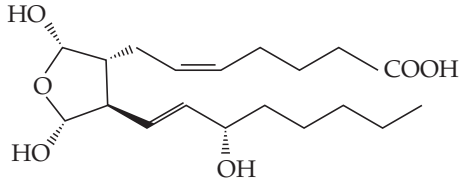
(a)



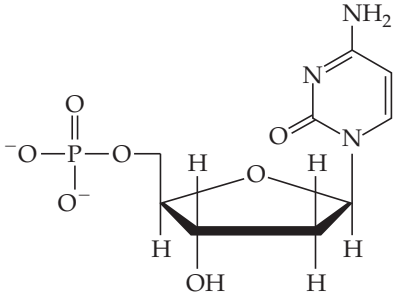
(b)



(c)



(d)



Continued

SOLUTION

Analyze We are asked to differentiate between compounds based on their functionality and to class them accordingly.

Plan By definition, *lipids* are naturally occurring substances that can be extracted from cells and tissue by non-polar organic solvents such as hexane. So we will use this definition as a means of classification.

Solve Structure **(a)** is a wax, similar to beeswax. It is soluble in hexane and so is classed as a lipid. Structure **(b)** is a member of the steroid hormones. Its large carbon framework suggests this compound will be soluble in non-polar solvents. Hence this compound can be generally classed as a lipid. Structure **(c)** is a prostaglandin. Despite the presence of three OH and a carboxylic acid group, the two large alkyl chains would suggest this molecule is hexane soluble. This compound is also a lipid. Structure **(d)** is a nucleotide. Its collection of nitrogen- and oxygen-containing heterocycles and polar phosphate group would mean this compound is more aqueous than hexane soluble. Therefore, this class of compound is not a lipid.

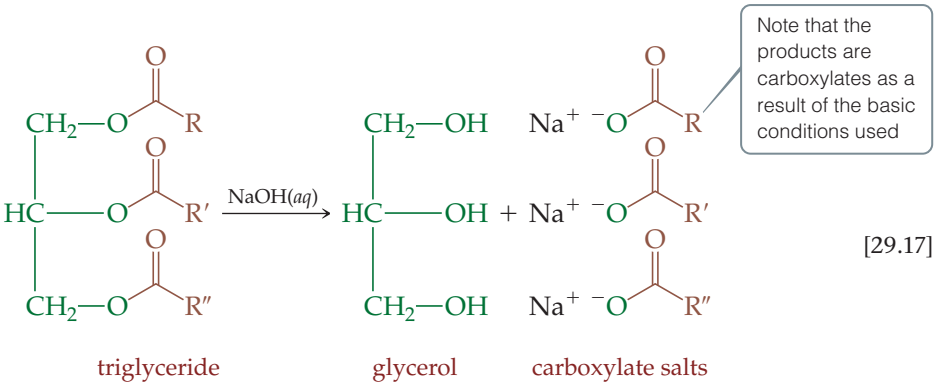
Practice Exercise
Draw the structure of a triglyceride containing lauric acid.

Soaps and Detergents

Historically, in the soap-making process a triglyceride (animal fat or a vegetable oil) was boiled with a strong base, usually NaOH. The resultant soap consisted of a mixture of sodium salts of long-chain carboxylic acids, the fatty acids, which formed during the saponification process (Figure 29.7).



▲ **Figure 29.7 Saponification.** Saponification of fats and oils has long been used to make soap. This etching shows a step in the soap-making process during the nineteenth century.



[29.17]

(R, R′, R″ are long alkyl chains)

The cleansing power of a soap is due to its ability to act as an emulsifying agent. That is, it is a substance that can sit at the interface between a hydrophobic liquid and a hydrophilic liquid, allowing the hydrophobic liquid to be dispersed in microscopic droplets. Many common forms of dirt (for example, grease, oil, fat) are hydrophobic and soaps allow them to be dispersed in waste water.

In water, soap forms a cloudy solution of **micelles**, as shown in Figure 29.8. Micelles form as a result of the hydrophobicity of the alkyl chains and the hydrophilicity of the polar carboxylate group. Micelles are stabilized by dispersion forces between alkyl groups and by hydrogen bonding between carboxylate anions and water molecules.

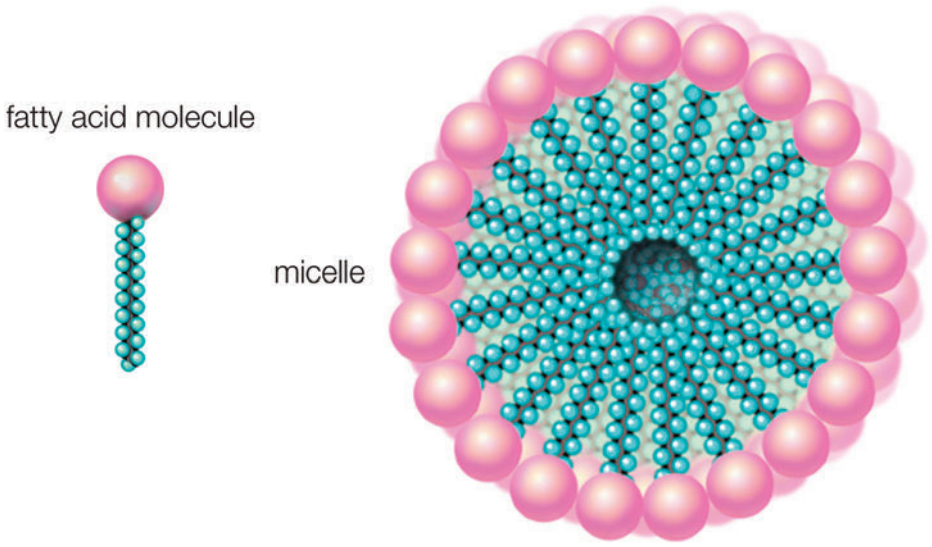
A common disadvantage of soap is the presence of *soap scum*, an insoluble precipitate or film that is difficult to remove from household areas such as bathrooms. This scum can be produced in two common ways. Foremost is the reaction of a fatty acid with Ca^{2+}, Mg^{2+} or Fe^{2+} ions found in *hard water*. This reaction, called a *counterion exchange* reaction, converts the sodium salt to the calcium salt, which is insoluble in water.

$$2\,CH_3(CH_2)_{16}COO^-\,Na^+ + Ca^{2+} \longrightarrow Ca[CH_3(CH_2)_{16}COO]_2 + 2\,Na^+$$

sodium salt of a fatty acid (soluble in water as micelles) → calcium salt of a fatty acid hard-water scum (insoluble in water)

[29.18]

The other common way of building up soap scum is through the precipitation of fatty acids in hard water that has been acidified by some means—for example, acid rain.



◀ **Figure 29.8 Soap micelle.** In water, soap forms a cloudy solution of micelles. The hydrophobic hydrocarbon chains cluster in the middle of the micelle and the polar (hydrophilic) carboxylate groups are on the surface. The Na^+ counterions are dissolved in the water around the micelle. Note: Micelles are not circular as drawn, but spherical (this is just a slice through a micelle).

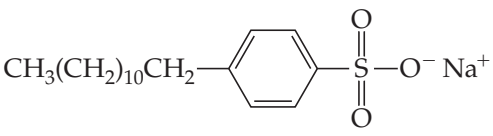
Without the ionisable carboxylate group, the fatty acid floats to the top of a water-based solution as a scum.

$$2\ CH_3(CH_2)_{16}COO^-\ Na^- \ +\ H^+ \longrightarrow CH_3(CH_2)_{16}COOH(s) + Na^+ \qquad [29.19]$$

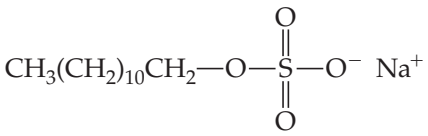
sodium salt of a fatty acid (soluble in water as micelles) — fatty acid acidic-water scum (insoluble in water)

Synthetic detergents have been designed with the problem of soap scum in mind. Essentially, the same desirable characteristics of a fatty-acid soap must be maintained; that is, the detergent should contain a long hydrocarbon chain and a polar head group. It is desirable that this polar head group should not form insoluble salts with Ca^{2+}, Mg^{2+} or Fe^{2+} ions, in particular. Sodium salts of sulfonic acids, called sulfonates or sulfates, provide useful analogues to the carboxylate group. Being stronger acids than carboxylic acids means that sulfonic acids are not as easily protonated, even under the lowest pH conditions found domestically. Of even greater significance is the fact that calcium, magnesium and iron salts of sulfonic acids are soluble in water.

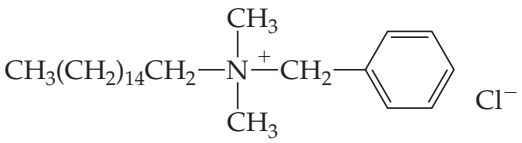
Not all detergents need to contain an anion. Benzalkonium chloride is one used in a variety of domestic liquid cleaning and disinfectant products. **Figure 29.9** illustrates some common examples of synthetic detergents.



sodium 4-dodecylbenzene sulfonate



sodium dodecyl sufate (SDS) (sodium lauryl sulfate)



benzylcetyldimethylammonium chloride (benzalkonium chloride)

◀ **Figure 29.9 Synthetic detergents.** Detergents can be anionic or cationic, but still retain the features of a soap derived from a fatty acid.

Sample Exercise 29.5

Soap Structure

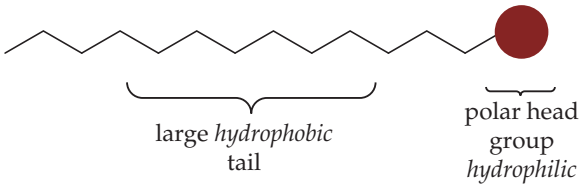
Draw the general structure of the main constituent of a soap micelle and indicate the hydrophilic and hydrophobic regions.

SOLUTION

Analyze We are asked to draw a schematic of the sodium or potassium salt of a fatty acid and indicate polar and non-polar regions.

Plan Since soaps are prepared from the carboxylate salt of a fatty acid, this question requires you to draw a long alkyl chain and a polar carboxylate head group.

Solve Using a simple circle for a head group and the line drawing of a long alkane, we get:

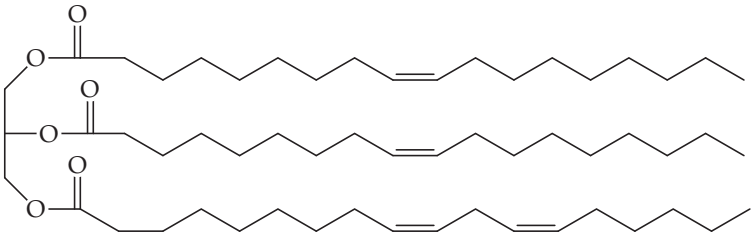


Practice Exercise

Detail the common features of a soap and a detergent.

Self-Assessment Exercise

29.17 Olive oil is composed of a number of fatty acids, but a typical molecule has the structure:



Name the fatty acids present in this structure.

(a) Stearic acid + 2 × oleic acid

(b) 2 × Oleic acid + linoleic acid

(c) 2 × Oleic acid + arachidonic acid

(d) Oleic acid + 2 × linoleic acid

Exercises

29.18 **(a)** What is the difference between a fat and an oil? **(b)** What is the difference between an fat and a wax? Draw an example of each to illustrate your point.

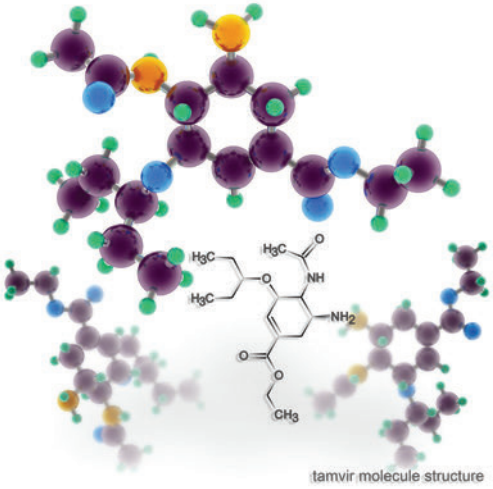
29.19 Write a balanced chemical equation using condensed structural formulas for **(a)** the formation of butyl propanoate from the appropriate acid and alcohol, **(b)** the saponification (base hydrolysis) of methyl benzoate.

29.20 Triglycerides are formed from fatty acids and glycerol (1,2,3-propanetriol). **(a)** Draw a general formula for the structure of a triglyceride. **(b)** Describe the difference between a saturated and an unsaturated fatty acid. **(c)** Indicate the difference in melting point between a saturated triglyceride and a comparable polyunsaturated triglyceride.

Answers to Self-Assessment Exercise

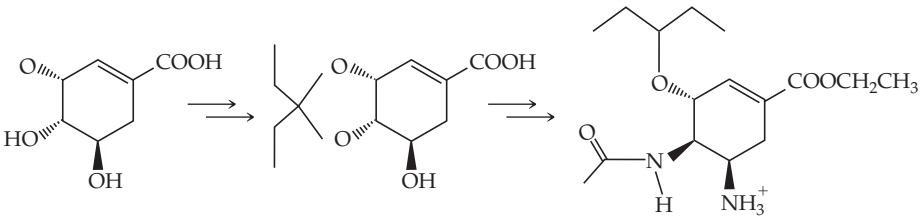
29.17 (b)

29.5 | Acid Chlorides, Anhydrides, and Nucleophilic Acyl Substitution



Most molecules around us contain more than one functional group. In our efforts to produce effective pharmaceuticals, we arrive at a substance that may have three, four, or more different functional groups in one molecule. This presents a difficulty in synthesis. How do we react one part of a molecule without affecting another functional group present? For example, treating a compound that contains both an aldehyde and a carboxylic acid group with an alcohol under acidic conditions will result in both an acetal and an ester being formed. As molecules become more complex and the number of functional groups they contain increases, the ability to do a reaction on one part of the molecule without interference from another functional group becomes increasingly difficult.

Sometimes the order in which we conduct a multi-stage synthesis allows us the selectivity we seek. In other cases, we may use "protecting groups". These are transformations that render one part of the molecule inactive while retaining the reactivity of another part. For example, a molecule that contains an alkene and a ketone will react with bromine by an electrophilic addition to the alkene and α-substitution to the carbonyl. If, however, we "protect" the ketone by forming an acetal first, bromination will only occur at the alkene, after which we can "deprotect" the acetal to re-form the original ketone. For this strategy to be efficient, the protecting group chemistry needs to be high-yielding and reversible. The formation of carboxylic acid derivatives, such as esters, is one example of the use of an effective protecting group. While protecting group chemistry is used extensively in a synthesis research laboratory, it is also employed in the manufacture of some pharmaceuticals such as oseltamivir—synthesized by Hoffmann-La Roche as an antiviral medication and marketed under the trade name of Tamiflu®.



(-)-Shickmic acid

The starting material contain three alcohol groups.
The formation of a "cyclic ketal" with the two *cis* OH groups allows the selcetive transformation of the third OH in high yield.

Oseltamivir

At the end of this section, you should be able to:

- Recognize the different functional groups that contain an acyl group
- Know the reagents necessary to convert between the different functional groups

Several functional group classes are derived from the carboxyl group. We have already introduced carboxylic acids and esters. Two others of note are the **acid anhydrides** and

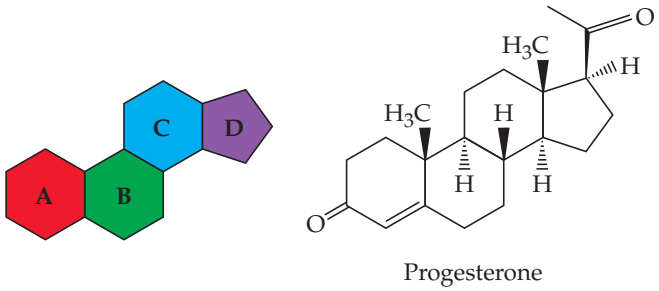
CHEMISTRY AND LIFE Steroids

Hormones are chemical messengers capable of stimulating or inhibiting particular biochemical processes. One major class of hormones is the steroids. Because steroids are non-polar compounds, they are considered lipids. Their non-polar character allows them to cross cell membranes so they can leave the cells in which they were synthesized and enter their target cells. There have been five Nobel prizes in the area of steroid chemistry giving it a rich and important history across chemistry and medicine.

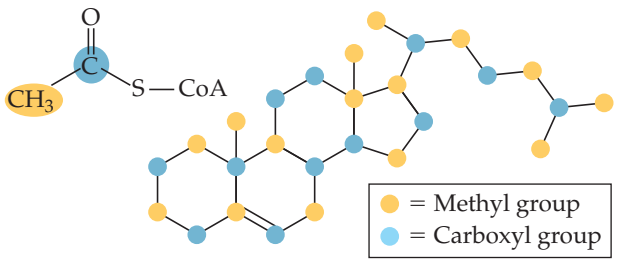
Bile salts are steroids with detergent properties able to emulsify lipids in foodstuff passing through the intestine to enable fat digestion and absorption through the intestinal wall. *Cholesterol* is a steroid found in animal tissues and various foods that is normally synthesized by the liver and is important as a constituent of cell membranes and influences membrane fluidity; it's actually a precursor to all steroid hormones. *Mineralcorticoids* such as aldosterone are secreted by the adrenal cortex and regulate the balance of water and electrolytes or salts (Na^+, Cl^-, HCO_3^-) in the body. The addition of aldosterone causes increased Na^+ readsorption, for example. *Glucocorticoids* such as cortisol (also called hydrocortisone) is also produced by the adrenal cortex and are involved in carbohydrate, protein and fat metabolism. They also have excellent anti-inflammatory properties. The most noted of the steroids are the sex hormones such as the estrogens (for example, progesterone and estrone) and the androgens (for example, testosterone). The estrogens and androgens affect the growth and function of the reproductive organs, the development of secondary sex characteristics and the behavioural patterns of animals. The structure of progesterone is shown in **Figure 29.10**. Anabolic steroids such as stanolozol aid in the development of muscles and are man made.

All steroids contain the characteristic rigid tetracyclic backbone based on the androstane ring system: the four rings are designated A, B, C and D as shown in Figure 29.10. The A, B and C rings are six-membered rings; D is a five-membered ring. In steroids, the rings are all fused with trans stereochemistry.

Steroids are made available from terpenes, which are readily made in nature from acetic acid.



▲ **Figure 29.10 The central tetracyclic structure to all steroids.** Progesterone is an estrone that plays a role in maintaining pregnancy.

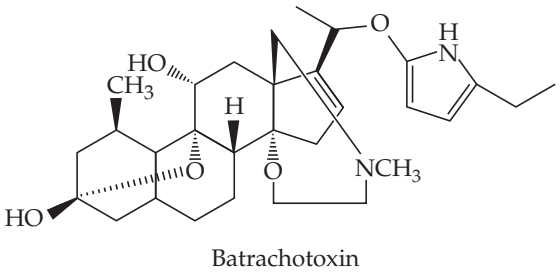


▲ **Figure 29.11 The tetracyclic backbone of all steroids can be traced back to acetic acid.** The methyl carbons in acetic acid are indicated as yellow dots, and the carbonyl carbons are represented in blue.

Figure 29.11 shows the origin of the acetic acid carbon atoms in a typical steroid structure. There are about 40 enzyme-catalyzed steps to prepare cholesterol from acetic acid through biosynthesis.

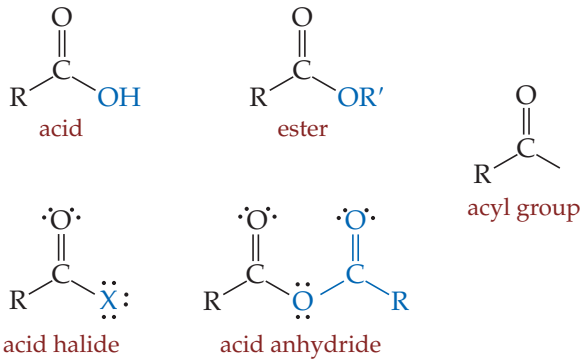
Poison dart frogs are fascinating creatures in that they secrete four steroid toxins from glands located on the back and behind the ears—one of them being among the most toxic substances known to man, batrachotoxin (**Figure 29.12**). Batrachotoxin contains the tetracyclic ring structure of the steroids. As a neurotoxin it affects the nervous system by increasing Na^+ permeability of cellular ion channels. It becomes lethal by permanently blocking nerve signal transmission to muscles, leading to cardiac arrest. The estimated lethal dose for this steroid poison in humans is somewhere between 2 and 200 μg.



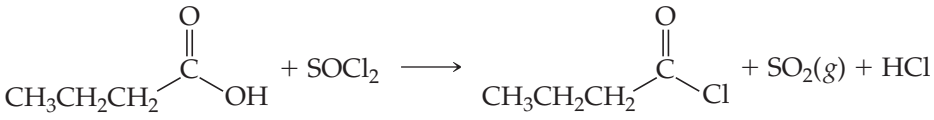


▲ **Figure 29.12 Poison dart frogs excrete batrachotoxin, a steroid-based structure and one of the most toxic compounds known.**

acid halides. The functional group known as an acid anhydride has two **acyl groups** (RCO–) linked by an oxygen atom. An acid halide has a single acyl group bonded to a halogen atom:



Acid chlorides, which are the most common and practical acid halides, are usually prepared by treatment of a carboxylic acid with thionyl chloride ($SOCl_2$). You may recall this reagent as a useful way of converting alcohols to chloroalkanes (Section 26.5). Acid chlorides are named by replacing the suffix *-oic acid* with *-oyl halide*. For example, $CH_3CH_2CH_2COCl$ is named butanoyl chloride and is derived from butanoic acid.

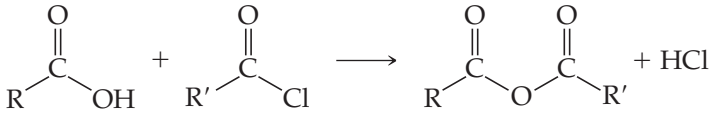


butanoic acid
a carboxylic acid

butanoyl chloride
an acid chloride

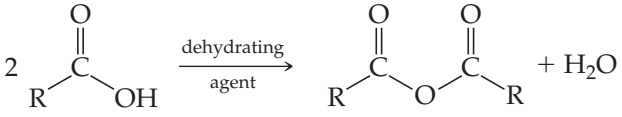
[29.20]

Acid anhydrides such as acetic anhydride, $(CH_3CO)_2O$, are usually prepared by reaction of a carboxylate anion with an acid chloride. In this way, both symmetrical anhydrides (same acyl group) and unsymmetrical anhydrides (different acyl groups) can be produced. Another general method is to dehydrate the carboxylic acid using a suitable dehydrating reagent, such as a more reactive anhydride. In some cases, especially 1,2-dicarboxylic acids such as phthalic acid or succinic acid, anhydrides can be formed by heating.



carboxylic acid acid chloride an acid anhydride

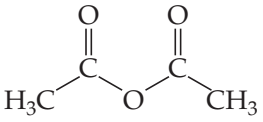
[29.21]



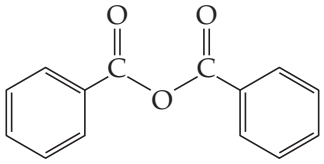
a carboxylic acid an acid anhydride

R = H, alkyl, aryl [29.22]

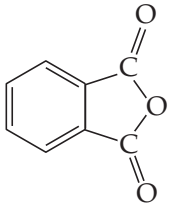
Anhydrides from simple carboxylic acids and cyclic anhydrides from dicarboxylic acids are named by replacing the word *acid* with *anhydride*.



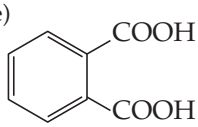
acetic anhydride
from acetic acid

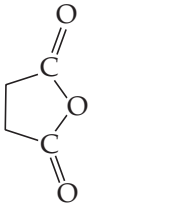


benzoic anhydride
from benzoic acid

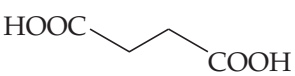


phthalic anhydride
from phthalic acid (accompanying figure)



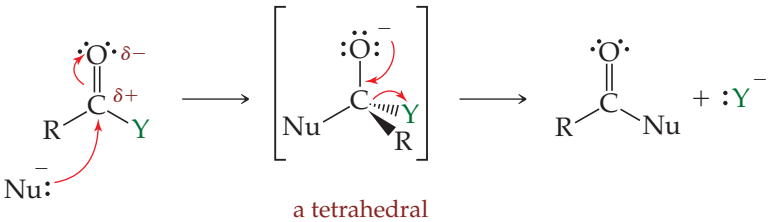


succinic anhydride
from succinic acid (accompanying figure)



Nucleophilic Acyl Substitution

Esters, acid chlorides and acid anhydrides all undergo nucleophilic substitution reactions at the acyl carbonyl group by the following general mechanism:



an acid chloride, anhydride or ester

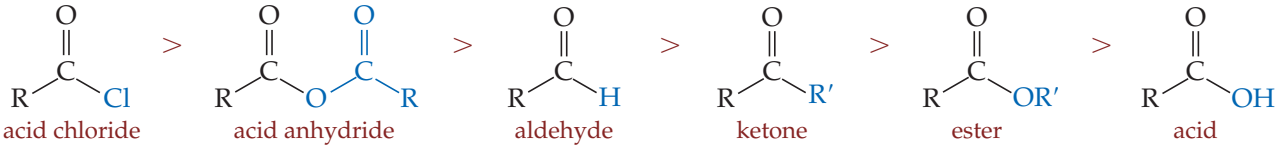
a tetrahedral intermediate

R = H, alkyl, aryl
Y = Cl, OR, OCOR

[29.23]

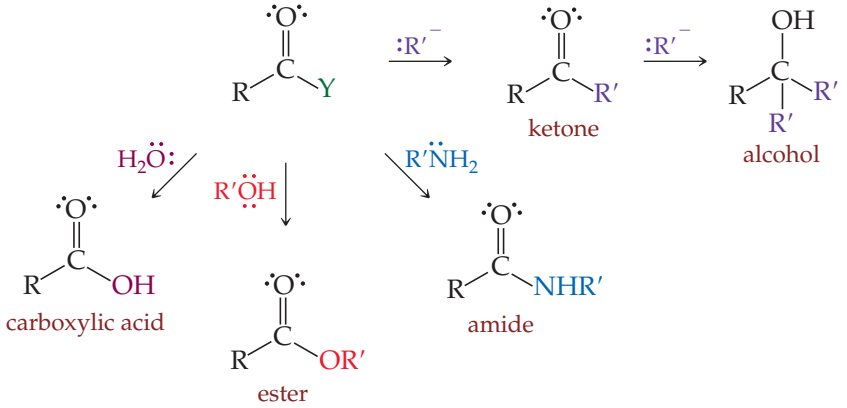
Such a reaction is called a **nucleophilic acyl substitution** and differs from nucleophilic reactions of aldehydes and ketones by the fate of the tetrahedral intermediate formed (compare the middle structure in equations 28.5 and 29.23). In this case, this intermediate collapses to regenerate the carboxyl group, thereby eliminating the group (Y)—which is typically a *good leaving group*—as a stable anion.

The reactivity of carbonyl compounds towards nucleophilic attack can be summarized as:

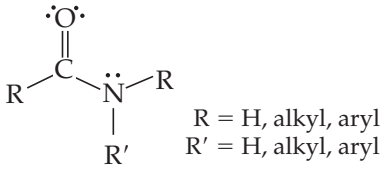


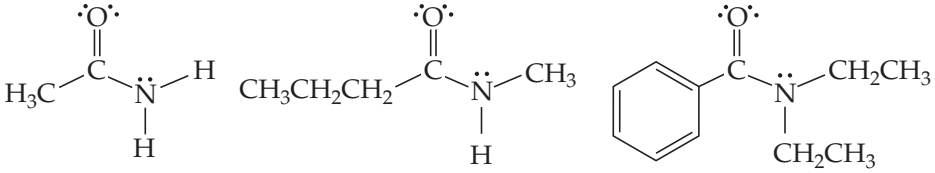
This relative reactivity is governed by two factors: the electropositive nature of the carbonyl carbon atom by substituent inductive effects, and the stability of the leaving group (Y^-) displaced by substitution. Some useful interconversions using this reaction type are shown in **Figure 29.13** including the reaction of amines with acid chlorides, anhydrides and esters to form **amides**. Amides have an acyl group bonded to a trivalent nitrogen atom, usually of the form RCONHR'. Amide bonds are the key structural features that join amino acids together to form polypeptides and proteins. Amides are named by replacing the suffix *-oic acid* with *amide*. The *N* in the names shown here refers to functionalization on nitrogen. So, for *N*-methylbutanamide, the methyl group is bonded to nitrogen.

Go Figure What role do water, alcohol and amine play in these interconversions?



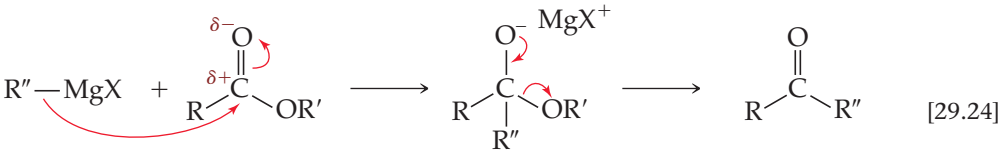
▲ **Figure 29.13 Functional group interconversions.** Acid halides, anhydrides and esters are versatile starting materials, leading to a range of different functional groups. Y = Cl, OR or OCOR.



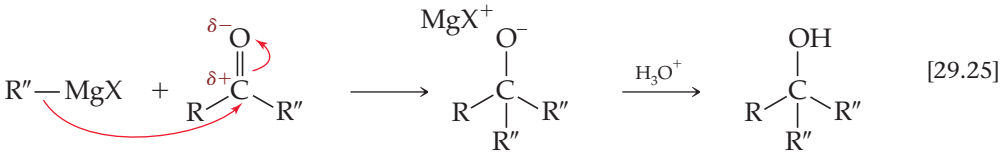


acetamide *N*-methylbutanamide *N,N*-diethylbenzamide

A second interconversion from Figure 29.13 to highlight involves the reaction of acid chlorides, anhydrides and esters with carbanions, such as those generated through Grignard reagents, to form alcohols via a ketone intermediate. The addition of a strong nucleophile such as a Grignard reagent to an ester (or acid chloride or anhydride) usually yields the corresponding 3° alcohol as the final product instead of the expected ketone (based on a stoichiometric addition). For this reason, usually two equivalents of the Grignard reagent are added to the reaction mixture to drive the reaction to completion. Mechanistically, collapse of the tetrahedral intermediate from the ester, after attack of the first equivalent of RMgX, yields a ketone. The ketone is more electrophilic than the ester (and so more reactive towards a second equivalent of RMgX), so it undergoes further reaction to yield the stable alkoxide in preference. Upon the addition of acid, the tertiary alcohol is formed.

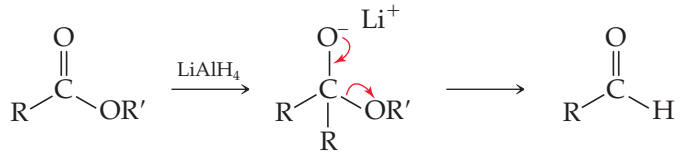


an ester a ketone [29.24]

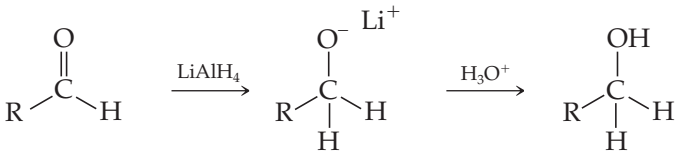


a ketone a tertiary alcohol [29.25]

We can extrapolate this result to other nucleophiles such as hydride (H^-), which comes in the form of lithium aluminum hydride ($LiAlH_4$), a powerful reducing agent. As shown in Equation 29.26, collapse of the tetrahedral intermediate from the ester yields an aldehyde, which again is more reactive than the ester, and which undergoes a second addition of hydride to form the alkoxide. The addition of mild acid protonates the alkoxide, forming a primary alcohol.



an ester an aldehyde [29.26]



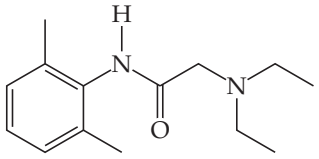
an aldehyde a primary alcohol [29.27]

Hence, by appropriate choice of nucleophile, esters can be easily converted into both primary and tertiary alcohols.

- Recognize the different functional groups that contain an acyl group
- Know the reagents necessary to convert between the different functional groups

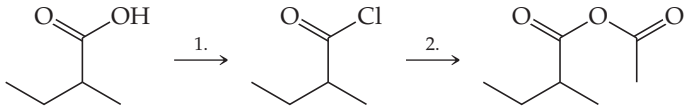
Self-Assessment Exercises

29.21 Lidocaine is used as a local anesthetic. What functional groups does it contains?



(a) amine and amide
(b) amine and ester
(c) carboxylic acid and amide

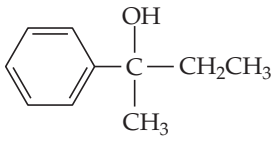
29.22 What reagents would carry out the following transformation?



(a) 1. Cl_2 2. CH_3COOH
(b) 1. $SOCl_2$ 2. CH_3COCH_3
(c) 1. $SOCl_2$ 2. CH_3COOH
(d) 1. HCl 2. CH_3COCl

Exercises

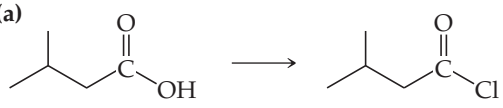
29.23 2-Phenyl-2-butanol can be synthesized by a combination of a Grignard reagent and an ester. Show the combination.

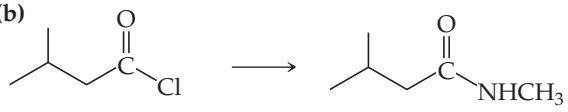


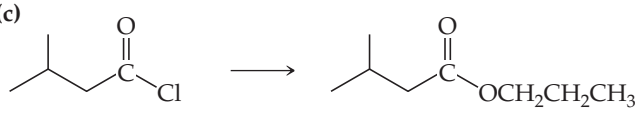
29.24 Draw the condensed structures of the products formed from **(a)** butanoic acid and methanol, **(b)** benzoic acid and 2-propanol, **(c)** the reaction of propanoic acid with $SOCl_2$ and then dimethylamine. Name the compound in each case.

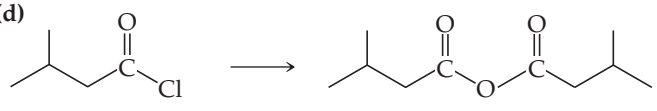
29.25 Acetic anhydride is formed from acetic acid in a condensation reaction that involves the removal of a mole of water from between two acetic acid molecules. Write the chemical equation for this process, and show the structure of acetic anhydride.

29.26 Suggest plausible reagents for the following transformations.

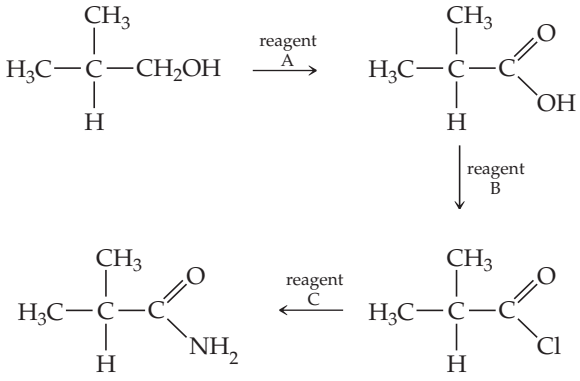
(a)


(b)


(c)


(d)


29.27 List the reagents necessary to undertake the following transformations:



Answers to Self-Assessment Exercises

29.21 (a) **29.22** (c)

29.6 | Condensation Polymerization



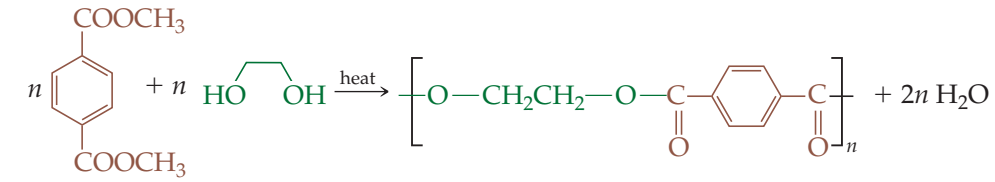
Polymers are an integral part of modern life. They are very large molecules constructed of just a few small molecules that are repeated many times. Their use in our lives is incredibly diverse and ranges from soft-drink bottles to components of life-saving heart valve replacements. A St Jude valve uses the polyester Dacron® to attach it to the surrounding heart tissue. Dacron® is Du Pont's trade name for the fiber formed from polyethene terephthalate (a polyester). About 250,000 valve-replacement procedures are performed annually worldwide, most using a St Jude valve. The valve is secured to the surrounding tissue via a biocompatible polyester sewing ring. The polar, oxygen-containing functional groups along the biocompatible polyester chain afford attractive interactions to facilitate tissue growth.

By the end of this section, you should be able to:

- Recognize the components of a condensation polymer.

In Chapter 26, we discussed one of the major classes of commercially important polymers and their formation by addition polymerization. A second general reaction used to synthesize commercially important polymers is **condensation polymerization** or *step-growth polymerization*. This type of polymerization usually employs difunctional molecules as the monomers, with each new bond being created in a separate step. We discuss two types of condensation polymers in this section: **polyesters** and **polyamides**.

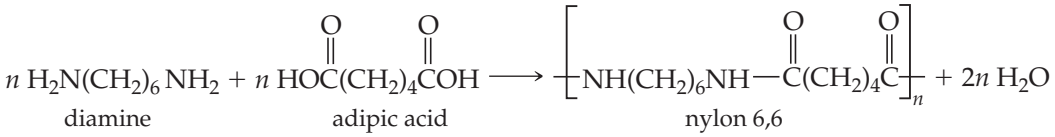
Polyesters are formed by the reaction of a diacid, diacid chloride or diester with a diol. Polymers formed from two different monomers are called **copolymers**. PET (polyethene terephthalate), or *Dacron*®, is the most common polyester copolymer used today.



dimethyl terephthalate | ethene glycol | PET (Dacron®)

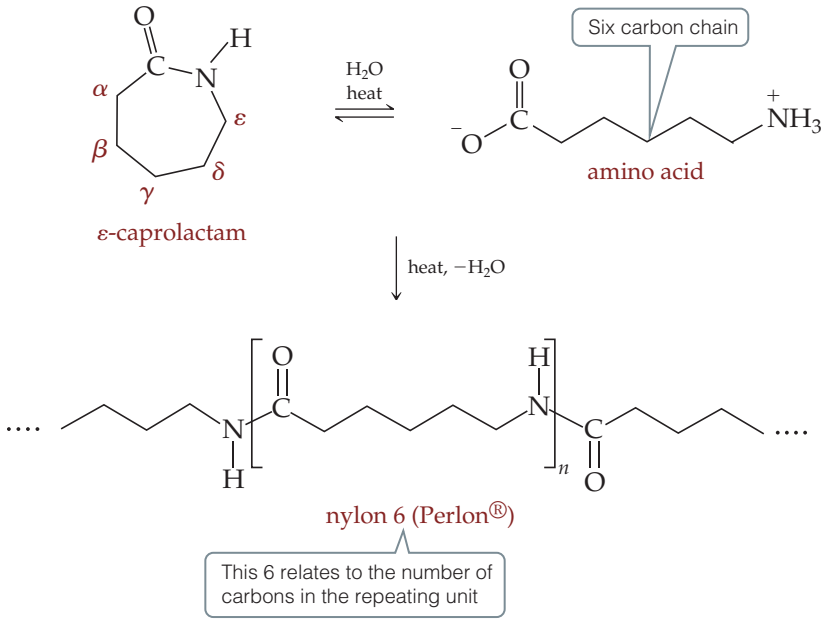
[29.28]

Polyamides are formed by the polycondensation of a diamine with a diacid, diacid chloride or diester. The best known of the polyamides is nylon 6,6, discovered by Wallace Carothers (1896–1937) and his associates at Du Pont in 1934. It is named with the notation 6,6 because it is made by the reaction of adipic acid (a diacid within a six-carbon chain) and 1,6-hexanediamine (a six-carbon chain diamine). Nylons are used in home furnishings, apparel, carpet, fishing line and toothbrush bristles, to name but a few.



[29.29]

Nylon 6, also called *Perlon*®, is made from ε-caprolactam, a cyclic amide. Its uses include ropes and ties. When ε-caprolactam is heated with a small amount of water, some of it is hydrolysed to the amino acid. Continued heating gives condensation and polymerization to yield molten nylon 6. Note that a single-digit notation is used because nylon 6 is a polymer made up of one monomer containing six carbons. The monomer can be symbolized as A, which in polymer form creates the same simple repeating unit -A-A-A-A-. Nylon 6,6 is a polymer comprising two different monomers, symbolized as A and B, which forms copolymers of the form -A-B-A-B-.



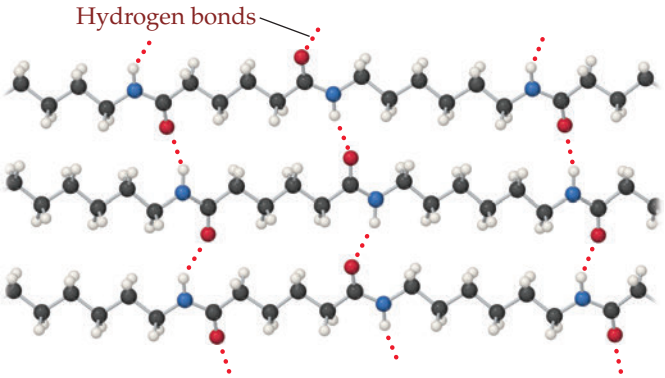
[29.30]

Polymers such as nylon and polyesters can also be formed into *fibres* that, like hair, are very long relative to their cross-sectional area and are not elastic. These fibres can be woven into fabrics or cords and fashioned into clothing and other useful objects.

Fibres of nylon 6,6 are cold-drawn, meaning they are drawn out at room temperature. As the fibres are drawn, hydrogen bonds form between individual polymer strands, such that the carbonyl of one amide bond hydrogen bonds to an amide hydrogen atom on another strand (**Figure 29.14**). The tensile strength and stiffness of nylon 6,6 are attributable to the hydrogen bonding that occurs in these fibres.

Various substances may also be added to polymers to provide protection against the effects of sunlight or against degradation by oxidation. For example, manganese(II) salts and copper(I) salts, in concentrations as low as $5-10^{-4}$ % (*w*/*w*), are added to nylons to provide protection from light and oxidation and to help maintain whiteness.

Go Figure What role do the hydrogen bonds play in a polymeric material such as nylon?



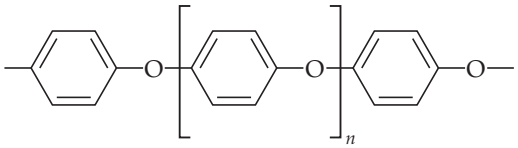
▲ **Figure 29.14 Hydrogen bonding in nylon 6,6.** The unusual and desirable physical properties of nylon 6,6 are a result of intermolecular hydrogen bonding.

CHEMISTRY AND LIFE Towards the Plastic Car

Many polymers can be formulated and processed to have sufficient structural strength, rigidity and heat stability to replace metals, glass and other materials in a variety of applications. The housings of electric motors and kitchen appliances such as coffee makers and can openers, for example, are now commonly made from specially formulated polymers. Engineering polymers are tailored to particular applications through choice of polymers, blending of polymers and modifications of processing steps. They generally have lower costs or superior performance over the materials they replace. In addition, shaping and colouring of the individual parts and their assembly to form the final product are often much easier.

The modern car provides many examples of the inroads engineering polymers have made in car design and construction. Car interiors have long been formed mainly of plastics. Through development of high-performance materials, significant progress has been made in introducing engineering polymers as engine components. **Figure 29.15**, for example, shows the manifold in a series of Ford V-8 utility and van engines. The manifold, which is made of nylon, must be stable at high temperatures. The use of an engineering polymer in this application eliminates machining and several assembly steps.

Car body parts can also be formed from engineering polymers. Components formed from engineering polymers usually weigh less than the components they replace, thus improving fuel economy. The bumper bars of Volkswagen's New Beetle (**Figure 29.16**), for example, are made of nylon reinforced with a second polymer, poly(phenylene ether) (PPE), which has the following structure:



Because the poly(phenylene ether) polymer is linear and rather rigid, it confers rigidity and ensures shape retention.

A big advantage of most engineering polymers over metals is that they eliminate the need for costly corrosion protection steps in manufacture. In addition, some engineering polymer formulations permit manufacturing with the colour built in, thus eliminating painting steps.



▲ **Figure 29.15 Plastic engines.** The intake manifold of some Ford V-8 engines is formed from nylon.

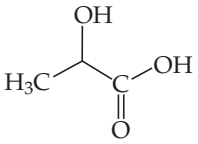


▲ **Figure 29.16 Plastic fenders.** The bumper bars of this Volkswagen Beetle are made of General Electric Noryl GTX, a composite of nylon and poly(phenylene ether).

Sample Exercise 29.6

Condensation Polymers

What is the structure of the polymer formed from lactic acid, a naturally occurring compound obtained from carbohydrates?

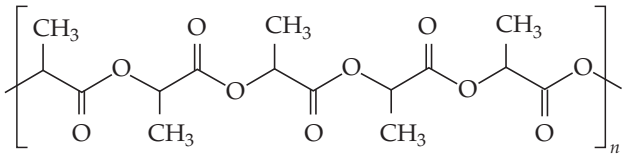


SOLUTION

Analyze We are given the structure of lactic acid and asked to derive the structure of the polymer made through self-condensation.

Plan Identify functional groups capable of forming a condensation polymer, then draw the polymer linking these functional groups up.

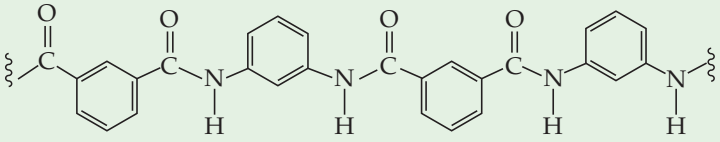
Solve Identification of the alcohol and carboxylic acid functional groups is important to determine the place of condensation. Condensation occurs by the formation of ester groups.

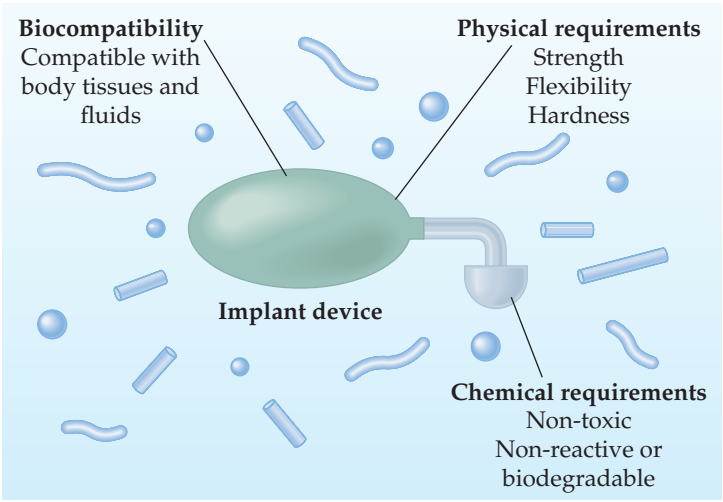


poly(lactic acid)

Practice Exercise

Indicate whether the following polymer is a step (condensation) or chain (addition) growth polymer. Draw the structure of the monomer/s used in the preparation of this polymer.





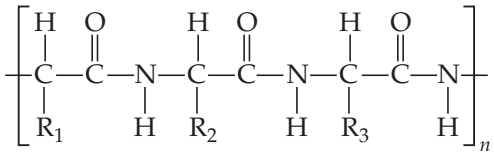
▲ **Figure 29.17 Schematic illustration of a human-made device implanted in a biological system.** To function successfully, the device must be biocompatible with its surroundings and meet the necessary physical and chemical requirements, some of which are listed for illustrative purposes.

Polymers for Medicine

Increasingly, modern synthetic materials such as polymers are being used in medical and biological applications. For our discussion here, a **biomaterial** is any material that has a biomedical application. The material might have a therapeutic use in a treatment, injury or disease or it might have a diagnostic use as part of a system for identifying a disease or for monitoring a quantity such as the glucose level in blood. Whether the use is therapeutic or diagnostic, the biomaterial is in contact with biological fluids, so it must have properties that meet the demands of that application. For example, a polymer used to make a disposable contact lens must be soft and have an easily wetted surface, whereas the polymer used to fill a dental cavity must be hard and wear resistant. The most important characteristics that influence the choice of a biomaterial are biocompatibility, physical requirements and chemical requirements, as illustrated in Figure 29.17.

Specialized polymers have been developed for a variety of biomedical applications. The degree to which the body accepts or rejects the foreign polymer is determined by the nature of the groups along the chain and the possibilities for interactions with the body's own molecules. Our bodies are composed largely of biopolymers such as proteins, polysaccharides (sugars) and polynucleotides (RNA, DNA). We will learn more about these molecules in Chapter 31. For now, we can simply note that the body's biopolymers have complex structures, with polar groups along the polymer chain. Proteins, for example,

are long strings of amino acids (the monomers) that have formed a condensation polymer. The protein chain has the following structure:

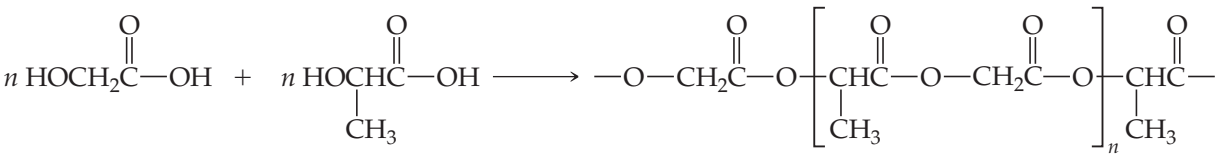


where the R groups vary along the chain ($-CH_3$, $-CH(CH_3)_2$, and so on). Twenty different amino acids are used in different combinations to make up proteins in humans. By contrast, synthetic polymers are simpler, formed from a single repeating unit or perhaps two different repeating units. This difference in complexity is one of the reasons why synthetic polymers are identified by the body as foreign objects. Another reason is that there may be few or no polar groups along the chain that can interact with the body's aqueous medium.

Polymers can be characterized by their physical properties. Elastomers are used as biomaterials in flexible tubing, over leads for implanted heart pacemakers and as catheters (tubes implanted into the body to administer a drug or to drain fluids). Thermoplastics, such as polyethene or polyesters, are employed as membranes in blood dialysis machines and as replacements for blood vessels. Thermoset plastics find limited, but important, uses. Because they are hard, inflexible and somewhat brittle, they are most often used in dental devices or in orthopedic applications, such as joint replacements. To fill a cavity, for example, the dentist may pack some material into the cavity, then shine an ultraviolet lamp on it. The light initiates a photochemical reaction that forms a hard, highly cross-linked thermoset polymer.

CHEMISTRY AND LIFE Biodegradable Sutures

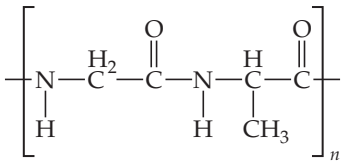
Until the 1980s, if you had to have stitches in a wound, you had to go back later to get the stitches removed. Stitches that are used to hold living tissue together are called *sutures*. Since the 1980s, biodegradable sutures have been available. After the sutures have been applied to the tissue, they slowly dissolve away and do not release any harmful by-products. Today biodegradable sutures are made out of lactic acid—glycolic acid copolymers that slowly hydrolyze over time.



glycolic acid lactic acid copolymer [29.31]

Self-Assessment Exercise

29.28 The material that makes up much of a spider's web is a polymer with the structure:



Identify the monomer units a spider uses to make its web.

(a) $NH_2-CH_2-NH_2$ and $HOOC-CH(CH_3)-COOH$

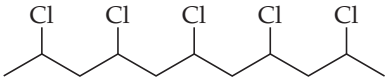
(b) $HOOC-CH_2-COOH$ and $NH_2-CH(CH_3)-NH_2$

(c) NH_2-CH_2-COOH and $NH_2-CH(CH_3)-COOH$

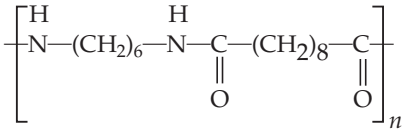
Exercises

29.29 Write a chemical equation for the formation of a polymer via a condensation reaction from the monomers succinic acid ($HOOCCH_2CH_2COOH$) and ethenediamine ($H_2NCH_2CH_2NH_2$).

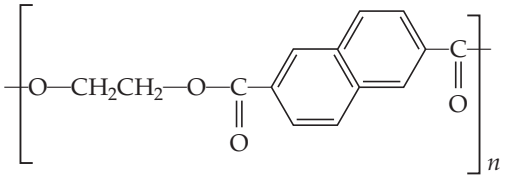
29.30 Draw the structure of the monomer/s employed to form each of the following polymers: **(a)** poly(vinyl chloride), **(b)** nylon 6,10 and **(c)** poly(ethene naphthalate).



poly(vinyl chloride)



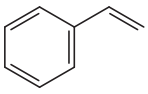
nylon 6,10



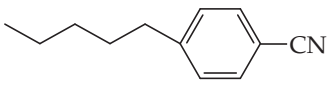
PEN

29.31 Consider the molecules shown here. **(a)** Which of these would be most likely to form an addition polymer? **(b)** Which would be most likely to form a condensation polymer?

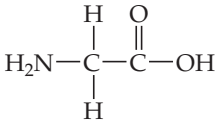
(i)



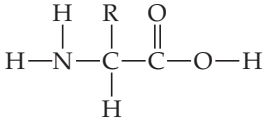
(ii)



(iii)

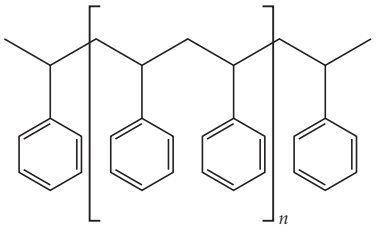


29.32 Proteins are polymers formed by condensation reactions of amino acids, which have the general structure

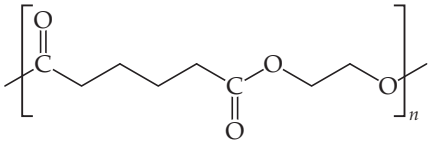


In this structure, R represents —H, $—CH_3$ or another group of atoms. Draw the general structure for a poly(amino acid) polymer formed by condensation polymerization of the molecule shown here.

29.33 On the basis of the structure of polystyrene and poly(ethene adipate) shown here, which class of polymer would you expect to form the most effective interface with biological systems? Explain.



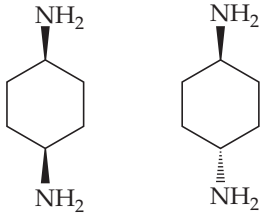
polystyrene



poly(ethene adipate)

29.34 If you were going to attempt to grow skin cells in a medium that affords an appropriate scaffolding for the cells and you had only two fabrics available, one made from polystyrene and the other from PET, which would you choose for your experiments? Explain.

29.35 **(a)** Draw the structure of Qiana®, a polyamide synthesized by the reaction of hexanedioic acid with *trans*-1,4-cyclohexanediamine. **(b)** What effect, if any, would there be in using *cis*-1,4-cyclohexanediamine instead of *trans*-1,4-cyclohexanediamine?



cis *trans*

1,4-cyclohexane diamine

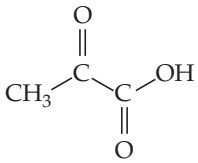
Answers to Self-Assessment Exercise

29.28 (c)

Sample Integrative Problem

Putting Concepts Together

Pyruvic acid has the following structure:



It is formed in the body from carbohydrate metabolism. In the muscle it is reduced to lactic acid in the course of exertion. The acid-dissociation constant for pyruvic acid is 3.2×10^{-3}. **(a)** Why does pyruvic acid have a higher acid-dissociation constant than acetic acid? **(b)** Would you expect pyruvic acid to exist primarily as the neutral acid or as dissociated ions in muscle tissue, assuming a pH of about 7.4 and an acid concentration of 2×10^{-4} M? **(c)** What would you predict for the solubility properties of pyruvic acid? Explain. **(d)** What is the hybridization of each carbon atom in pyruvic acid? **(e)** Assuming H atoms as the reducing agent, write a balanced chemical equation for the reduction of pyruvic acid to lactic acid. (Although H atoms don't exist as such in biochemical systems, biochemical reducing agents deliver hydrogen for such reductions.)

SOLUTION

(a) The acid ionization constant for pyruvic acid should be somewhat greater than that of acetic acid because the carbonyl function on the α-carbon atom exerts an electron-withdrawing effect on the carboxylic acid group. In the C—O—H bond system, the electrons are shifted from hydrogen, facilitating loss of the hydrogen as a proton.

(b) To determine the extent of ionization, we first set up the ionization equilibrium and equilibrium constant expression. Using HPv as the symbol for the acid, we have

$$\text{HPv} \rightleftharpoons \text{H}^+ + \text{Pv}^-$$

$$K_a = \frac{[\text{H}^+][\text{Pv}^-]}{[\text{HPv}]} = 3.2 \times 10^{-3}$$

Let $[\text{Pv}^-] = x$. Then the concentration of undissociated acid is $2 \times 10^{-4} - x$. The concentration of $[\text{H}^+]$ is fixed at 4.0×10^{-8} (the antilog of the pH value). Substituting, we obtain

$$3.2 \times 10^{-3} = \frac{[4.0 \times 10^{-8}][x]}{[2 \times 10^{-4} - x]}$$

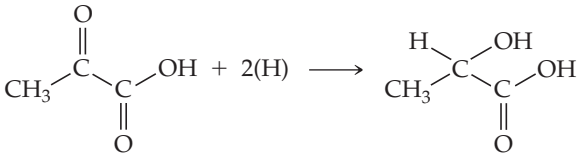
Solving for x, we obtain $x[3.2 \times 10^{-3} + 4.0 \times 10^{-8}] = 6.4 \times 10^{-7}$

The second term in the brackets is negligible compared with the first, so $x = [\text{Pv}^-] = 6.4 \times 10^{-7}/3.2 \times 10^{-3} = 2 \times 10^{-4}$ M. This is the initial concentration of acid, which means that essentially all the acid has dissociated. We might have expected this result because the acid is quite dilute and the acid-dissociation constant is fairly high.

(c) Pyruvic acid should be quite soluble in water because it has polar functional groups and a small hydrocarbon component. It is miscible with water, ethanol and diethyl ether.

(d) The methyl group carbon has sp^2 hybridization. The carbon carrying the carbonyl group has sp^2 hybridization because of the double bond to oxygen. Similarly, the carboxylic acid carbon is sp^2 hybridized.

(e) The balanced chemical equation for this reaction is



Essentially, the ketonic functional group has been reduced to an alcohol.

Chapter Summary and Key Terms

SECTION 29.1 **Carboxylic acids** are weak acids. They react with bases to form **carboxylate anions**, which are very stable due to resonance. Carboxylic acids readily form hydrogen bonded dimers in concentrated solution or neat.

SECTION 29.2 Carboxylic acids are commonly prepared by oxidation of primary alcohols or aldehydes or by the oxidation of benzylic carbon atoms, yielding benzoic acid derivatives. They can also be prepared by hydrolysis of nitriles, amides and esters.

SECTION 29.3 **Esters** are formed by the condensation reaction of carboxylic acids and alcohols. This reaction is called the **Fischer esterification**. Esters can form amides by a condensation reaction with amines. Esters undergo hydrolysis, called **saponification**, in the presence of strong bases.

SECTION 29.4 Esters such as **fats**, **oils**, **waxes** and **triglycerides** are abundant in biological systems. They form part of a general class called **lipids**. Lipids come in two forms; **complex** and **simple**, depending on

the chemical properties of the lipid. Polyunsaturated triglycerides can be hardened by catalytic hydrogenation, which changes the texture of the triglyceride from a liquid form to a solid/semi-solid form. This process is called **hardening**. The saponification of a triglyceride leads to a **soap**. In water, soaps form a **micelle**, encapsulating dirt particles. Hard waters that contain Ca^{2+} often leave an insoluble scum. **Synthetic detergents** are designer soaps that eliminate the unwanted properties associated with the formation of calcium salts.

SECTION 29.5 **Acid anhydrides** and **acid halides** also contain an **acyl group** and are more reactive than their ester or carboxylic acid analogues. Both the anhydrides and acid halides are useful starting materials with which to make esters and **amides** through **nucleophilic acyl substitution** reactions.

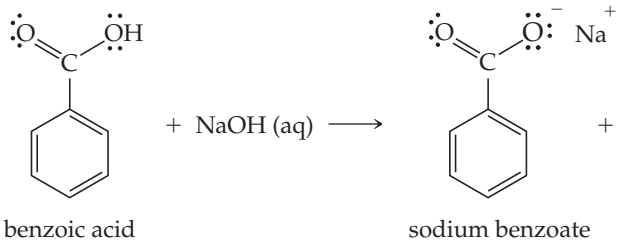
SECTION 29.6 A **condensation polymerization** occurs when a small molecule is lost upon reaction. The two main types of condensation polymers are **polyesters** and **polyamides**. A polymer formed from two different monomers is called a **copolymer**. A **biomaterial** is any biocompatible material that has a biomedical application. Biomaterials are commonly polymers with special properties matched to the application.

Key Skills

- Be able to prepare carboxylic acids from a range of starting materials. (Section 29.2)
- Know how to name carboxylic acids, esters, amides and acid chlorides and to discern these functional groups. (Sections 29.3–29.5)
- Be able to define terms such as lipid, oil and fat and reference these terms to classes of compounds. (Section 29.4)
- Understand the differences and similarities between a soap and a detergent. (Section 29.4)
- Be able to determine the products of acyl nucleophilic substitution of esters, acid chlorides and anhydrides with a range of nucleophiles. (Section 29.5)
- Be familiar with the chemistry of carboxylic acids—including their acidity, the stability of carboxylate salts, their reaction with alcohols to form esters and their reaction with amines to form amides. (Sections 29.2–29.5)
- Be able to draw and name polyesters from monomers and identify monomers within polyesters. (Section 29.6)

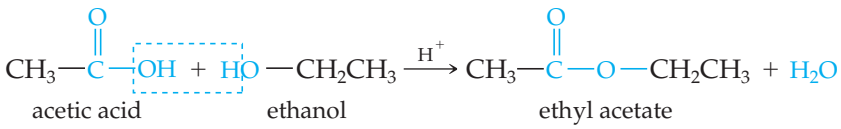
Key Equations

- Acid–base reaction



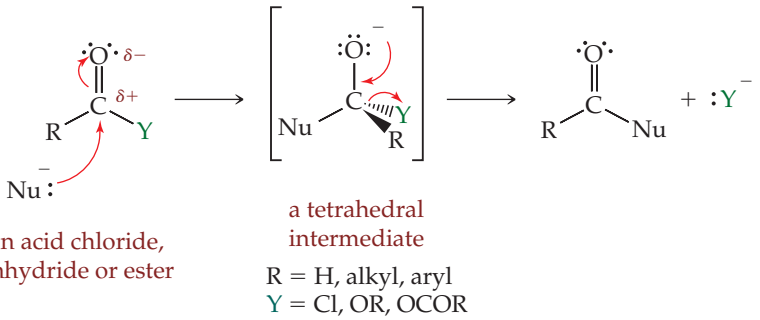
[29.2]

- Esterification



[29.14]

- Nucleophilic acyl substitution



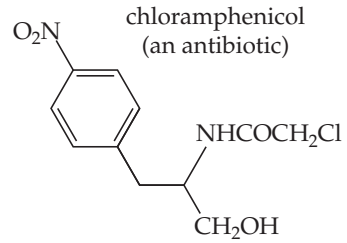
[29.23]

Exercises

Visualizing Concepts

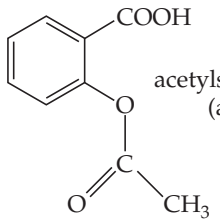
29.36 Identify each of the functional groups in the following molecules. [Sections 29.1 and 29.2]

(a)



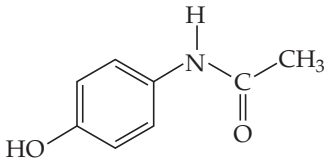
chloramphenicol (an antibiotic)

(b)



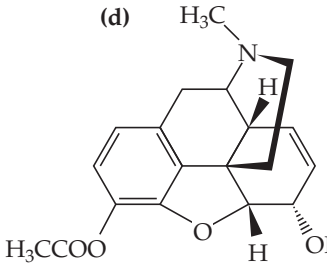
acetylsalicylic acid (aspirin)

(c)



paracetamol

(d)



heroin

29.37 What features must a molecule have to participate in hydrogen bonding with other molecules of the same kind? Which of the following compounds would you expect to **(a)** have the highest melting point, **(b)** be most soluble in mild aqueous base? Explain. [Section 29.1]



(i) (ii) (iii) (iv)

29.38 Draw the structure of the alcohol precursor, its systematic name and the reaction conditions you might use to obtain the following compounds by oxidation. [Section 29.1]

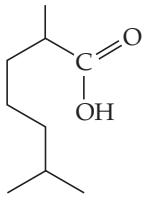
(a)



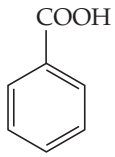
(b)



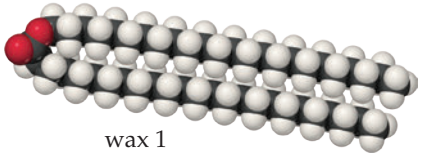
(c)



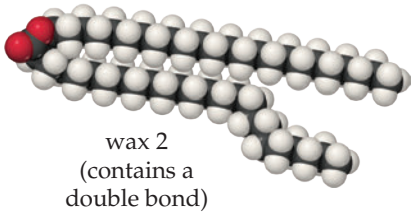
(d)



29.39 Which of the following waxes will have the lower melting point? [Section 29.4]



wax 1

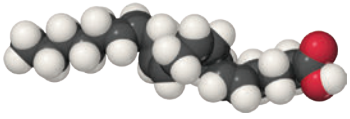


wax 2 (contains a double bond)

29.40 Which of the following fatty acids, when reacted with potassium hydroxide, would form better micelles and hence make the best soap? Explain. [Section 29.4]

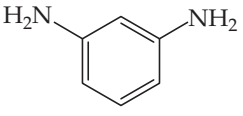


arachidic acid

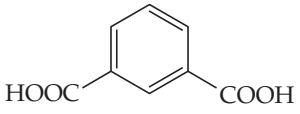


arachidonic acid

29.41 The polyamide Nomex is prepared from the condensation polymerization of 1,3-benzenediamine with 1,3-benzenedicarboxylic acid. **(a)** Draw a structural formula representation of the polymer, being sure to indicate the repeat unit. **(b)** Would you expect such a polymer to have applications requiring high strength and high temperature, or to be more useful as a *glad-wrap* alternative? Explain your answer. [Section 29.6]



1,3-benzenediamine



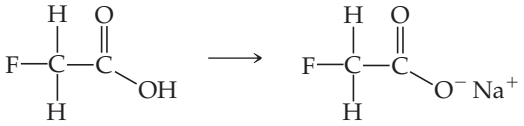
1,3-benzenedicarboxylic acid

Carboxylic Acids (Section 29.1)

29.42 Although carboxylic acids and alcohols both contain an −OH group, one is acidic in water and the other is not. Explain the difference.

29.43 "Bath bombs" contain calcium carbonate and citric acid. When placed into water, they fizz and dissolve rapidly. What are the products of this reaction?

29.44 **(a)** Sodium monofluoroacetate, known as "1080", is a commonly used rabbit and fox poison. What reagent could be used to convert fluoroacetic acid into 1080? **(b)** Explain why the pK_a for fluoroacetic acid ($pK_a = 2.59$) is lower than the pK_a of acetic acid (CH_3COOH, $pK_a = 4.76$).



fluoroacetic acid 1080

29.45 **(a)** The structural formula for acetic acid is shown in this table. Replacing hydrogen atoms on the carbon with chlorine atoms causes an increase in acidity, as follows:

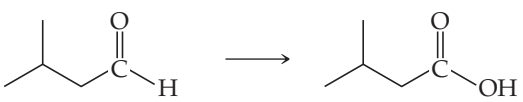
Acid	Formula	K_a (25 °C)
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

Using Lewis structures as the basis of your discussion, explain the observed trend in acidities in the series. Calculate the pH of a 0.010 *M* solution of each acid.

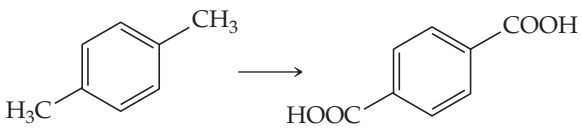
Preparation of Carboxylic Acids (Section 29.2)

29.46 Suggest plausible reagents for the transformations shown here.

(a)



(b)



29.47 Describe methods for preparing butanoic acid from each of the following:

(**a**) butan-1-ol

(**b**) butanal

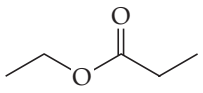
(**c**) methyl butanoate

(**d**) butanoyl chloride

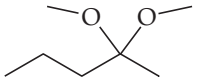
Esters and Esterification (Section 29.3)

29.48 Classify the following compounds as acetals, alcohols, hemiacetals, carboxylic acids, esters or ethers:

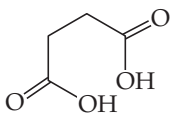
(a)



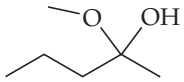
(b)



(c)



(d)



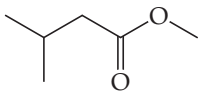
29.49 Name the following esters and draw the starting materials needed to synthesize them.



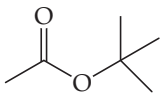
(a) **(b)** **(c)**

29.50 Draw the products of the following hydrolysis reactions.

(a)

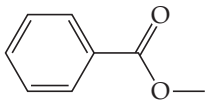


(b)



(c) $CH_3CH_2COOCH_2CH_2CH_3$ $\xrightarrow{H^+(aq)}$

(d)

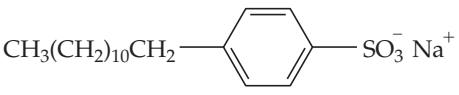


Fats, Oils, and Waxes (Section 29.4)

29.51 Write a balanced chemical equation using condensed structural formulas for the saponification (base hydrolysis) of **(a)** methyl propionate, **(b)** phenyl acetate.

29.52 Locate the stereogenic center/s in a triglyceride bearing one palmitic acid, one stearic acid and one arachidic side chain (see Table 29.5).

29.53 The structure of a synthetic detergent is shown here. **(a)** What features make this compound act like a natural soap? **(b)** Draw a simple micelle using this molecule to demonstrate the detergent's application. Label the hydrophobic and hydrophilic regions of the micelle.

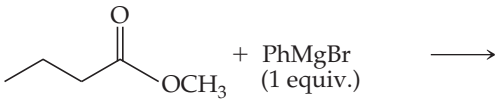


sodium 4-dodecylbenzene sulfonate (SDS)

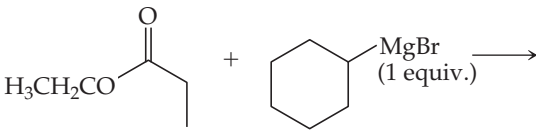
Nucleophilic Acyl Substitution (Section 29.5)

29.54 Draw the major product expected under the following conditions (Ph = C_6H_5):

(a)



(b)

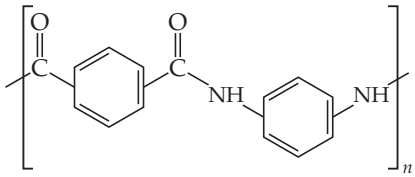


29.55 Draw the condensed structure of the compounds formed by reactions between **(a)** benzoic acid and ethanol, **(b)** ethanoyl chloride and methylamine, **(c)** acetic acid and phenol. Name the compound in each case.

29.56 γ-Hydroxybutanoic acid (GHB) can be prepared enzymatically from 1,4-butanediol. **(a)** Devise a method of preparing GHB in the laboratory from 1,4-butanediol. What compromise did you have to make? **(b)** GHB can form a cyclic ester under acidic conditions. Draw the structure of this ester.

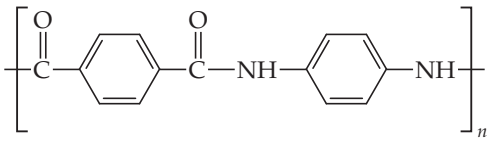
Condensation Polymerization (Section 29.6)

29.57 The nylon Nomex®, a condensation polymer, has the following structure:



Draw the structures of the two monomers that yield Nomex®.

29.58 Kevlar®, a high-performance polymer, has the following structure:



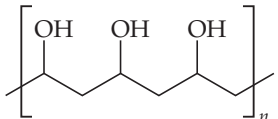
Write the structural formulas for the two compounds that are condensed to form this polymer.

29.59 In addition to the condensation of dicarboxylic acids with diamines, nylons can also be formed by the condensation reactions of aminocarboxylic acids with themselves. Nylon 4, for example, is formed by the polycondensation of 4-aminobutyric acid ($NH_2CH_2CH_2CH_2COOH$). Write a chemical equation to show the formation of nylon 4 from this monomer.

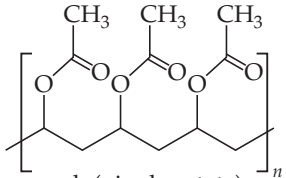
29.60 Briefly explain why it is important to achieve correct 1:1 stoichiometry of monomers in a condensation polymerization.

29.61 PET soft drink bottles can be recycled by heating the PET with methanol in the presence of an acid catalyst. The result of this reaction is the isolation of ethene glycol and dimethyl terephthalate (the dimethyl ester of terephthalic acid). These compounds are then reused in the manufacture of new PET-containing products. Write a reaction for the acid-catalyzed degradation of PET with methanol.

29.62 Poly(vinyl alcohol), PVA, is a useful water-soluble polymer. It cannot be prepared directly from vinyl alcohol, because vinyl alcohol tautomerizes spontaneously to acetaldehyde. It can, however, be prepared from poly(vinyl acetate). Design an experiment for the conversion of poly(vinyl acetate) to poly(vinyl alcohol).



poly(vinyl alcohol)



poly(vinyl acetate)

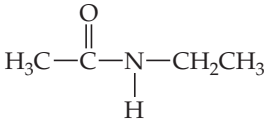
29.63 Glyptal® resin makes a strong thermoset polymer with applications in the electronics and car industries. It is prepared by the condensation of terephthalic acid and glycerol. Draw the structure of Glyptal® and explain its remarkable strength and rigidity.

Integrative Exercises

29.64 Bromobenzene is reacted first with magnesium, then carbon dioxide followed by dilute acid in a Grignard reaction. **(a)** Draw the structure of the product of this reaction. A 0.0050 *M* solution of the product has a pH of 3.25. **(b)** What is the K_a of the product? **(c)** The conjugate base of the product is a resonance-stabilized anion. Draw all the major resonance structures of this anion.

29.65 Many esters are volatile compounds with distinct fragrances. The boiling point of an ester is often lower than you might expect from the boiling points of the carboxylic acid and alcohol from which it is derived. For example, ethyl methanoate has a boiling point of 54 °C and the boiling points of ethanol and methanoic acid are 78 °C and 100 °C, respectively. **(a)** Draw the structure of ethyl methanoate and indicate the approximate bond angle associated with the carbonyl carbon and ether oxygen atom. **(b)** What intermolecular force is responsible for an increase in boiling point as molecular mass increases in a series of similar compounds? **(c)** What additional intermolecular forces are present in carboxylic acids and alcohols that are not present in the related ester?

29.66 Ethene is an important product from the petrochemical industry. Devise a synthesis of *N*-ethyl acetamide using ethene as the only carbon source. [*Hint*: NH_2^- is a powerful nucleophile.]

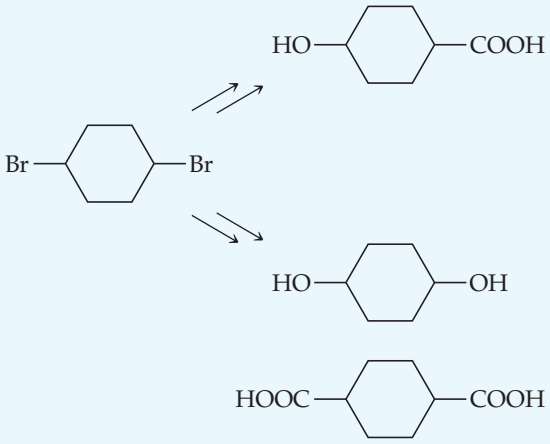


N-ethyl acetamide

Design an Experiment

Imagine you are a materials chemist working on a new polyester based on cyclohexane. You want to investigate the difference between a copolymer formed from a dicarboxylic acid with a diol and the polymer formed from a single monomer unit containing both carboxylic acid and alcohol functional groups. For economy of manufacture, you start with 1,4-dibromocyclohexane to make both types of monomer.

How do you synthesize the starting monomers? Do you need to pay attention to the relative quantities of reagents that you use? When making 4-hydroxycyclohexanecarboxylic acid is it important which order you use to install the two different functional groups? How might you carry out the polymerization reaction? What sort of properties do you anticipate for your polymer?



30

BENZENE AND ITS DERIVATIVES

WHAT'S AHEAD

30.1 The Structure of Benzene

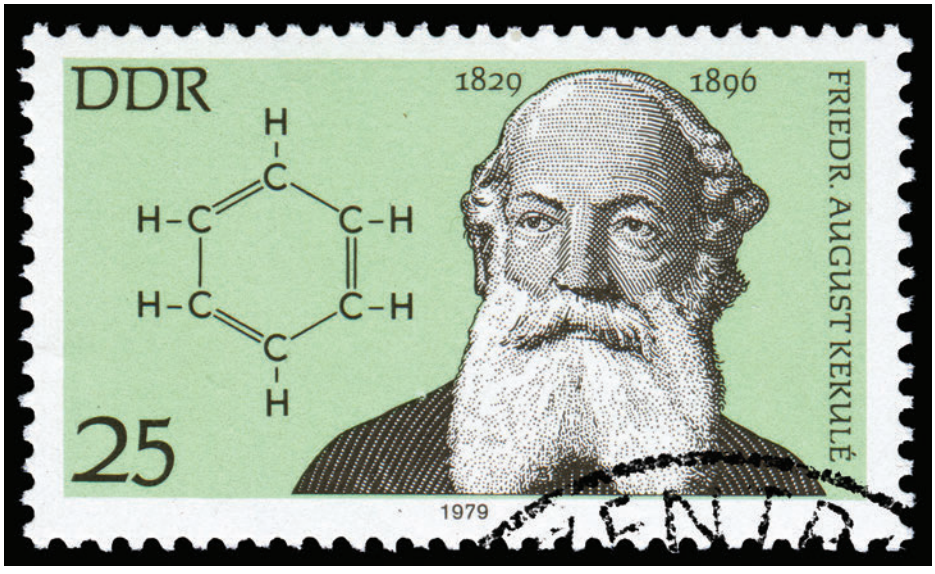
30.2 Isomerism and Nomenclature in Aromatic Compounds

30.3 Aromaticity

30.4 Acidity of Phenols

30.5 Electrophilic Aromatic Substitution (EAS) Reactions

30.1 The Structure of Benzene



The history of benzene and the discovery of its unusual structure is an interesting story. In 1825, Michael Faraday isolated a pure compound from the oily mixture that condensed from illuminating gas, the fuel burned in gaslights common at the time in England. The compound had a boiling point of 80 °C and a pungent odour. Elemental analysis of the compound showed it had a carbon-to-hydrogen ratio of 1:1, corresponding to an empirical formula of CH. About nine years later, German chemist Eilhard Mitscherlich (1794–1863) synthesized the same compound by heating benzoic acid in the presence of lime:

$$\underset{\text{gum of benzoin (benzoic acid)}}{C_6H_5COOH} + \underset{\text{calcium oxide}}{CaO} \xrightarrow{\text{heat}} \underset{\text{benzene}}{C_6H_6} + \underset{\text{calcium carbonate}}{CaCO_3}$$

He further used vapor-density measurements to determine the molecular weight of 78 u. He named the new compound *benzin*, after the gum benzoin from which he derived it. We now know this compound as benzene.

However, benzoic acid had been known for several hundred years before Mitscherlich's experiment. Benzoic acid is the white odourless compound isolated from benzoin resin, a substance extruded by several types of Southeast Asian trees of the genus *Styrax*. It is often used as a topical fungicide.

Although the experiments of Mitscherlich showed that benzene must have the formula C_6H_6, it was not clear what the structure of the molecule could be. Only after 1860, when the concept of unsaturation was introduced, did August Kekulé (1829–1896) propose a suitable model. Kekulé was instrumental in developing much of the structural theory of organic chemistry, but he is best known for his work on benzene (1865). How he came to propose the structure of benzene is the truly fascinating part of this story. Kekulé recalled falling asleep on a London bus, and while he was dozing, he conjured images of "dancing atoms" that connected into snakes. As the snakes twisted and turned, eventually one caught its own tail, giving the image leading to the now famous structure of alternating double and single bonds. In his theory, however, two interconvertable structures were possible. As we know now, the structure is subtly different, but considering the level of chemical knowledge at this point in time, and more importantly, on the chemistry of benzene, Kekulé's proposed structure was revolutionary.

By the end of this section, you should be able to:

- Understand the unusual structure that benzene possesses.

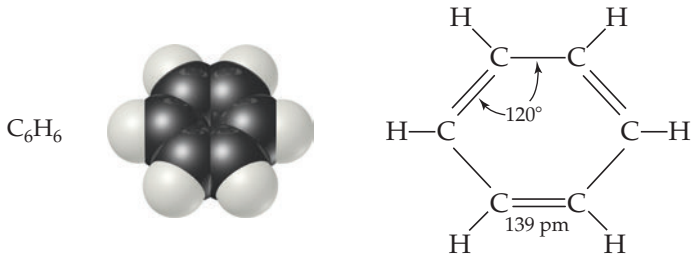
In Chapter 26, we discussed the structure of both alkenes and alkynes and described the carbon atoms that form the molecular skeleton as *unsaturated*. The trigonal-planar bonding geometry of an alkene carbon was rationalized based on the hybridization of one 2*s* and two 2*p* orbitals available to carbon. Recall that the overlap of unhybridized *p* orbitals forms a π-bond. One other class of hydrocarbon also takes advantage of π-bonding—the *aromatic hydrocarbons*.

Benzene is the simplest example of an **aromatic hydrocarbon** (also called an **arene**). This class of hydrocarbon contains a planar ring structure, usually drawn with either a circle in the middle (for reasons we discuss shortly), or alternating single and double bonds (**Figure 30.1**). Although aromatic hydrocarbons involve sp^2-hybridized carbons, they are not alkenes, and undergo very different chemical reactions.

Bonding in Benzene

In many of the molecules we have discussed so far, the bonding electrons are *localized*. By this we mean that the σ- and π-electrons are associated totally with the two atoms that form the bond. In some molecules, however, we cannot adequately describe the bonding as being entirely localized. One molecule that cannot be described with localized π-bonds is benzene (C_6H_6).

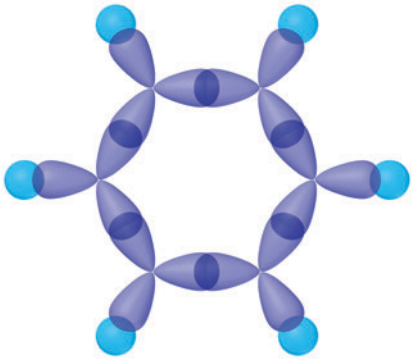
Go Figure How does the structure of benzene relate to cyclohexane?



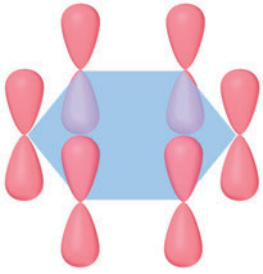
▲ **Figure 30.1 Benzene.** Molecular formulas and geometrical representations for benzene.

To describe the bonding in benzene, we first choose a hybridization scheme consistent with the geometry of the molecule (see Figure 30.1). As each carbon is surrounded by three atoms at 120° angles, the appropriate carbon hybrid orbital set is sp^2. Six localized C—C σ-bonds and six localized C—H σ-bonds are formed from the sp^2 hybrid orbitals, as shown in **Figure 30.2(a)**. This leaves a $2p$ orbital on each carbon atom that is oriented perpendicularly to the plane of the hydrocarbon ring. The situation is very much like that in ethene, except we now have six carbon $2p$ orbitals arranged in a ring (Figure 30.2(b)). Each of the unhybridized $2p$ orbitals is occupied by one electron, meaning a total of six electrons have to be accounted for by π-bonding.

We could imagine using the unhybridized $2p$ orbitals of benzene to form three *localized* π-bonds—that is, π-bonds defined formally between neighboring carbon atoms. As shown in **Figure 30.3(a) and (b)**, there are two equivalent ways to make these localized bonds and each diagram corresponds to one of the resonance structures of the molecule. A representation that reflects *both* resonance structures has the six π-electrons distributed among all six carbon atoms, as shown in Figure 30.3(c). Notice how this figure corresponds to the "circle-in-a-hexagon" drawing often used to represent benzene.

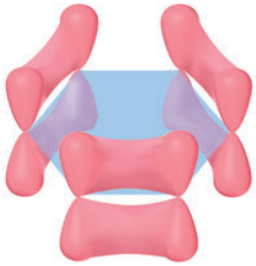


(a) σ-bonds

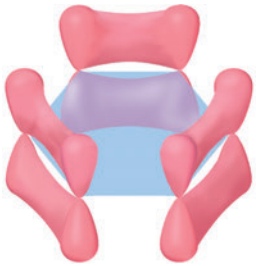


(b) $2p$ atomic orbitals

◀ **Figure 30.2 The σ- and π-bond networks in benzene, C_6H_6.** (a) The C—C and C—H σ-bonds all lie in the plane of the molecule and are formed by using carbon sp^2 hybrid orbitals. (b) Each carbon atom has an unhybridized $2p$ orbital that lies perpendicular to the molecular plane. These six $2p$ orbitals form the π-orbitals of benzene.



(a) Localized π-bonds

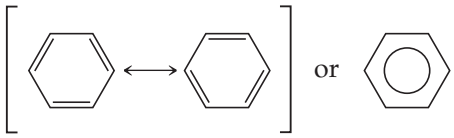


(b) Localized π-bonds



(c) Delocalized π-bonds

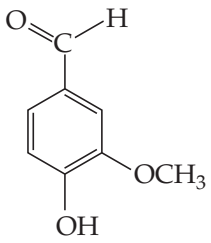
◀ **Figure 30.3 Delocalized π-bonds in benzene.** (a) The six $2p$ orbitals of benzene, shown in Figure 30.2(b), can be used to make three C—C π-bonds. (a) and (b) show two equivalent ways to make localized π-bonds. These π-bonds correspond to the two resonance structures for benzene. (c) A representation of the delocalization of the three C—C π-bonds among the six C atoms.



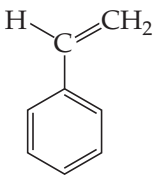
The model described in Figure 30.3(c) leads to the description of each carbon–carbon bond as having an identical bond length, which is between the length of a carbon–carbon single bond (154 pm) and the length of a carbon–carbon double bond (134 pm). This is consistent with the observed bond lengths in benzene (139 pm).

Since we cannot describe the π-bonds in benzene as individual electron-pair bonds between neighboring atoms, we say that the π-bonds are *delocalized* among the six carbon atoms. In Section 30.3 we investigate the effects of delocalization on reactivity and the concept of *aromaticity*. **Figure 30.4** shows the structures of some common aromatic compounds.

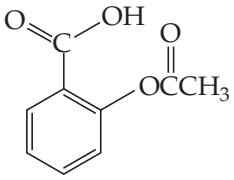
Go Figure Identify the functional groups attached to benzene in these examples.



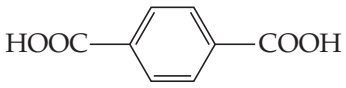
vanillin
(from vanilla beans)



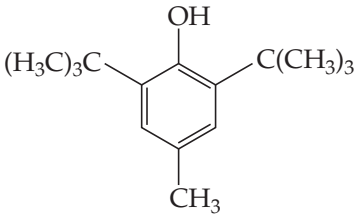
styrene
(used to make polystyrene)



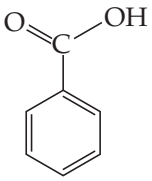
acetylsalicylic acid
(aspirin)



terephthalic acid
(used in forming sails for windsurfers)



2,6-di-*tert*-butyl-4-methylphenol
(BHT—a widely used antioxidant)



benzoic acid
(a fungicide)

▲ **Figure 30.4 Important aromatic compounds.** A small sample of common aromatic compounds containing benzene. These compounds are important in biochemistry, as pharmaceuticals, and in the production of modern materials.

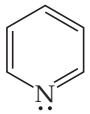
Self-Assessment Exercise

30.1 Naphthalene, $C_{10}H_8$, has two benzene rings fused together along a common edge. How many π-electrons are there in naphthalene?

(a) 6
(b) 8
(c) 10
(d) 12

Exercises

30.2 Pyridine is an analog of benzene in which one of the sp^2 carbon atoms is replaced by nitrogen. **(a)** Does this molecule have delocalized π-bonds? **(b)** Draw a representation for pyridine that illustrates how this delocalization comes about. **(c)** How might the lone pair on nitrogen orientate itself within pyridine?



30.3 What structural features help us identify a compound as an aromatic hydrocarbon?

30.4 Name another compound that has the same empirical formula as benzene.

Answers to Self-Assessment Exercises

30.1 (c)

30.2 Isomerism and Nomenclature in Aromatic Compounds



Benzene and its derivatives play an important role in much of society. For example, when polymerized styrene forms polystyrene, a substance used for insulation and as a building material; tyrosine and phenylalanine are important naturally occurring amino acids that are benzene derivatives; phenols, the hydroxylated form of benzene, are the principal components of the tannins and are responsible for the antioxidant capacity of red wine; vanillin is the compound responsible for the very pleasant sweet, buttery smell associated with the extract of the vanilla plant. Finally, many drugs are composed around a benzene core, including aspirin and paracetamol.

Aspirin, for example, is the common name of acetylsalicylic acid, a benzene-containing compound used commonly as an analgesic for pain relief. Aspirin was developed by Bayer in 1853 though salicylic acid present in willow bark had been known to relieve headaches since around 450 BCE.

Many other compounds isolated during the 19th century were related to benzene. For example, toluene was extracted by distillation from the balsam of the tolu tree in the 1840s. Each of these compounds had a low C : H ratio and many, such as vanillin, had pleasant rather than pungent aromas. As a result, this group of compounds were called aromatic compounds. We will see in Section 30.3 that, as the unusual properties of aromatic compounds were investigated, the term "aromatic" came to be applied to compounds with an unusual stability, regardless of their odor.

By the end of this section, you should:

- Know the names of simple aromatic compounds

Aromatic compounds or *arenes* are a large and important class of organic compounds. The simplest member of the series is benzene (C_6H_6) and further arenes are formed essentially by fusing another C_6 skeleton to benzene. Each aromatic ring

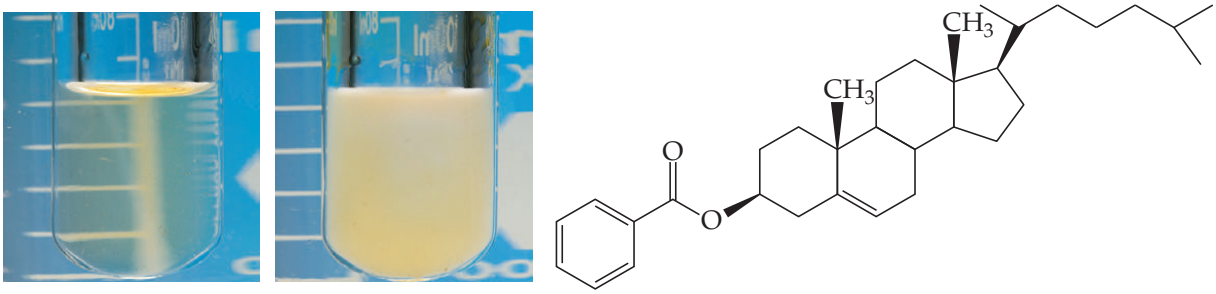
CHEMISTRY AND LIFE The Discovery of Liquid Crystals

In 1888 Frederick Reinitzer (1857–1927), an Austrian botanist, discovered that an organic compound he was studying, cholesteryl benzoate, had interesting and unusual properties. When heated, the substance melts at 145 °C to form a viscous milky liquid; at 179 °C the milky liquid suddenly becomes clear. When the substance is cooled, the reverse process occurs. Reinitzer's work represents the first systematic report of what we now call a *liquid crystal* (Figure 30.5).

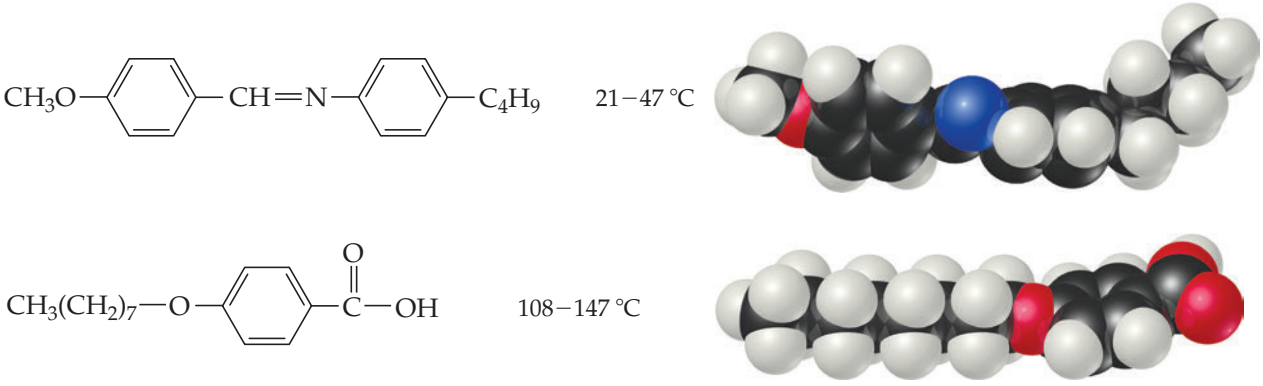
Instead of passing directly from a solid to the liquid phase when heated, some substances, such as cholesteryl benzoate, pass through an intermediate liquid crystalline phase that has some of the structure of solids and some of the freedom of motion possessed by liquids. Because of partial ordering, liquid crystals may be very viscous and possess properties between that of a solid and a liquid. The region in which they exhibit these properties is marked by sharp transition temperatures, as in Reinitzer's example of cholesteryl benzoate.

From the time of their discovery in 1888 until about 30 years ago, liquid crystals were largely a laboratory curiosity. However, researchers found that the weak intermolecular forces that hold the molecules together in a liquid crystal are easily affected by changes in temperature, pressure and electric fields. As a result, liquid crystals are now widely used as temperature and pressure sensors and in the displays of electrical devices such as digital watches, calculators, mobile phones and laptop and hand-held calculators.

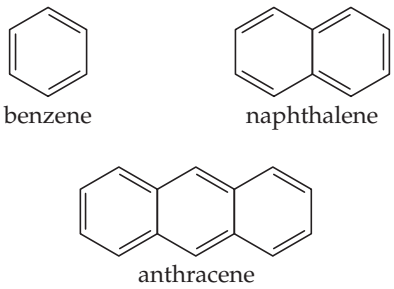
Substances that form liquid crystals are often composed of long, rod-like molecules. They usually contain a long-chain alkane component (minimum chain length of five carbons) linked to an aromatic group such as benzene (Figure 30.6). The liquid crystalline properties they exhibit are in fact due to the ordered interplay of London dispersion forces and aromatic–aromatic interactions, also called π–π interactions.



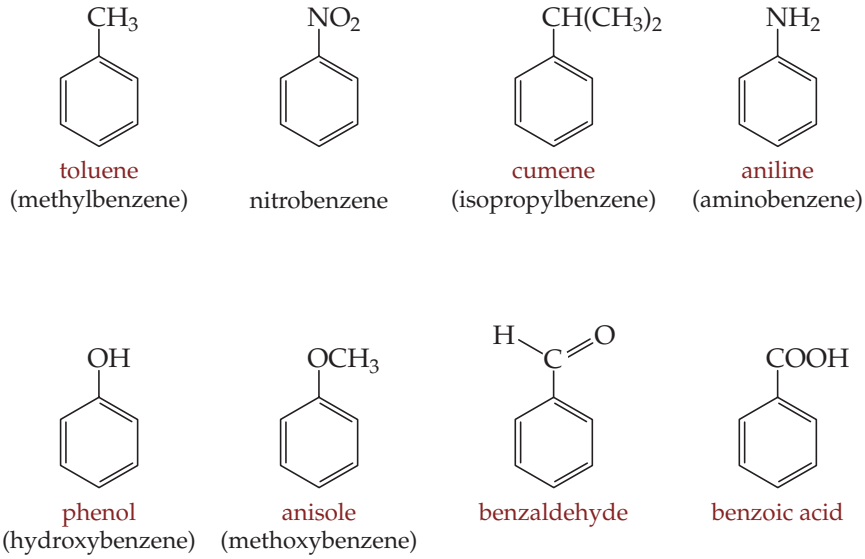
▲ **Figure 30.5 Liquid and liquid crystal.** (a) Molten cholesteryl benzoate at a temperature above 179 °C. In this temperature region the substance is a clear liquid. Note that the printing on the surface of the beaker behind the sample test tube is readable. (b) Cholesteryl benzoate at a temperature between 179 °C and its melting point, 145 °C. In this temperature interval, cholesteryl benzoate exists as a milky liquid crystalline phase. (c) The structure of cholesteryl benzoate.



▲ **Figure 30.6 Structures and liquid crystal temperature intervals of two typical liquid crystalline materials.** The temperature interval indicates the temperature range in which the substance exhibits liquid crystalline behavior.



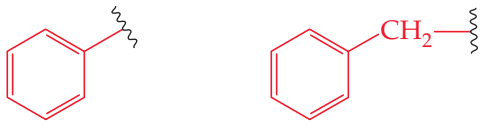
▲ **Figure 30.7 Condensed structural formulas and common names of several aromatic compounds.** The aromatic rings are represented by hexagons with a circle inscribed inside to denote aromatic character. Each corner represents a carbon atom. Each carbon is bound to three other atoms—either three carbons or two carbons and a hydrogen. The hydrogen atoms are not shown.



▲ **Figure 30.8 Benzene derivatives containing a single functional group.** The eight most common monosubstituted benzenes are listed together with their systematic and common names.

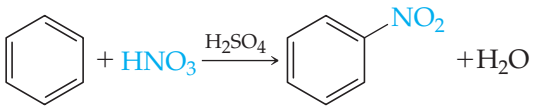
system is given a common name, as shown in **Figure 30.7**. The systematic names of monosubstituted benzenes are usually derived from benzene, although some common names are still used. For example, methylbenzene is known more commonly as toluene. The common names phenol, anisole, benzaldehyde, benzoic acid and aniline are also retained. **Figure 30.8** illustrates some systematic and common names.

The substituent group C_6H_5 formed by the loss of a hydrogen atom from benzene is called a **phenyl group**. The loss of a hydrogen atom from toluene leads to a **benzyl group**.



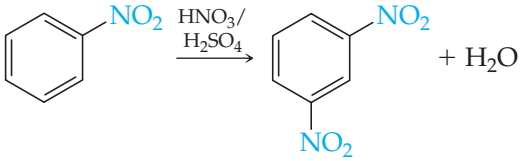
phenyl group benzyl group

When a benzene ring has two substituents, they can form three possible constitutional isomers—*ortho*, *meta* and *para* (**Figure 30.9**). When benzene is warmed in a mixture of nitric and sulfuric acids, for example, hydrogen is substituted by the nitro group, NO_2:



[30.1]

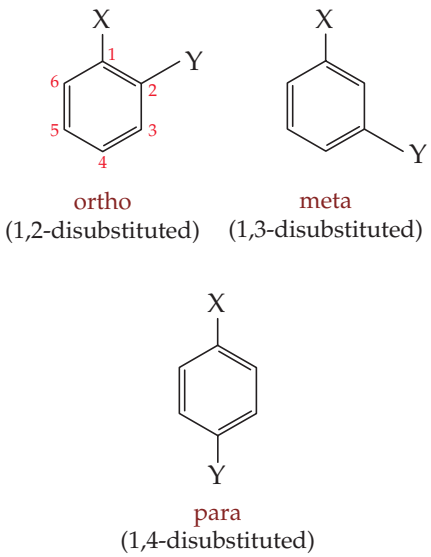
More vigorous treatment results in substitution of a second nitro group into the molecule:



[30.2]

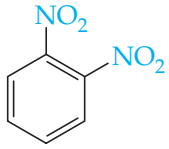
Go Figure

How many *ortho*, *meta* and *para* positions exist in a monosubstituted benzene?

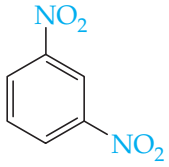


▲ **Figure 30.9 Substitution on benzene.** There are three ways of arranging two substituents on benzene—as *ortho*, *meta* and *para* substitution. Each isomer has different physical and chemical properties.

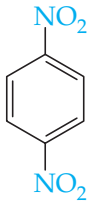
The three possible isomers of benzene with two nitro groups attached are *ortho*-, *meta*- and *para*-dinitrobenzene:



ortho-dinitrobenzene
mp 118 °C



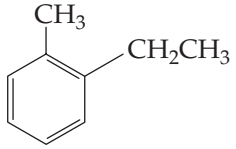
meta-dinitrobenzene
mp 90 °C



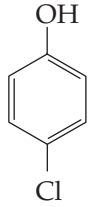
para-dinitrobenzene
mp 174 °C

The *meta* isomer is formed as the major product of the reaction of nitric acid with nitrobenzene. We will explore the reason for this further in Section 30.5.

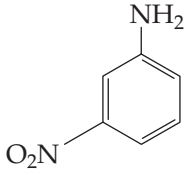
When one of the two substituents on the ring is able to impart a common name (for example, aniline, toluene, phenol), the compound is named based on that parent molecule. The substituent that imparts the common name occupies position number 1. When neither group imparts a common name, the two substituents are listed alphabetically (with the lowest position numbers possible) before ending in *benzene*. The same rules apply to three or more substituents.



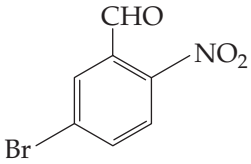
2-ethyltoluene or
o-ethyltoluene



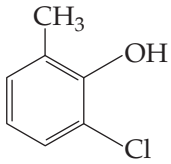
4-chlorophenol or
p-chlorophenol



3-nitroaniline or
m-nitroaniline



5-bromo-2-nitrobenzaldehyde



2-chloro-6-methylphenol

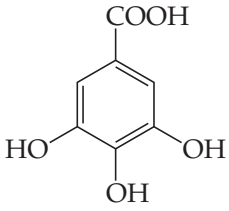
In naming disubstituted benzenes, either position numbers or the use of *o* for *ortho*, *m* for *meta* and *p* for *para* is acceptable. For the more substituted benzenes, only position numbers are used. As with other nomenclature we have studied, these position numbers need to be made as small as possible while maintaining the parent molecule group at position 1. Where a choice of parent group exists, there is a hierarchy similar to that used for multifunctional alkanes. For example, 2-chloro-6-methylphenol is named as such and not as 3-chloro-2-hydroxytoluene. This hierarchical method of naming is based on which functional group is of higher order. A useful, though not exhaustive, order is:

$$\textit{toluene} < \textit{aniline} < \textit{phenol} < \textit{benzaldehyde} < \textit{benzoic acid}$$

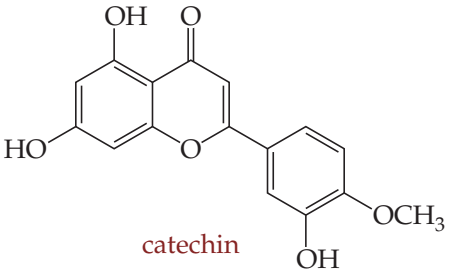
Phenols

Phenols, or hydroxybenzenes, are named after the parent compound, phenol, which was first isolated from coal tar in 1834. The phenol structure is based on the direct attachment of the OH group to a benzene ring. This connectivity confers unique properties on phenols. Some phenol derivatives are named as substituted phenols, others as hydroxy compounds, depending on which other functional groups are present. Many have trivial names.

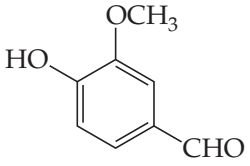
Phenols are an important class of natural product, widely distributed throughout nature. Several examples of naturally occurring phenols are shown here and in **Figure 30.10**. Gallic acid and catechin are phenols found in wines. One of their properties is to act as an antioxidant. Compare their structure with another phenolic antioxidant, vitamin E. Vanillin is the compound responsible for the odour produced by vanilla beans. The cresols, of which *p*-cresol is shown, are isolated from coal tar. They found use in the 1960s–1980s as a wood preservative. There is evidence to suggest that due to their antioxidant properties, the polyphenols in fruit and vegetable juice, and in wine, may play an important role in delaying the onset of colds and in more specific conditions such as Alzheimer's disease.



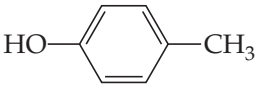
gallic acid



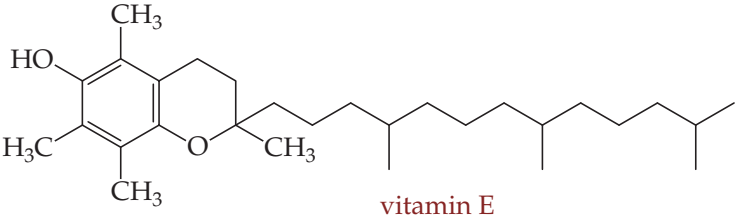
catechin



4-hydroxy-
3-methoxybenzaldehyde
(vanillin)

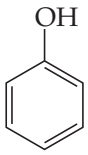


p-cresol or
4-methylphenol

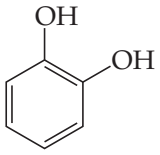


vitamin E
(*lipid soluble*)

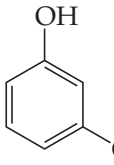
The largest single use of phenol is as an intermediate in the production of low-cost thermoset resins (called *phenolic resins*), used in the production of plywood adhesive as well as in the construction and car industries. Medicinally, phenol and its derivatives have been used in the past as a disinfectant and as a topical anesthetic in preparations such as ointments, ear and nose drops, cold sore lotions, throat lozenges and antiseptic lotions.



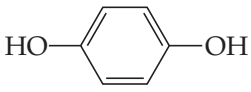
phenol



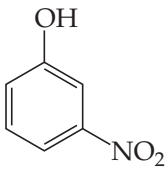
1,2-dihydroxybenzene
or
o-dihydroxybenzene
(catechol)



1,3-dihydroxybenzene
or
m-dihydroxybenzene
(resorcinol)



1,4-dihydroxybenzene
or
p-dihydroxybenzene
(hydroquinone)



m-nitrophenol
or
3-nitrophenol

▲ **Figure 30.10** **Common phenols.**

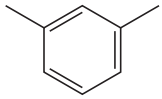
Self-Assessment Exercise

30.5 Dimethylbenzene is usually called xylene. Which name unambiguously describes the following structure?

(a) o-xylene

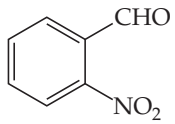
(b) m-xylene

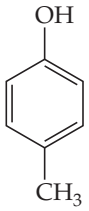
(c) p-xylene

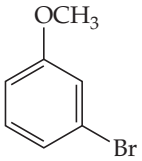


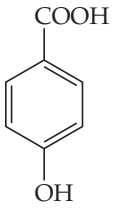
Exercises

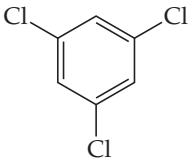
30.6 Name the following structures.

(a) 

(b) 

(c) 

(d) 

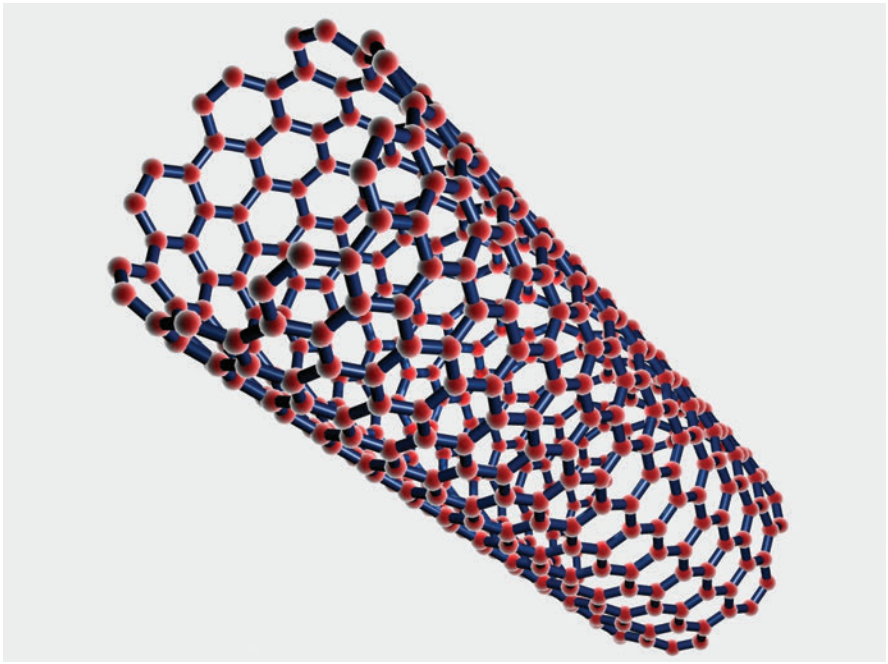
(e) 

30.7 When naphthalene is reacted with nitric and sulfuric acids, two compounds containing one nitro group are formed. Draw the structures of these two compounds.

Answers to Self-Assessment Exercises

30.5 (b)

30.3 | Aromaticity



The illustration portrays an atomic model of a carbon nanotube. The fact that carbon nanotubes can be made either semiconducting or metallic is unique among all solid-state materials. Because the basic elements of the transistor are semiconductors and metals, there is great interest in building nanoscale electronic circuits using only carbon nanotubes. Carbon nanotubes are also being explored for their mechanical properties. Experiments on individual carbon nanotubes suggest that they are stronger than steel of the same dimensions. Carbon nanotubes have also been spun into fibres with polymers, adding great strength and toughness to the composite material.

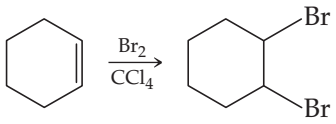
By the end of this section, you should be able to:

- Recognize an aromatic compound based on three criteria

The planar, highly symmetrical structure of benzene, with its 120° bond angles, suggests a high degree of unsaturation. You might therefore expect benzene to resemble the unsaturated hydrocarbons and be highly reactive. The chemical behavior of benzene, however, is unlike that of alkenes or alkynes. Benzene and the other aromatic hydrocarbons are much more stable than alkenes and alkynes because the π-electrons are delocalized in the unhybridized *p* orbitals (Section 30.1).

Let's consider two molecules, cyclohexene and benzene, and their reactions with bromine. Although cyclohexene reacts readily with bromine at room temperature, benzene does not react with bromine at all under these conditions.

The systematic and common names are listed.



[30.3]



[30.4]

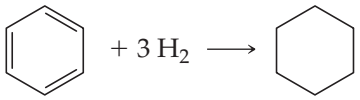
FIGURE 30.12 illustrates the structure of cyclohexatriene and its difference from benzene. This difference is due to the property of **resonance**. Resonance is an extremely important concept in describing the bonding in and stability of organic molecules, particularly aromatic and other highly conjugated molecules. For many molecules and ions, no single Lewis structure provides a truly accurate representation, so a set of **resonance structures** is often used to describe a molecule or ion. For example, there are two equivalent Lewis structures for benzene, each of which satisfies the octet rule. These two structures are in resonance, each resonance structure showing three C—C single bonds and three C—C double bonds, but the double bonds are in different places in the two structures. The actual structure is neither of these two but somewhere intermediate to both.

In the case of benzene, curved arrows can also be used to interconvert the two canonical structures as shown in **FIGURE 30.13**.

So far we have discussed benzene as an aromatic compound, but what is aromaticity? Originally, molecules derived from benzene were called aromatic purely because of their smell. Later, however, the German chemist Eric Hückel (1896–1980) defined what an aromatic compound is through a set of criteria. It must:

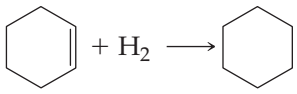
1. be cyclic and planar;
2. have at least one unhybridized *p* orbital on each atom of the ring; and
3. have $[4n + 2]$ π-electrons, where n is an integer $n = 0, 1, 2, 3 \ldots$

Aromatic molecules resist any move to break that aromaticity. This resistance is quantified as aromatic stabilization or **resonance energy**. We can estimate the stabilization of the π-electrons in benzene by comparing the energy released when hydrogen gas reacts with benzene (a reaction known as *hydrogenation*) to form a saturated compound, with the energy required to hydrogenate certain alkenes. The hydrogenation of benzene to form cyclohexane can be represented as



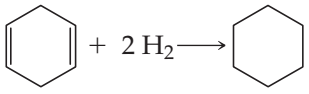
$$\Delta H^\circ = -208 \text{ kJ/mol} \qquad [30.5]$$

The enthalpy change in this reaction is −208 kJ/mol. The heat of hydrogenation of the cyclic alkene cyclohexene is −120 kJ/mol:



$$\Delta H^\circ = -120 \text{ kJ/mol} \qquad [30.6]$$

Similarly, the heat released on hydrogenating 1,4-cyclohexadiene is −232 kJ/mol^{-1}:



$$\Delta H^\circ = -232 \text{ kJ/mol} \qquad [30.7]$$

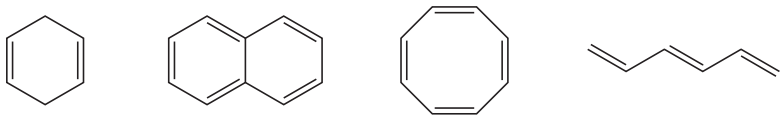
From these last two reactions, it appears that the heat of hydrogenating each double bond is roughly −116 kJ/mol. Since benzene has the equivalent of three double bonds, we might expect that the heat of hydrogenating benzene would be about three times −116 kJ/mol (or −348 kJ/mol). Instead, the heat released is 140 kJ less, indicating that benzene is more stable than would be expected for three double bonds. The difference of 140 kJ/mol^{-1} between the "expected" heat of hydrogenation, −348 kJ/mol, and the

observed heat of hydrogenation, −208 kJ/mol, is due to stabilization of the π-electrons through delocalization.

Many other molecules apart from aromatic hydrocarbons show aromaticity. These molecules typically contain one or more **heteroatoms** (for example, O, N, S). Such compounds, called **heterocyclic compounds**, tend to be biologically active and are dealt with in more detail in Chapter 31.

Self-Assessment Exercise

30.8 Which of the following compounds is aromatic?



(a) (b) (c) (d)

Exercises

30.9 **(a)** Use the concept of resonance to explain why all six C—C bonds in benzene are equal in length. **(b)** The C—C bond lengths in benzene are longer than C—C single bonds but shorter than C—C double bonds. Use the resonance model to explain this observation.

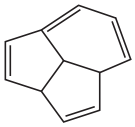
30.10 **(a)** Briefly discuss some of the evidence that has been used to demonstrate the phenomenon of aromaticity. **(b)** Briefly discuss the valence-bond model of aromaticity.

30.11 **(a)** What *two* experimental results prove that cyclohexatriene is a poor representation of the real structure of benzene? **(b)** Benzene has six sp^2-hybridized carbons. How many electrons are left in each of the six *p* orbitals of benzene? How many electrons in the π-system of benzene? **(c)** With the aid of resonance structures, describe how the structure of benzene and the hypothetical cyclohexatriene differ.

30.12 **(a)** Draw a benzylic cation. **(b)** Use arrow notation to describe why this intermediate is more stable than that for the corresponding methylcyclohexane primary carbocation.

30.13 List the criteria that compounds must meet in order to be considered aromatic.

30.14 **(a)** How many π-electrons should an aromatic molecule contain? **(b)** Is the following molecule aromatic?



Answers to Self-Assessment Exercise

30.8 (b)

30.4 | Acidity of Phenols

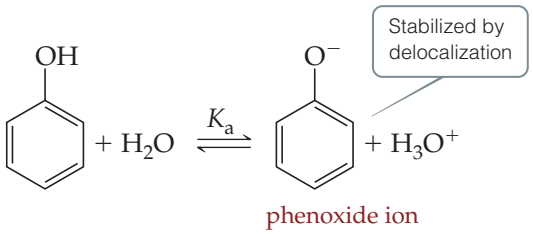


In 1907, the New York–based chemist Leo Baekeland invented the first plastic to be made from synthetic components. He named it Bakelite, after himself, and was granted a patent two years later. It is a thermosetting plastic, which means that, once made, it cannot be melted and reshaped. It is made from phenol and formaldehyde in the presence of a catalyst and a filler such as wood dust or asbestos fibers to form a rigid, highly cross-linked polymer resin. The components can be mixed and even formulated into a powder with the final stage of the curing process being conducted in a mold involving both heat and pressure. Only a couple of minutes were required for the resin to set into a hard, durable, solvent resistant, slightly shiny material which could be turned from the mold while still hot. This made production rapid and the electrical insulating properties of Bakelite meant it was quickly adopted for casings of electrical equipment such as telephones, radios, and light switches. This was expanded to include a lot of household items, toys and games, equipment, and jewelry.

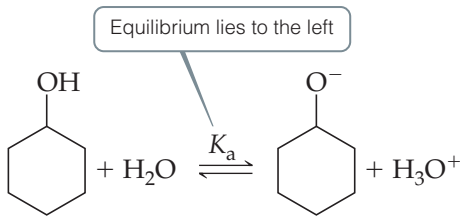
In this section, we look at phenol and, in particular, the acidity of phenol and its derivatives. By the end of the section, you should be able to

- Understand the factors that affect the acidity of a phenol.

Phenols are approximately 10^6 times stronger acids than alcohols. Phenol was originally named carbolic acid, due to its unusually high acidity for an alcohol. To illustrate the difference in acidity of alcohols and phenols, let us consider two molecules: phenol and cyclohexanol. The chemical equations for their acid-dissociation constants are:



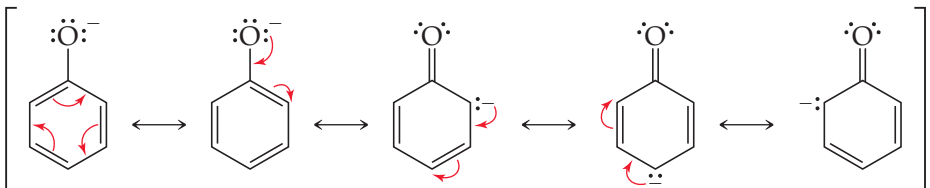
phenoxide ion [30.8]



cyclohexoxide ion [30.9]

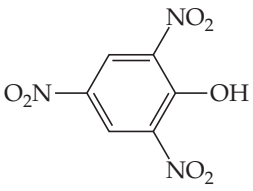
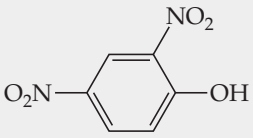
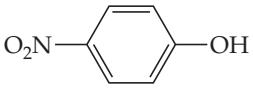
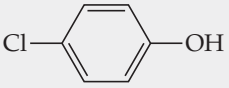
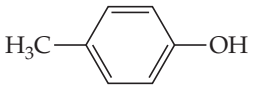
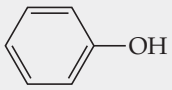
The pK_a of phenol is about 10, while that for cyclohexanol is about 16 (recall that $pK_a = -\log_{10}K_a$). The difference in acidity between phenol and cyclohexanol is due to the stability of the corresponding anion products. Phenols are more acidic because of the **resonance-stabilized** nature of the anion formed upon deprotonation relative to the alkoxide. This delocalization can be seen in the contributing structures illustrated in **Figure 30.11**.

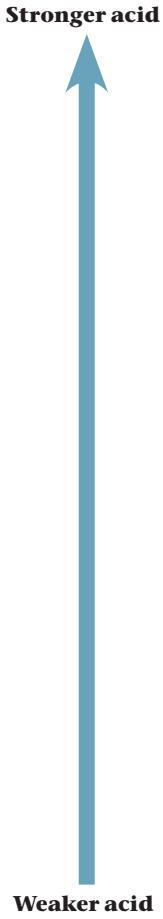
The stability of the phenoxide ion arises from resonance. The last three structures on the right in Figure 30.11 illustrate, using curved arrow notation, how the charge is



▲ **Figure 30.11 Resonance stabilization.** Phenoxide ions are stabilized relative to alkoxide ions because phenoxide ions are able to resonance stabilize the negative charge around the aromatic ring.

TABLE 30.1 Relative pK_a values for selected alcohols and phenols*

Compound	Structural formula	pK_a
Hydrogen chloride	HCl	−7
Picric acid		0.5
2,4-Dinitrophenol		4
4-Nitrophenol		7
4-Chlorophenol		9
p-Cresol		10
Phenol		10
Water	H_2O	15.7
1-Propanol	$CH_3CH_2CH_2OH$	16



* Error in measurement ±0.2.

distributed to the *ortho* and *para* positions of the aromatic ring. This charge distribution through resonance is important to the reactivity of aromatic compounds.

In contrast to phenoxide, the cyclohexoxide ion doesn't allow for charge delocalization; the charge is localized on oxygen. Although arrow notation and the use of contributing structures allow us to rationalize why phenols are more acidic, they do not give us quantitative information on how strong an acid they might be. The pK_a value needs to be determined experimentally.

Table 30.1 compares the pK_a of several alcohols and phenols. Electron-withdrawing groups on the phenyl ring of phenol increase the acidity through **inductive effects**. **Electron-withdrawing groups** are those that are more electronegative than carbon. They can be atoms (for example, F, Cl, Br) or a collection of atoms such as the *nitro group*, NO_2, which, combined, are electron deficient. Each of these groups is able partially to withdraw electron density out of the O—H bond, making this bond weaker and hence the phenol more acidic. They can also contribute to the charge delocalization of the resulting phenoxide ion.

Sample Exercise 30.1

Utilizing the acidity difference

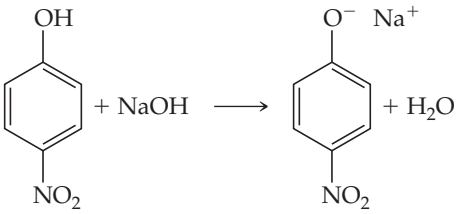
Suggest a method of separating 4-nitrophenol (pK_a = 7) and cyclohexanol (pK_a = 16) in a solution of diethyl ether.

SOLUTION

Analyze We are asked to find a way of separating a phenol and alcohol in an organic solution.

Plan Take advantage of the difference in pK_a between the two compounds and use the extraction method to remove one from the ether. Sodium phenoxides are salts, and many salts (including organic salts) are soluble in water. Cyclohexanol is not soluble in water because of the large cyclohexyl ring, which makes this compound more hydrophobic. The result is that the phenol can be separated into the water layer while the cyclohexanol stays in the diethyl ether layer.

Solve The pK_a of phenols is such that an aqueous 1 M sodium hydroxide (NaOH) solution is basic enough to deprotonate the phenol, but not the cyclohexanol, by the following chemical equation:



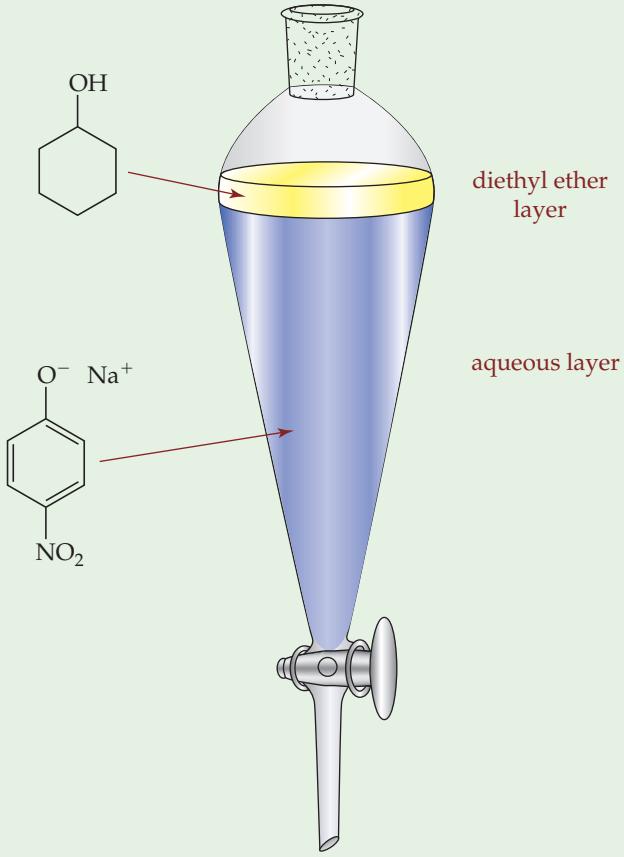
a sodium phenoxide

Once reaction has occurred, two layers are formed—an diethyl ether layer and an aqueous layer. The layers are then separated using a separating funnel.

Once the two solutions are separated, the diethyl ether can be distilled off (bp 35 °C) to leave the pure cyclohexanol. Acidification of the aqueous layer using 1 M HCl yields 4-nitrophenol as a solid, which can be filtered off and dried.

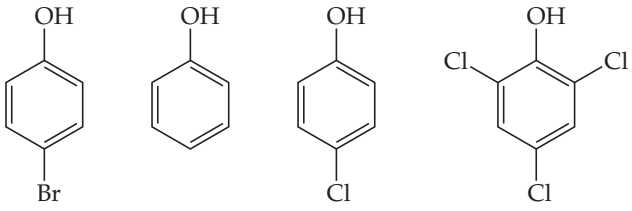
Practice Exercise

Arrange these compounds in increasing order of acidity: 2,4-dichlorophenol, phenol, 2,6-dinitrophenol and 4-nitro-2-chlorophenol, using the trends in Table 30.1.



Self-Assessment Exercise

30.15 Order the following in terms of increasing acidity.



(A) **(B)** **(C)** **(D)**

(a) A < B < C < D
(b) B < A < C < D
(c) B < C < D < A
(d) D < C < A < B

Exercises

30.16 The phenolate ion gains stability through contributing resonance structures unlike the alkoxides ion. What does this tell you about the relative basicity of the alkoxide and phenolate ions?

30.17 The acidity of the chlorophenols increases in the order *p*-chlorophenol < *m*-chlorophenol < *o*-chlorophenol. Explain this effect.

30.18 Draw a flow diagram to show how you could separate *p*-chlorophenol from *p*-chlorotoluene.

Answers to Self-Assessment Exercise

30.15 (b)

30.5 Electrophilic Aromatic Substitution (EAS) Reactions



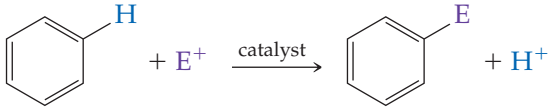
In the mid-1939s, Louis Hammett conducted pioneering work on what became known as linear free-energy relationships. His starting point was to look at how the acidity of benzoic acid changed when substituents were placed in either the *meta* or *para* positions. He then examined different reactions of aromatic compounds and determined how their rates compared for a particular substituent. This enabled him to construct a set of constants, one of which depended on the substituent present and the other on the type of reaction conducted. In this way, he was able to quantify, and understand better, the effect that a substituent has on the reaction of an aromatic compound. He coined the term "physical organic chemistry" to describe this area of the physical measurements of organic reactions.

In this section, we look at the substitution reactions of aromatic compounds and see that they are influenced by what is already attached to the ring. A patten emerges! By the end of this section, you should:

- Have a basic knowledge of the scope of the substitution reactions of aromatic compounds
- Be able to predict the effect a substituent has on the rate and position of substitution in EAS reactions

Although aromatic hydrocarbons are unsaturated, they do not readily undergo addition reactions. The delocalized π-bonding causes aromatic compounds to behave quite differently from alkenes and alkynes.

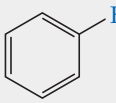
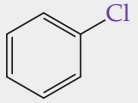
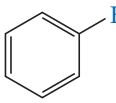
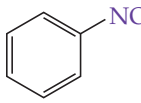
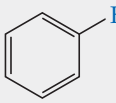
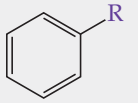
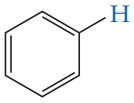
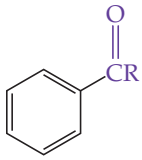
Benzene, for example, does not react with Cl_2 or Br_2 under ordinary conditions. In contrast, aromatic hydrocarbons undergo substitution reactions relatively easily. Such a reaction is called an **electrophilic aromatic substitution (EAS)** reaction. In a substitution reaction, one atom of a molecule is replaced (substituted) by another atom or group of atoms. These reactions occur in the presence of an electrophile, usually given the symbol E^+. A catalyst is usually needed to generate the electrophile.



[30.10]

Table 30.2 illustrates the four most common EAS reactions, their names and the nature of the electrophile used. Halogenation, employing either the *bromonium ion* (Br^+)

TABLE 30.2 The four most common forms of electrophilic aromatic substitution reaction

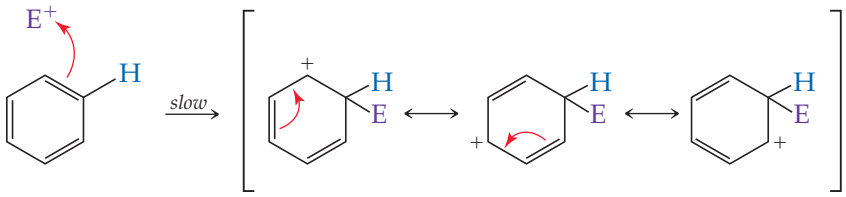
Reaction name	E^+	Reagent	Catalyst	Products
Halogenation	Cl^+ chloronium		$FeCl_3$	 + HCl
Nitration	NO_2^+ nitronium		H_2SO_4	 + H_2O
Friedel–Crafts alkylation	R^+ alkyl carbocation		$AlCl_3$	 + HX
Friedel–Crafts acylation	 acylium ion		$AlCl_3$	 + HX

Note: The R group represents a general group (for example, alkyl, aryl).

or *chloronium ion* (Cl^+), and nitration, employing the *nitronium ion* (NO_2^+), are useful ways of introducing new functionality to the benzene ring.

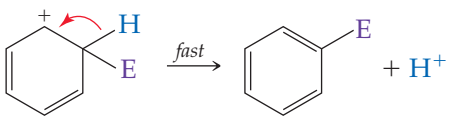
The Friedel-Crafts alkylation and acylation reactions generate new C—C bonds. Discovered in the late 1870s, they are two of the most important methods in forming new C—C bonds to the aromatic ring. The alkylation reaction uses carbocations to accomplish the substitution reaction. Tertiary carbocations react more cleanly and more efficiently than 2° or 1° carbocations. The *acylium ion* is formed from an activated carboxylic acid as the electrophile in a Friedel-Crafts acylation. This reaction generates aromatic ketones in high yields.

The mechanism of an electrophilic aromatic substitution reaction involves two steps. The initial step is rate-determining and leads to the formation of a resonance-stabilized carbocation intermediate, sometimes called a Wheland intermediate or sigma complex.



[30.11]

This resonance stabilized intermediate is able to lose H^+ to regain aromaticity—the driving force in making this reaction a substitution rather than an addition reaction.



[30.12]

Sample Exercise 30.2

Electrophilic aromatic substitution

Draw the structural formula for the major product formed when *p*-xylene (1,4-dimethylbenzene) is reacted with HNO_3/H_2SO_4. Justify your choice for the major product.

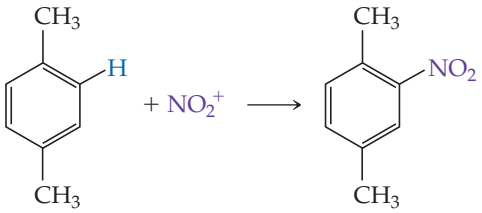
Continued

SOLUTION

Analyze We are asked to determine the major product of the reaction of 1,4-dimethylbenzene with a mixture of nitric and sulfuric acid.

Plan The reaction of nitric acid with sulfuric acid yields the nitronium ion, NO_2^+, which is a useful electrophile. We will use this electrophile in a reaction with 1,4-dimethylbenzene.

Solve The major product is identified through the following reaction:



Because of the symmetry of *p*-xylene, substitution occurs in one of four equivalent positions.

Practice Exercise

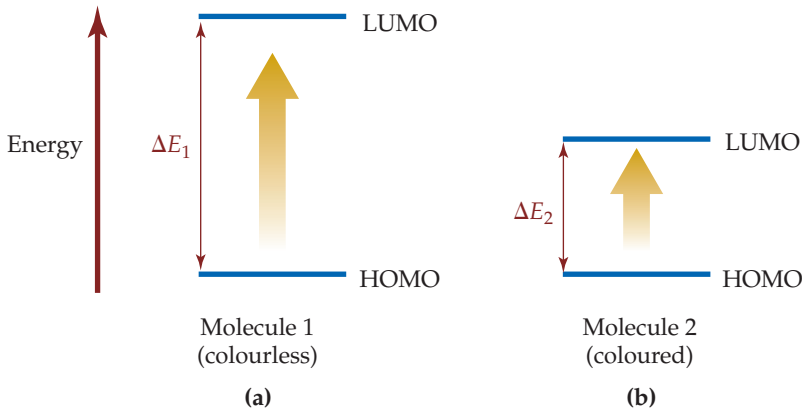
Addition of iodomethane to an aromatic compound, in the presence of $AlCl_3$, yields significant amounts of 4-chlorotoluene. What is the aromatic compound?

A CLOSER LOOK Organic Dyes

Light excites electrons in molecules. In a molecular orbital picture, we can envisage light exciting an electron from a filled molecular orbital (MO) to an empty one at higher energy. Because the MOs have definite energies, only light of the proper wavelength can excite electrons. The situation is analogous to that of atomic line spectra. If the appropriate wavelength for exciting electrons is in the visible portion of the electromagnetic spectrum, the substance will appear colored as certain wavelengths of white light are absorbed, whereas others are not.

In using MO theory to discuss the absorption of light by molecules, we focus on two MOs in particular. The *highest occupied molecular orbital* (HOMO) is the MO of highest energy that has electrons in it. The *lowest unoccupied molecular orbital* (LUMO) is the MO of lowest energy that does not have electrons in it. The energy difference between the HOMO and the LUMO—known as the HOMO–LUMO gap—is related to the minimum energy needed to excite an electron in the molecule. Colorless or white substances usually have such a large HOMO–LUMO gap that visible light is not energetic enough to excite an electron to the higher level (**Figure 30.12**). For example, the typical energy needed to excite an electron in naphthalene corresponds to light with a wavelength of 200–300 nm, which is far into the ultraviolet part of the spectrum. As a result, naphthalene cannot absorb any visible light and is therefore colorless.

Many of nature's rich colors, such as the green of plants and the bright hues of flowers, and the colors found in an ink-jet printer, are due to *organic dyes* **Figure 30.13**, organic molecules that strongly absorb selected wavelengths of visible light. Organic dyes contain extensively delocalized π-electrons as a result of *conjugation*. The HOMO–LUMO gap in such molecules decreases as the number of conjugated double bonds increases, making it easier to excite the molecule with lower-energy (longer-wavelength) radiation (Figure 30.12). Generally, then, the more conjugated a compound is, the more colored that compound will be.



▲ **Figure 30.12 Molecules absorbing light.** The smaller the energy gap between the HOMO and LUMO within a molecule, the greater the likelihood that the molecule is colored. This is because a light of longer wavelength (lower energy) can be absorbed by the molecule to allow the excitation.

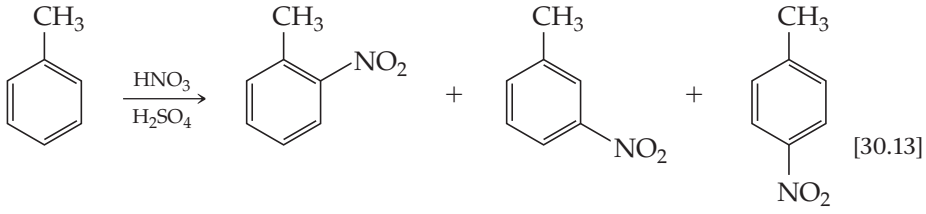


▲ **Figure 30.13 Organic dyes.** Many of the bright colors we see in our lives are a result of aromatic compounds.

Directing Groups and Substitution Effects

So far we have only considered benzene as the starting material for an electrophilic aromatic substitution reaction. Now we ask, what effects will other functional groups have on electrophilic aromatic substitution?

Let us begin to answer this question by looking at the nitration of toluene. In this case, three products, corresponding to the three possible isomers, are formed.



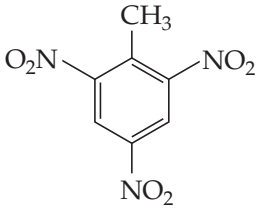
[30.13]

toluene — 2-nitrotoluene (60%) *ortho* — 3-nitrotoluene (5%) *meta* — 4-nitrotoluene (35%) *para*

Two things are to be noted here:

1. The nitration of toluene is approximately 25 times faster than that of benzene. In this case we say that toluene is **activated** towards electrophilic aromatic substitution. Therefore the methyl group can be classed as an **activating group**. The fact that nitration only occurs once (dinitration does not happen easily under these conditions) suggests that the nitro group is a **deactivating group**. Further nitration is possible under forcing conditions to give 2,4,6-trinitrotoluene (TNT) (**Figure 30.14**).
2. The product ratio strongly favors both *ortho* and *para* substitution. If all positions on the phenyl ring of toluene were equally reactive, the ratio of nitration at *ortho*: *meta*: *para* should be statistical at 40: 40: 20 (there are two *ortho* and *meta* positions to one *para* position). This is not the case, so this means that the methyl group is an ***ortho*, *para*-director**. In other words, the methyl group directs a second substituent to the *ortho* and *para* positions, but not to the *meta* position.

Go Figure Why might TNT be explosive?

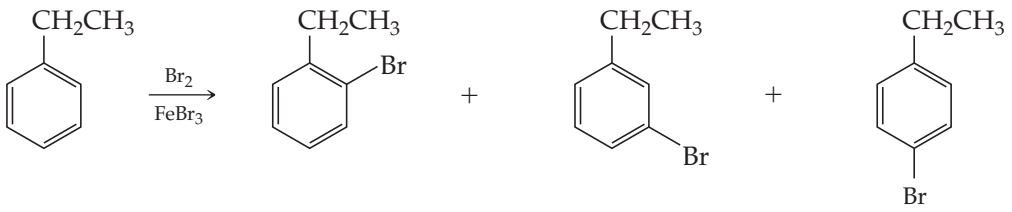


▲ **Figure 30.14 TNT.** Actually TNT is an acronym for 2,4,6-trinitrotoluene, a highly unstable and explosive compound if a force is applied to it.

Both the activation and product distribution can be rationalized by looking at the intermediates formed after the addition of the electrophile and their relative stabilities, and then comparing this to the nitration of benzene (**Figure 30.15**). We can look at these intermediates because the rate-determining step in this reaction is the addition of the electrophile rather than the re-aromatization leading to the nitrobenzene product.

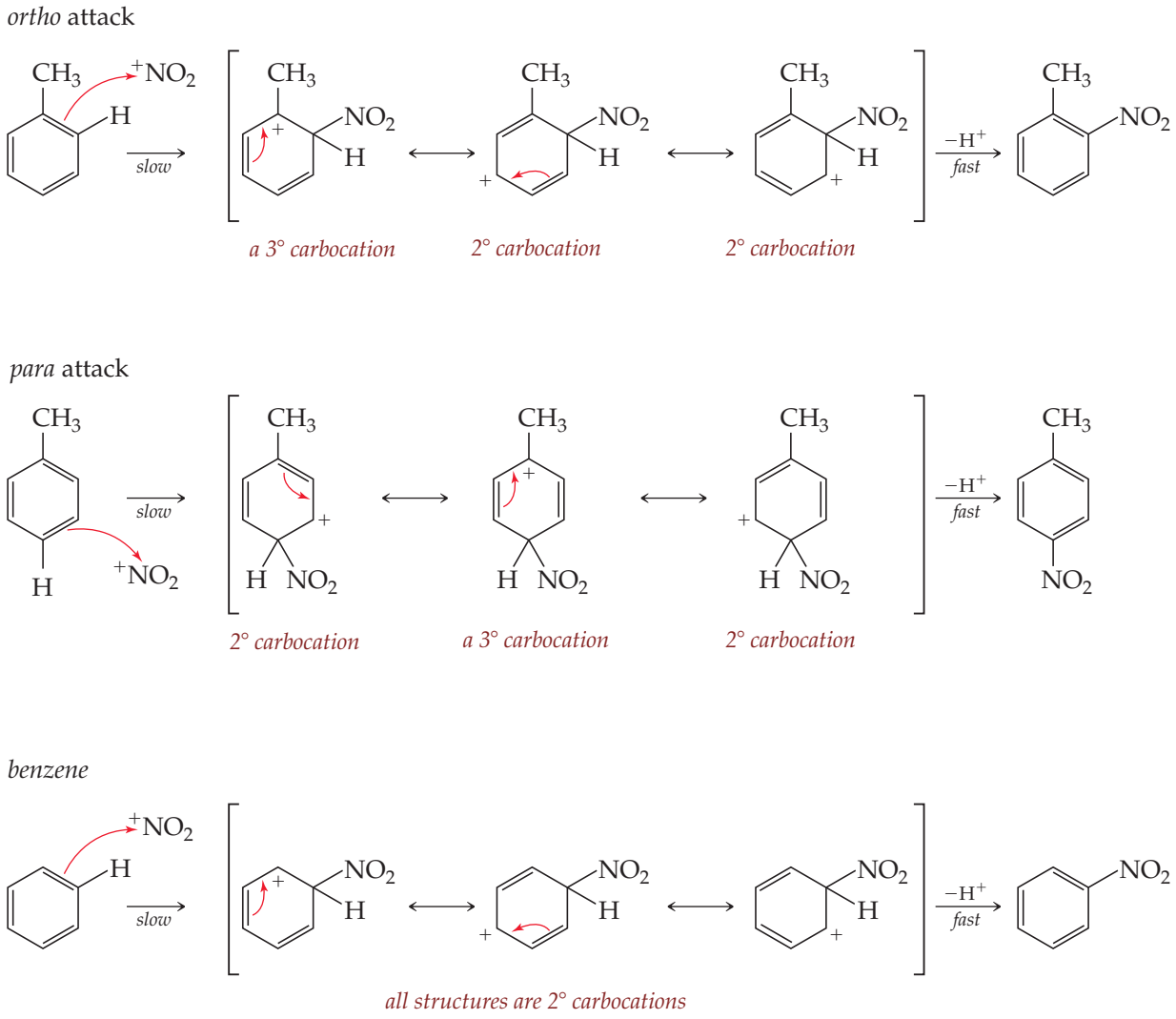
In both *ortho*- and *para*-attack, an intermediate resonance contributor can be drawn that form a 3° carbocation. As we saw in previous chapters, tertiary carbocations are more stable than either primary or secondary carbocations. In the case of benzene (shown) and for *meta*-attack, only 2° carbocation intermediates are formed. As a result, the overall stability of the intermediates for *ortho*- and *para*-attack are both favored and lower in energy.

Bromination of ethylbenzene using bromine and iron(III) tribromide (ferric bromide) also follows the same trend, with *ortho*- and *para*-substituted isomers favored. Here, because of steric effects around the ethyl group, the *para*-isomer is favored over the *ortho*-isomer.



toluene — 2-bromoethylbenzene (38%) *ortho* — 3-bromoethylbenzene (<1%) *meta* — 4-bromoethylbenzene (62%) *para*

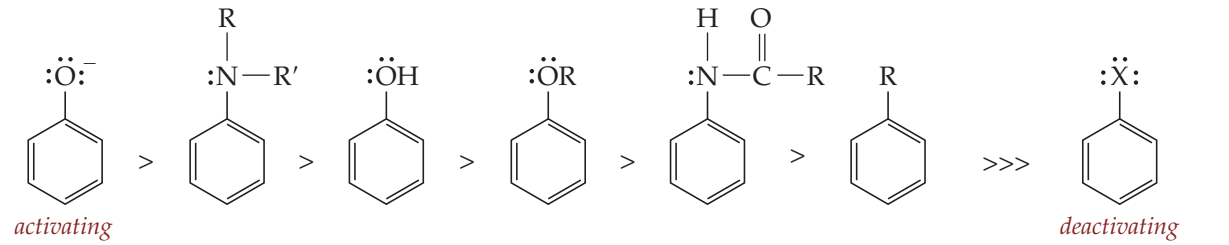
The methyl group in toluene or the ethyl group in ethylbenzene are slightly electron donating, stabilizing the intermediates formed upon the first step of an EAS reaction.



▲ **Figure 30.15 Intermediates of nitrating toluene and benzene.** The intermediates of electrophilic aromatic substitution reactions reveal information about which isomer dominates in a reaction.

Generally speaking, *electron-donating groups are ortho, para-directors and activating towards electrophilic aromatic substitution.*

Ortho-, *para*-directing groups and their relative activation for EAS are:

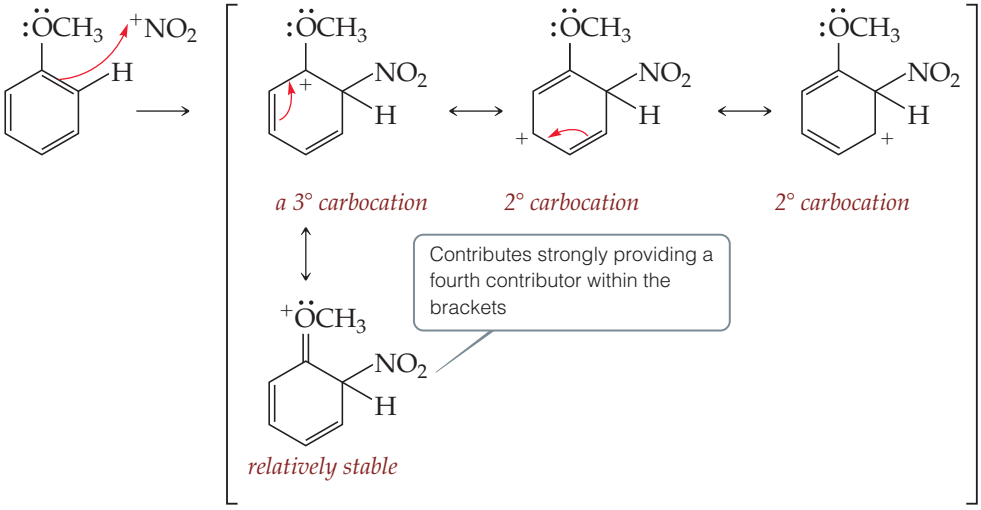


Notice that in many of these cases, the functional group contains a lone pair capable of playing a stabilizing role in the intermediates of an EAS reaction. This effect, which occurs in the first five examples and halobenzenes, is called *resonance stabilization*. In the case of alkylbenzenes, the donation of electron density into the ring is called *inductive stabilization*. In each case, however, some electron density is donated into the ring to stabilize the positive charge generated in the intermediates.

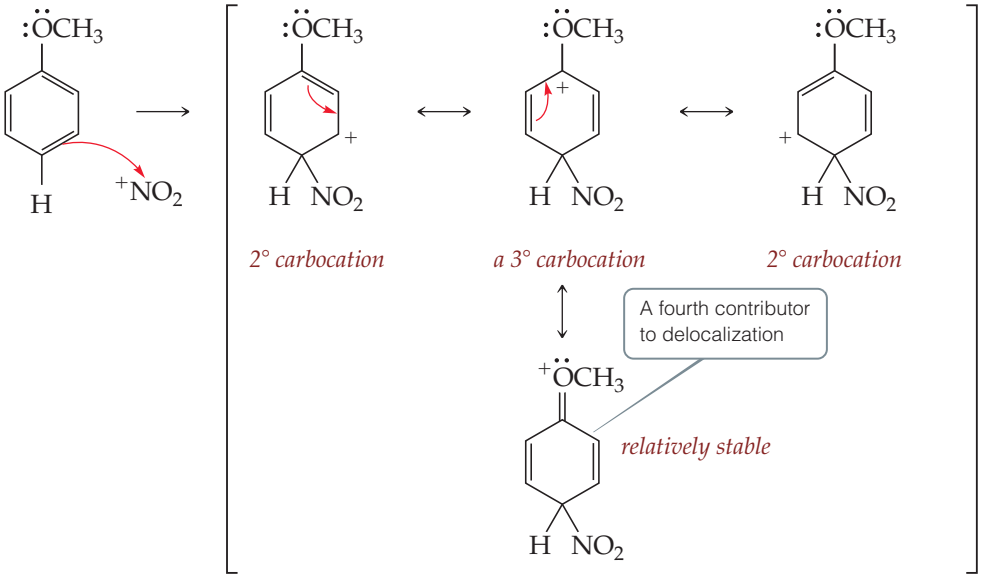
Although the halobenzenes (F, Cl, Br, I) are weakly deactivating by virtue of their inductive electron-withdrawing effects, they are still *o,p*-directing because of their ability to resonance stabilize the cationic intermediates.

To help with your understanding of resonance stabilization, let's look at the intermediates of the nitration of anisole. Here, the alkoxy group (—OR) is able to use its non-bonding lone pair to participate in resonance stabilization, forming a very stable fourth contributor in both *ortho*- and *para*-intermediates that is not available in the *meta* case. This difference in the number of contributors is used to rationalize the product distribution. The effect of the methoxy group's activation is such that anisole nitrates 10 000 times faster than benzene.

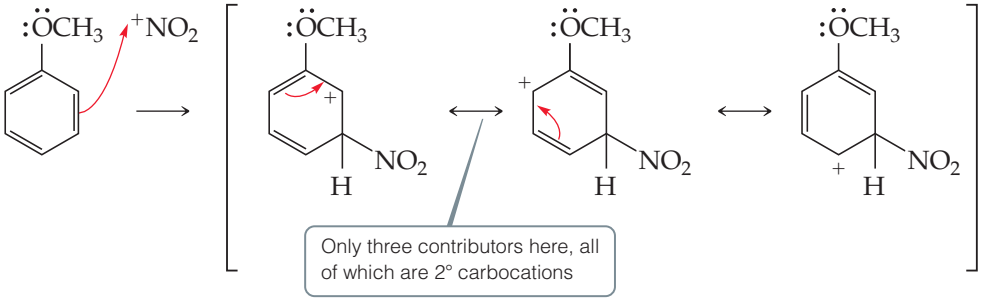
ortho-attack



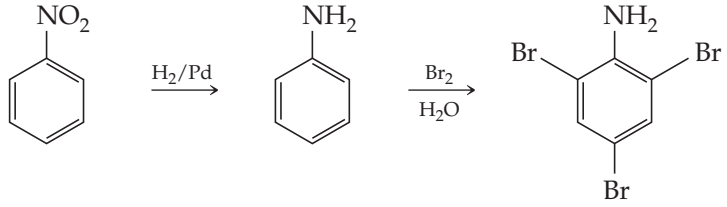
para-attack



meta-attack



Anilines are very reactive towards EAS and are highly activated *ortho*-, *para*-directors. For example, the bromination of aniline occurs rapidly and without the addition of a catalyst to give the tribromoaniline in excellent yield:



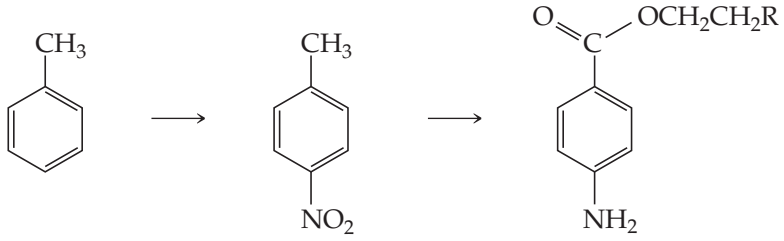
[30.14]

nitrobenzene aniline 2,4,6-tribromoaniline (>95%)

Sample Exercise 30.3

EAS reaction

4-Nitrotoluene is the starting material for the synthesis of the local anaesthetics benzocaine and procaine. Describe a synthesis of 4-nitrotoluene starting from toluene.



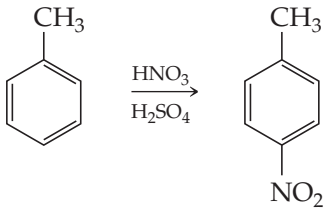
benzocaine (R=H)
procaine (R=NEt_3)

SOLUTION

Analyze We are asked to synthesize 4-nitrotoluene from toluene.

Plan To begin this exercise we look at the functional group differences between starting materials and products. In this reaction, the introduction of a *para*-nitro substituent is made, which can be achieved by EAS.

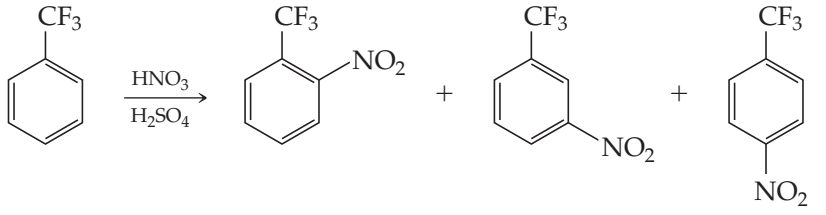
Solve Since methyl groups are *ortho*-, *para*-directing, 4-nitrotoluene can be formed by nitration of toluene and separation of the *ortho*- and *para*-isomers:



Practice Exercise

(a) Would *tert*-butylbenzene (2-methyl-2-phenylpropane) be more or less reactive than benzene towards nitration?
(b) Comment on which position would be favored and why.

So far we have dealt with electron-donating substituents. Now let's see what happens with the nitration of (trifluoromethyl)benzene, an analogue of toluene where each of the methyl hydrogens is replaced with fluorine. In this case, the *meta* product 3-nitro(trifluoromethyl)benzene is almost exclusively formed (~90% yield).

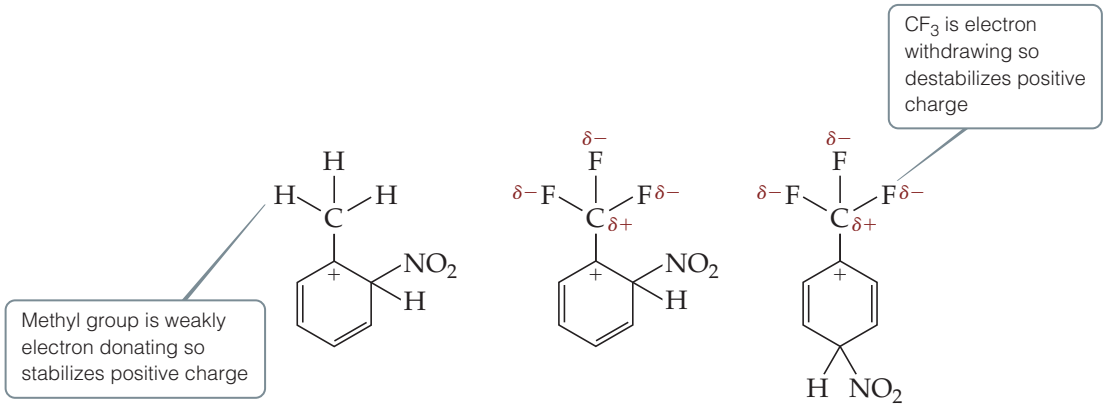


[30.15]

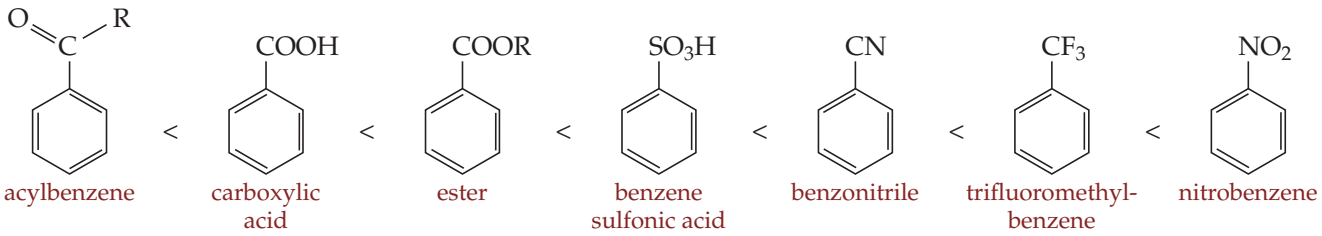
(trifluoromethyl) benzene *ortho* (~5%) *meta* (~90%) *para* (~5%)

The near exclusive formation of the *meta* isomer means that the trifluoromethyl group is a ***meta*-director**. Though similar in size, there is a marked difference between the inductive properties of methyl and trifluoromethyl groups. The electronegativity of F compared to H means that inductively the trifluoromethyl group is electron withdrawing. This has two implications.

1. The electron-withdrawing nature means that attack on the electrophile by the electrons of the aromatic ring is impeded. This leads to deactivation.
2. The second is that in the case of *ortho*- and *para*-attack, the once favorable 3° carbocation of toluene is now significantly destabilized by the CF_3 group. This makes the *meta* substitution pathway more favorable. The instability relates to the neighboring location of the carbocation with the electropositive carbon bearing the three fluoro groups. This situation is analogous to that for carbonyl compounds attached to an aromatic ring where the carbonyl carbon is also δ+.

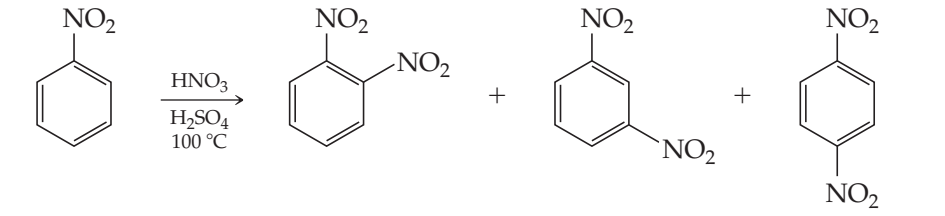


Many groups are *meta*-directing and deactivating. A series of mono-substituted benzenes and their relative deactivation for EAS include:



Generally speaking, electron-withdrawing groups are *meta*-directors and deactivating towards electrophilic aromatic substitution.

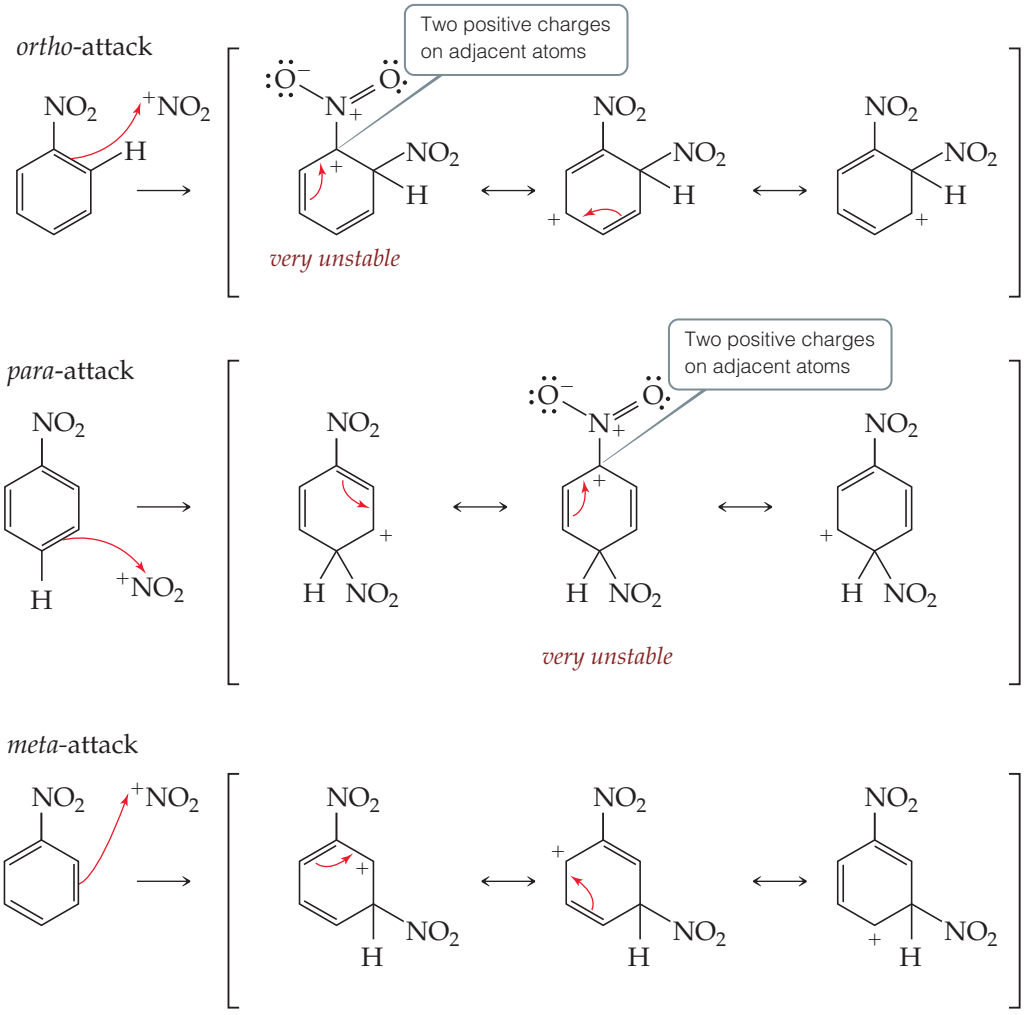
Let us complete our appreciation of directing groups by studying the nitration of nitrobenzene. The nitration of nitrobenzene is approximately 100 000 times slower than the nitration of benzene. In this case, the nitro group is said to be *strongly deactivating* and more forcing conditions are required to nitrate. This is due to the inductive electron-withdrawing effects of the nitro group, weakening the attack of the aromatic ring on the electrophile.



[30.16]

nitrobenzene — 1,2-dinitrobenzene (6%) — 1,3-dinitrobenzene (93%) — 1,4-dinitrobenzene (>1%)

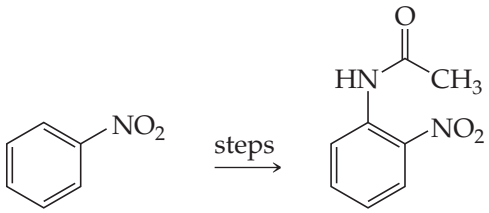
The reason why nitro groups are *meta*-directors becomes more obvious when investigating the resonance forms of the intermediates upon nitration. The proximity of the two positive charges in one resonance form of the *ortho* and *para* cases, in which they are on adjacent atoms, severely destabilizes this group of intermediates, disfavoring *ortho*-, *para*-attack in favor of *meta*-attack.



Sample Exercise 30.4

Directing groups

Determine a suitable pathway for forming 2-nitrophenylacetamide from nitrobenzene.



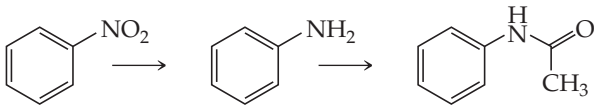
SOLUTION

Analyze We are asked to form 2-nitrophenylacetamide from nitrobenzene.

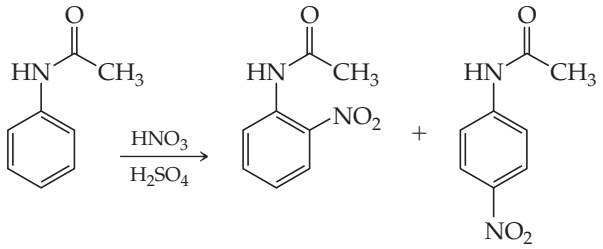
Plan Identify the differences in structure to determine what functionality needs to be added. Our knowledge of directing groups will also play a significant role in the pathway we follow. We also need to have some idea of synthetic transformations.

Solve The acetamide group can be formed in two steps from the nitro group by reduction, using catalytic hydrogenation or $SnCl_2$ forming the amine (aniline in this case). Acetylation using acetic anhydride or acetyl chloride leads to the acetamide:

Continued



Acetamides and anilines are *o*-, *p*-directing and activating but nitro groups are *m*-directing and deactivating. Hence it makes sense to nitrate either the aniline or acetamide to give the desired product. You will need to separate the *o*- from *p*-isomer, however.



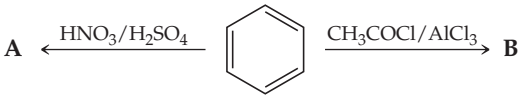
Trying to elaborate a synthesis from the nitrobenzene will undoubtedly lead to *meta* substitution, so this pathway should not be followed in this case.

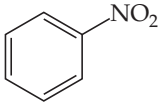
Practice Exercise

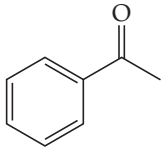
Which reacts more rapidly with HNO_3/H_2SO_4: anisole, toluene or nitrobenzene?

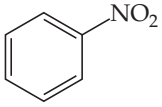
Self-Assessment Exercise

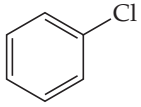
30.19 What product is formed in each of the following reactions?

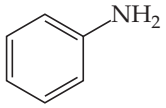


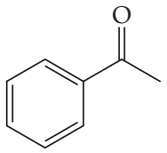
(a) A 

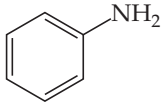
B 

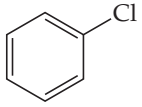
(b) A 

B 

(c) A 

B 

(d) A 

B 

30.20 What is the major product of the nitration of benzonitrile (cyanobenzene)?

(a) *ortho*-nitrobenzonitrile

(b) *meta*-nitrobenzonitrile

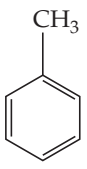
(c) *para*-nitrobenzonitrile

Exercises

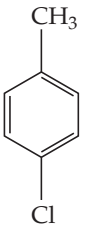
30.21 **(a)** What is the difference between a substitution and an addition reaction? Which one is commonly observed with alkenes and which one with aromatic hydrocarbons? **(b)** Using condensed structural formulas, write the balanced equation for the addition reaction of 2,4-dimethyl-2-pentene with Br_2. **(c)** Write a balanced equation for the substitution reaction of Cl_2 with *para*-dichlorobenzene in the presence of $FeCl_3$ as a catalyst.

30.22 Write a series of reactions leading to *para*-bromoethylbenzene, beginning with benzene and using other reagents as needed.

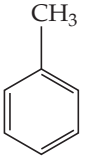
30.23 Suggest a suitable product for each of the following transformations. Also, give the name of the reaction type exemplified.

(a) 

+ Br_2 $\xrightarrow[\text{show } para \text{ substitution}]{FeBr_3}$

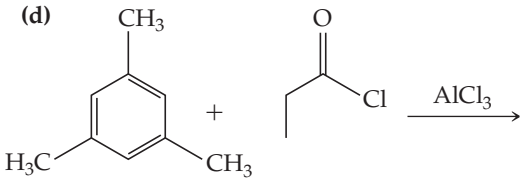
(b) 

+ HNO_3 $\xrightarrow[\text{show } ortho \text{ substitution to methyl group}]{H_2SO_4}$

(c) 

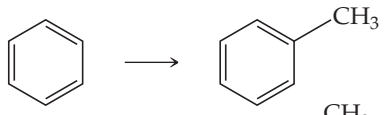
+ CH_3CH_2Br $\xrightarrow[\text{show } meta \text{ substitution}]{AlCl_3}$

(d)

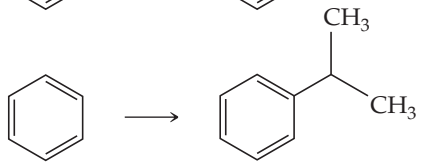


30.24 Suggest ways of conducting the transformations shown here.

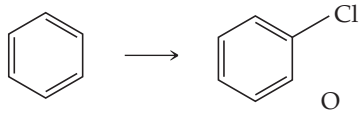
(a)



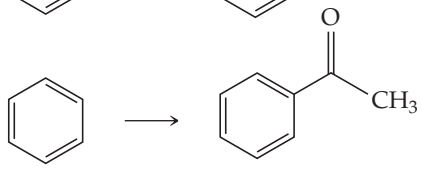
(b)



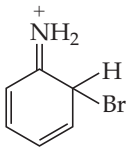
(c)



(d)

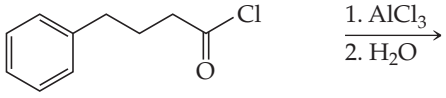


30.25 Draw all the resonance structures of the species shown here.

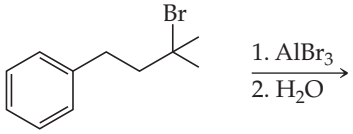


30.26 Provide the major organic product of the following reactions. [*Hint*: Think intramolecular.]

(a)



(b)



30.27 Which of the following functional groups is the most deactivating for EAS? **(a)** methoxy, **(b)** phenol **(c)** ethyl, **(d)** acetamide, **(e)** benzene?

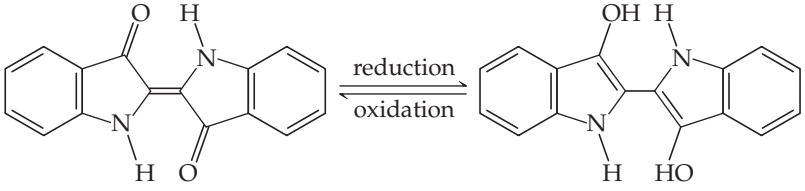
Answers to Self-Assessment Exercises

30.19 (a) **30.20** (b)

Sample Integrative Exercise

Putting concepts together

Indigo is a dark blue dye with the following structure.



Indigo Indigo white

(a) Classify the central double bond as either *E* or *Z*. **(b)** Intramolecular hydrogen bonding occurs in indigo but only intermolecular hydrogen bonding occurs in the related diastereoisomer. Explain why this is so. **(c)** The ring containing the nitrogen atom in indigo is planar. What does this suggest about the hybridization of the nitrogen atom? **(d)** Indigo is very insoluble in water. In order for it to be used as a dye, it is first converted to a water-soluble form (indigo white). The cloth is impregnated with solution and, upon oxidation, the blue dye is precipitated in the cloth. What structural feature of indigo white is responsible for the increase in water solubility? **(e)** Is indigo white aromatic?

SOLUTION

Analyze This exercise focuses on the structure of indigo and the effect this has on hydrogen bonding and solubility.

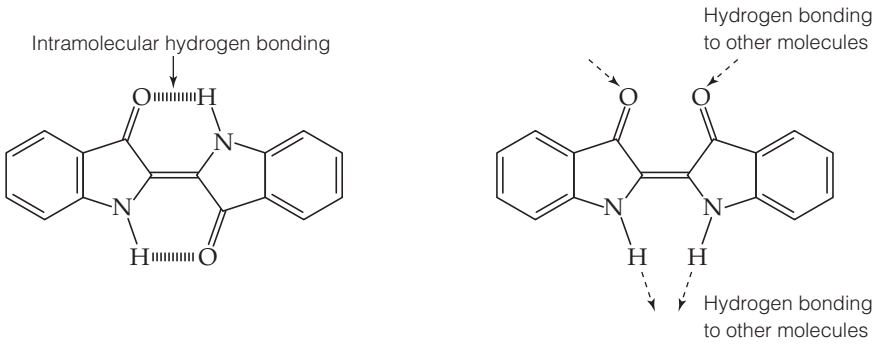
Plan Determine the priority of the groups attached to the central double bond in order to classify it as *E* or *Z* then identify hydrogen bonding sites within the molecule and its isomer. Work out the hybridization of the N atom and examine factors that may influence water solubility.

Continued

Solve

(a) In assigning priorities to the groups at either end of the central double bond, nitrogen has a higher priority than carbon. Consequently indigo has the two high priority groups in an *E* arrangement.

(b) The hydrogen bonding in indigo forms six-member rings which are stable. In the *Z* isomer of this compound the hydrogen bond donor atoms and hydrogen bond acceptor atoms are not matched with each other and consequently can only hydrogen bond to appropriate surrounding molecules.



(c) A planar nitrogen atom with three bonds suggests sp^2 hybridization with the lone pair in a *p* orbital.

(d) Reduction of a ketone to an alcohol group will be accompanied by an increased opportunity for hydrogen bonding and will increase the water solubility of the material.

(e) Yes, it follows the $(4n + 2)$ rule for aromaticity. The lone pair on nitrogen forms part of the aromatic structure.

Chapter Summary and Key Terms

SECTION 30.1 **Aromatic hydrocarbons**, or **arenes**, are compounds containing multiple sp^2-hybridized carbons, most often in a six-membered ring, which we call benzene. They are less reactive than alkenes and undergo very different chemical reactions because of the delocalization of their π-electrons.

SECTION 30.2 Aromatic hydrocarbons larger than benzene that incorporate multiple rings are given trivial names. Simple aromatic hydrocarbons bearing a single substituent are named based on benzene—for example, nitrobenzene. The substituent C_6H_5 is called a **phenyl group**. Loss of a hydrogen from toluene leads to a **benzyl group**. **Phenols** are a benzene derivative bearing a hydroxyl group. Disubstituted benzenes occur as three isomers labelled *ortho*, *meta*, *para*.

SECTION 30.3 Aromatic compounds are stabilized by the contributions of two or more **resonance structures**. **Resonance** is an extremely important concept in describing the bonding and stability of aromatic compounds. The **resonance energy** associated with benzene is the difference in energy between hydrogenating benzene and the theoretical molecule 1,3,5-cyclohexatriene. Compounds are aromatic if they follow Hückel's criteria. The major criterion states that a compound is aromatic if it has $[4n + 2]$ π-electrons and is cyclic. **Heterocyclic compounds** contain a **heteroatom**—that is, an atom other than carbon.

SECTION 30.4 Phenols are an unusual class of compound prevalent in nature. Their acidity differs greatly from another common and closely related class, the alcohols, because of the relative stability of the phenoxide ion. The anion is **resonance-stabilized** as a result of the phenolate's ability to distribute the electron density around the aromatic ring. **Electron-withdrawing groups** on the phenyl ring of phenol increase the acidity through **inductive effects**.

SECTION 30.5 Addition reactions are difficult to carry out with aromatic hydrocarbons, but **electrophilic aromatic substitution (EAS) reactions** are easily accomplished in the presence of a catalyst. Two general reactions are halogenation, which substitutes hydrogen for a single halogen (typically Cl or Br), and nitration, which substitutes a hydrogen for NO_2. Two new types of reactions discussed are the **Friedel–Crafts alkylation** and **acylation reactions**. Each of these reaction types is useful as they produce new C—C bonds. Substituted benzenes also undergo EAS, though the substituent can act as an **activating** or **deactivating** depending on whether it is electron donating or electron withdrawing. Generally, electron-donating groups are ***ortho-***, ***para-*directing** whereas electron-deficient groups are ***meta-*directing**.

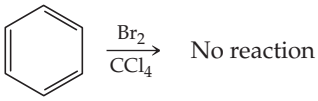
Key Skills

- Know how to derive the name of simple mono- and disubstituted aromatic compounds by positional numbering, for example 1,2-dibromobenzene, as well as by *ortho*, *meta* and *para* nomenclature, for example *o*-dibromobenzene. (Section 30.2)
- Learn the common names such as toluene, phenol, aniline, etc. and the hierarchy of functional groups. (Section 30.2)
- Be able to use the curved arrow notation introduced in Chapter 26 to understand the stability and directive properties of different functional groups on the aromatic structure. (Section 30.5)

- Be able to draw Wheland intermediates to show the directive influences of substituents on benzene in EAS. (Section 30.5)
- Understand why phenols are acidic and be able to describe this through drawing resonance contributors to an intermediate structure. (Section 30.4)
- Be able to identify electrophiles from a given set of reagents, and in the case of substituted benzenes understand qualitatively their directive influences on the product outcome. (Section 30.5)

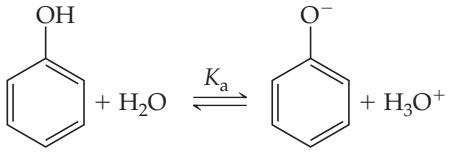
Key Equations

- Aromaticity



[30.4]

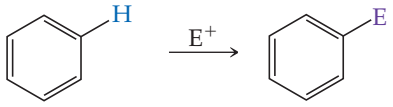
- Acidity



phenoxide ion

[30.8]

- Electrophilic aromatic substitution



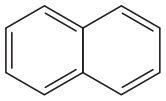
[30.10]

Exercises

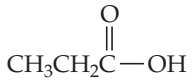
Visualizing Concepts

30.28 **(a)** Draw a six-membered ring as a line drawing and demonstrate how sp^2 hybrid orbitals interact, as in benzene. **(b)** Illustrate how the p orbitals overlap to form a stable aromatic structure. [Section 30.1]

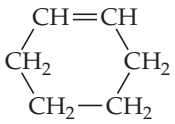
30.29 Which of the following molecules will readily undergo an electrophilic substitution reaction? [Section 30.5]



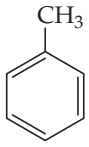
(a)



(b)

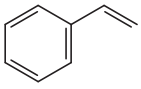


(c)

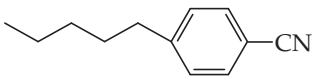


(d)

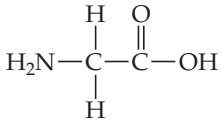
30.30 Consider the following molecules. Which of these would be most likely to exhibit liquid crystalline behavior? [Section 30.3]



(i)

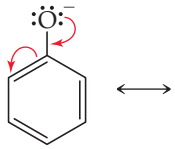


(ii)



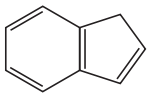
(iii)

30.31 Draw the product of the following valence electron movements. [Section 30.4]

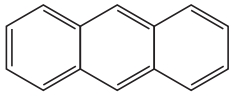


30.32 Which of the following structures is aromatic? [Section 30.3]

(a)



(b)



(c)



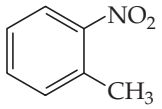
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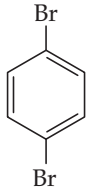
Benzene Structure and Nomenclature (Sections 30.1 and 30.2)

30.33 Name the following compounds systematically:

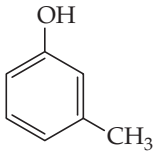
(a)



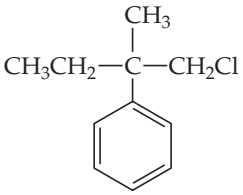
(b)



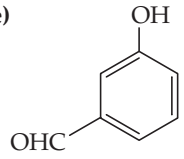
(c)



(d)



(e)



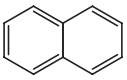
30.34 What observations made by Reinitzer on cholesteryl benzoate suggested that this substance possesses a liquid crystalline phase?

30.35 In contrast to ordinary liquids, liquid crystals are said to possess "order". What does this mean?

Aromaticity (Section 30.3)

30.36 Which hydrogens are more acidic, those of cyclohexane or benzene? Why?

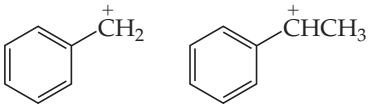
30.37 Mothballs are composed of naphthalene, $C_{10}H_8$, the structure of which consists of two six-membered rings of carbon that are fused along an edge, as shown in the following incomplete Lewis structure:



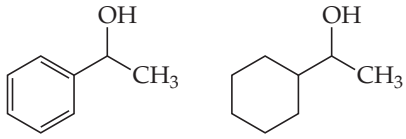
(a) Write two different complete Lewis structures for naphthalene. **(b)** The observed C—C bond lengths in the molecule are intermediate between C—C single and C—C double bonds. Explain. **(c)** Represent the resonance in naphthalene in a way analogous to that used to represent it in benzene.

30.38 **(a)** What is the difference between a localized π-bond and a delocalized one? **(b)** How can you determine whether a molecule or ion will exhibit delocalized π-bonding? **(c)** Demonstrate with the aid of a diagram the delocalization in benzene. **(d)** Is the π-bond in $CH_3CO_2^-$ localized or delocalized?

30.39 Which of the following compounds is more stable? Explain.



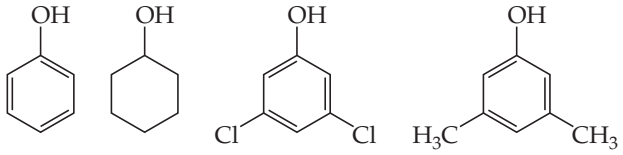
30.40 Which of the following alcohols undergoes dehydration more rapidly when heated with H_2SO_4? Why?



30.41 **(a)** One test for the presence of an alkene is to add a small amount of molecular bromine and look for the disappearance of the brown color. This test does not work for detecting the presence of an aromatic hydrocarbon. Explain.

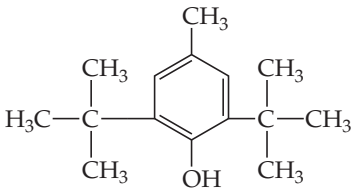
Properties of Phenols (Section 30.4)

30.42 Place the following in decreasing order of acidity:



30.43 **(a)** Draw the structure of phenoxide. **(b)** Use arrow notation to describe why this intermediate is more stable than that for the corresponding cyclohexanol anion.

30.44 Butylated hydroxytoluene (BHT) has the following molecular structure:



BHT

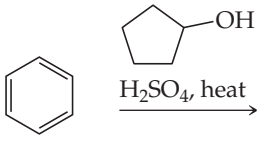
It is widely used as a preservative in a variety of foods, including dried cereals. **(a)** Based on its structure, would you expect BHT to be more soluble in water or in hexane (C_6H_{14})? Explain. **(b)** Identify phenol within this structure.

Electrophilic Aromatic Substitution Reactions (Section 30.5)

30.45 Using condensed structural formulas, write a chemical equation for each of the following reactions: **(a)** hydrogenation of cyclohexatriene; **(b)** bromination of 1,4-dimethoxybenzene using $FeBr_3$ as a catalyst; **(c)** reaction of 2-chloropropane with benzene in the presence of $AlCl_3$.

30.46 Suggest a method of preparing ethylbenzene, starting with benzene and ethene as the only organic reagents.

30.47 **(a)** What would be the electrophile in the following reaction? **(b)** What is the EAS product?



30.48 Rank the following groups in order of increasing activating power in electrophilic aromatic substitution reactions: $-OCH_3$, $-CH_2CH_3$, $-Br$.

30.49 Draw the most important contributor to the resonance hybrid formed when toluene undergoes *para* nitration.

30.50 What factors affect the *ortho*:*para* ratio in electrophilic aromatic substitution reactions?

30.51 **(a)** What is the effect of a chlorine substituent on EAS? **(b)** What is the effect of a nitro substituent on EAS?

30.52 What is the *major* product (including regioisomer) when ethylbenzene is reacted with $Br_2/FeBr_3$?

30.53 Give a reason why nitrobenzene can be used as a solvent for Friedel-Crafts alkylation.

30.54 Give an explanation why direct nitration of aniline using HNO_3 yields, among other products, *m*-nitroaniline.

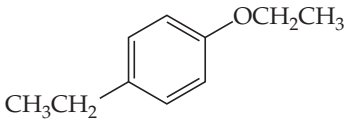
30.55 Devise a method for preparing *m*-chloroaniline from benzene.

30.56 Provide a series of synthetic steps by which 2-bromo-4-nitrobenzoic acid can be prepared from toluene.

30.57 What is the *major* product of the bromination of 4-methylphenol by Br_2 in the presence of $FeBr_3$?

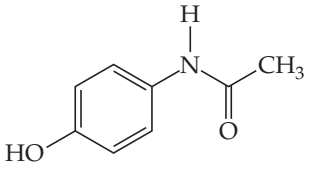
30.58 What is the *major* product of the nitration of 4-bromoanisole?

30.59 What is the major mononitration product of 1-ethoxy-4-ethylbenzene?



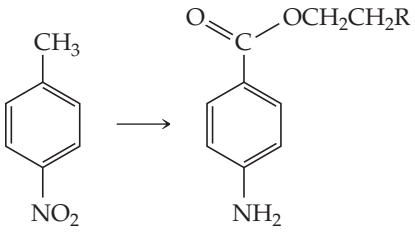
Integrative Exercises

30.60 **(a)** Devise a synthesis of the analgesic acetaminophen (paracetamol) from phenol.



(b) Does the name *paracetamol* tell you anything about the structure of the molecule?

30.61 4-Nitrotoluene is the starting material for the synthesis of the local anaesthetics benzocaine and procaine. Describe a synthesis of benzocaine starting from 4-nitrotoluene.



benzocaine (R=H)
procaine (R=NEt_3)

30.62 The heat of combustion of decahydronaphthalene ($C_{10}H_{18}$) is -6286 kJ mol^{-1}. The heat of combustion of naphthalene ($C_{10}H_8$) is -5157 kJ mol^{-1}. (In both cases, CO_2(g) and H_2O(l) are the products.) Using these data and data in Appendix C, calculate the heat of hydrogenation of naphthalene. Does this value provide any evidence for aromatic character in naphthalene?

30.63 The *cyclopentadienide ion* has the formula $C_5H_5^-$. The ion consists of a regular pentagon of C atoms, each bonded to two C neighbors, with a hydrogen atom bonded to each C atom. All the atoms lie in the same plane. **(a)** Draw a Lewis structure for the ion. According to your structure, do all five C atoms have the same hybridization? Explain. **(b)** Chemists generally view this ion as having sp^2 hybridization at each C atom. Is that view consistent with your answer to part (a)? **(c)** Your Lewis structure should show one non-bonding pair of electrons. Under the assumption of part (b), in what type of orbital must this non-bonding pair reside? **(d)** Are there resonance structures equivalent to the Lewis structure you drew in part (a)? If so, how many? **(e)** The ion is often drawn as a pentagon enclosing a circle. Is this representation consistent with your answer to part (d)? Explain. **(f)** Both benzene and the cyclopentadienide ion are often described as systems containing six π-electrons. What do you think is meant by this description?

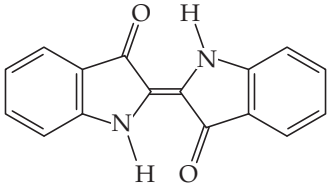
30.64 Both 3-aminobenzoic acid and 4-aminobenzoic acid are precursors to condensation polymers. **(a)** What type of isomers are these molecules? **(b)** Draw the structure of both of these molecules and the repeating unit of the polymer each forms. **(c)** Both compounds may be synthesized from toluene using the following reactions (not given in the correct order).

- Reduction of a nitro group using hydrogen gas and a palladium catalyst.
- Nitration using concentrated nitric acid and concentrated sulfuric acid.
- Oxidation of the aromatic alkyl group with acidified potassium permanganate.

Use your knowledge of the directing effect of a substituent to give the correct sequence of reactions for the synthesis of both compounds.

30.65 The pK_b of methylamine and analine is 3.36 and 9.40 respectively. Which molecule is the stronger base? Explain the reason for this difference.

30.66 Indigo is a blue dye that was originally extracted from plants but now is produced synthetically.



Indigo

(a) List the functional groups present in indigo. **(b)** What is the hybridization of the carbon atoms? **(c)** Explain why the overall shape of indigo is planar. **(d)** The molecule absorbs at 613 nm in the visible region of the spectrum. What energy does this correspond to?

Design an Experiment

There is often more than one way to prepare a compound and a research scientist has to consider the advantages and drawbacks of each route. For example, you are asked to prepare 3-nitrobenzoic acid from benzene. How do you do it? Note the carboxylic acid group cannot be introduced into the ring directly but could be obtained by either a Grignard reaction on a halobenzene or the oxidation of an alkylbenzene. You need to consider the directing effect of a group prior to installing the second substituent onto the ring and whether the group is activating or deactivating. An activating group will give a product under much milder conditions that may have economic advantages. Draw out as many different routes to 3-nitrobenzoic acid as you can and assess each one for its viability. At what point do you purify your compound to remove unused reagents and biproducts? How might you do the purification? If you started with 78 g of benzene, what quantities of reagents do you need for each route?

WHAT'S AHEAD

31.1 ▶ Amines and the Amide Bond

31.2 ▶ Amino Acids

31.3 ▶ Proteins, Peptides, and Enzymes

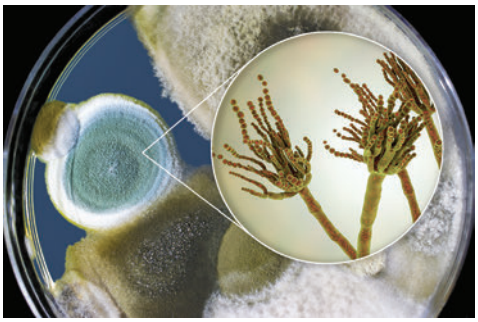
31.4 ▶ Nucleic Acids and DNA

31

NITROGEN-CONTAINING ORGANIC COMPOUNDS

31.1 | Amines and the Amide Bond





The discovery of penicillin in 1928 by Alexander Fleming was serendipitous. He had left an uncovered petri dish containing staphylococci bacteria on the windowsill of his laboratory at the St. Mary's Medical School of London University. Mold spores blew in through the open window and started to grow on the culture medium. Some days later, Fleming observed that the bacteria surrounding the mold was dying. He surmised that it was not the mold itself (from the *Penicillium* genus), but a metabolite of the mold that was causing the effect and named it penicillin. Fleming did little to capitilize on his discovery, but Ernst Chain, a biochemist working at Oxford University's Sir William Dunn School of Pathology, as well as Howard Florey, who headed the school, recognized the enormous potential of the discovery to medicine. Work commenced on isolating this "mold juice" and involved fermenting thousands of liters of mold broth in vessels exposed to air. By 1945, Dorothy Hodgkin had determined the chemical structure of penicillin using X-ray crystallography and found it was a relatively small molecule centered around a four membered ring containing a cyclic amide called a β-lactam. The 1945 Nobel prize in physiology or medicine was awarded jointly to Fleming, Florey, and Chain.

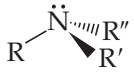
Chapters 27–29 introduced the chemistry of oxygen-containing compounds; in this chapter we will examine the complementary role played by nitrogen-containing molecules. In fact, nitrogen-containing organic compounds form an incredibly large and important class in their own right.

By the end of this section, you should be able to

- Name simple amines and amides
- Recognize several methods by which amines may be synthesizes
- Understand the acid-base properties of amines

Amines

Amines are organic bases with the general formula

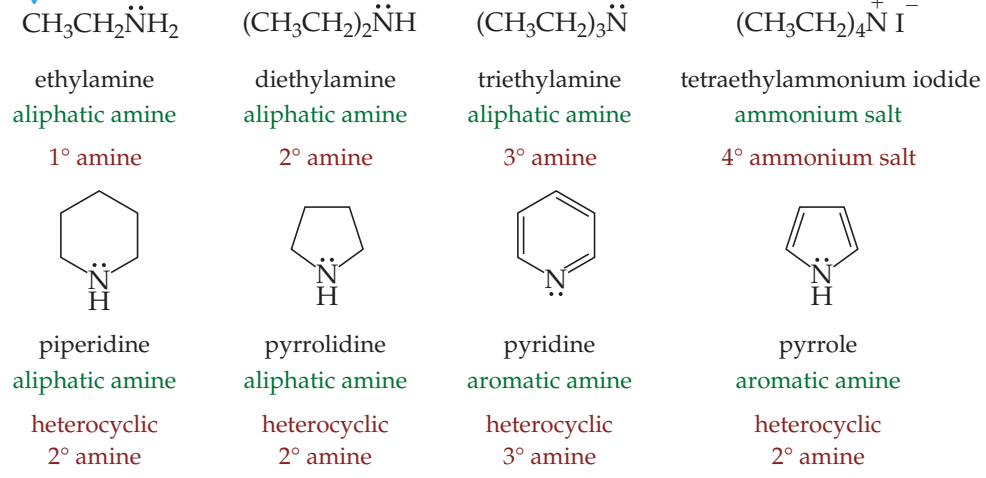


where R, R′ and R″ may be H or a hydrocarbon group. Amines containing alkyl groups are called **aliphatic amines**. Aniline is the parent molecule of a class of amines known as **aromatic amines**. This class is characterized by a covalent bond between the nitrogen atom and at least one aromatic group (for example, phenyl or naphthyl). Amines that form part of a cyclic structure are called **cyclic amines** or *heterocycles*. A special class of heterocyclic compounds contains a nitrogen atom within an aromatic ring (for example, pyridine). We also class these amines as aromatic amines. In many cases the lone pair found on nitrogen in an aromatic amine can contribute to the aromaticity. Figure 31.1 gives some examples of amine classes, including the five- and six-membered heterocycles pyrrolidine and piperidine, and the aromatic heterocycles pyrrole and pyridine.

Amines are further classified as primary, secondary or tertiary.

- **Primary (1°) amine**: contains *one* alkyl or aryl group bonded to nitrogen.
- **Secondary (2°) amine**: contains *two* alkyl or aryl groups bonded to nitrogen.
- **Tertiary (3°) amine**: contains *three* alkyl or aryl groups bonded to nitrogen.
- **Quaternary (4°) ammonium salts**: contain *four* alkyl or aryl groups directly attached to nitrogen.

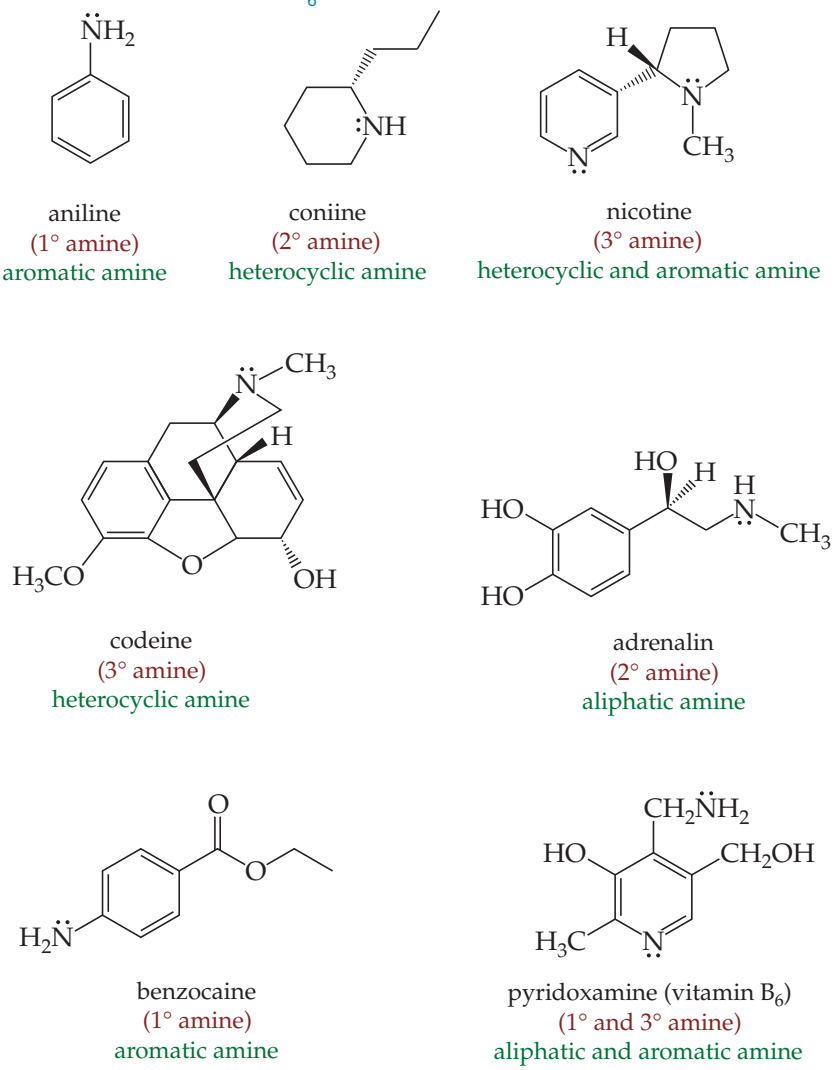
Go Figure What makes an amine secondary?



▲ **Figure 31.1** **Amine classes.**

Figure 31.2 shows the structure of some industrially and biologically important amines. Aniline, for example, is an aromatic amine used extensively in the manufacture of dye stuffs. A significant number of amines are derived from plant material, such as roots, leaves and bark. Amines that are derived from plant material and contain a basic nitrogen atom are commonly called **alkaloids**. Alkaloids form an enormous class of compounds whose physiological properties have been studied intensively for over 150 years. Coniine, for example, is a highly toxic alkaloid, found to be the active ingredient in "poison hemlock", which was responsible for the death of Socrates. Nicotine is a highly addictive alkaloid found in tobacco leaves. Codeine and morphine, are both analgesics and alkaloids extracted from opium poppies. Adrenaline is a principal compound in a group of compounds known as the *phenylethylamines*. Adrenaline is not an alkaloid; it is a *hormone* that is released into the body in response to stress. It causes increased blood flow to the muscles and brain, accelerates respiration and heart rate, and stimulates the release of stored energy into the blood. When injury to the body occurs, it potentiates the healing process. At times, adrenaline also functions as a neurotransmitter. Pyridoxamine, or vitamin B_6, is a water soluble vitamin that exists in three major chemical forms: pyridoxine, pyridoxal

Go Figure Can you identify which amine is 1° and which is 3° in vitamin B_6?

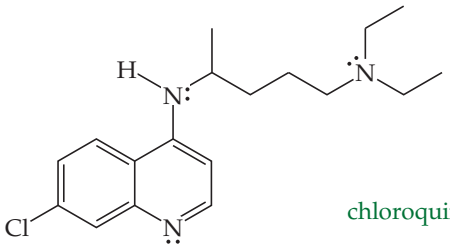


▲ **Figure 31.2 Industrially and biologically important amines.** The lone pair on nitrogen has been added to highlight its position in these compounds.

Sample Exercise 31.1

Classifying Amines

Classify each amino group of chloroquine, a compound used for the treatment of malaria, as primary, secondary or tertiary. Comment also on whether they are aliphatic or aromatic amines.



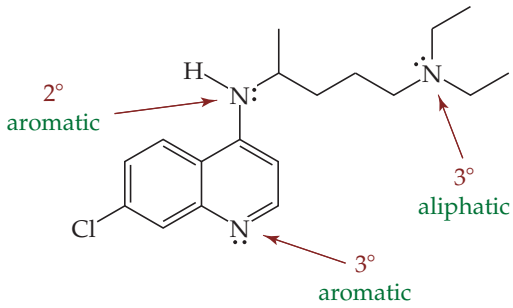
chloroquine

SOLUTION

Analyze We are asked to classify each amine in chloroquine.

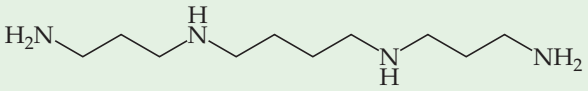
Plan Look for each nitrogen atom and determine if aromatic or aliphatic as a result of the nature of the bonding around them. Classify each as primary, secondary or tertiary by determining how many N—C bonds exist.

Solve



Practice Exercise

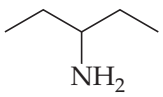
Classify each amino group of spermine, a compound isolated from semen, as primary, secondary or tertiary.



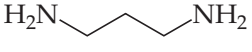
spermine

and pyridoxamine. Its role in the body is varied but essential for good health. Benzocaine is an effective local and topical anesthetic used in sting medication, sunburn cream and by dentists in mucosal tissue.

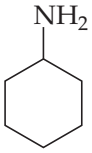
The systematic naming of simple monoaliphatic amines follows the same guidelines as for alcohols. The *e* of the parent alkane is replaced by *amine* (as opposed to *ol* for alcohols). Otherwise, the name is derived from the alkyl group attached to nitrogen and named as the alkylamine. For example:



3-pentanamine

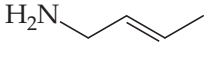


propane-1,3-diamine

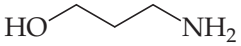


cyclohexylamine

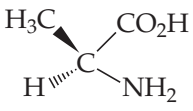
For amines containing multiple alkyl groups bonded to carbon, the amine is named based on those alkyl groups (Figure 31.1). Amines have a low priority in the nomenclature hierarchy. In many instances, the **amino group** is named as a substituent rather than as the class of an organic compound:



1-aminobut-2-ene



3-aminopropan-1-ol



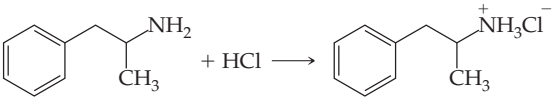
(*S*)-2-aminopropanoic acid

CHEMISTRY AND LIFE Amines and Amine Hydrochlorides

Many amines with low molecular weights have unpleasant "fishy" odors. Amines and ammonia (NH_3) are produced by the anaerobic (absence of O_2) decomposition of dead animal or plant matter. Two such amines with very disagreeable odors are $H_2N(CH_2)_4NH_2$, known as *putrescine*, and $H_2N(CH_2)_5NH_2$, known as *cadaverine*. Despite their usually unpleasant odors, amines and the products of their reactions are very important compounds in biological systems.

The pigment of vision, rhodopsin, is prepared by the formation of an imine bond between the biologically active aldehyde 11-*cis*-retinal and the protein opsin (**Figure 31.3**). When rhodopsin absorbs a photon of light, the *cis* double bond at C11 undergoes an isomerization to the *trans* geometry, which triggers a change in the shape of rhodopsin, leading to nerve impulses that are detected by the brain as a visual image.

Many drugs, including quinine, codeine, caffeine and amphetamine (benzedrine), are amines. Like other amines, these substances are weak bases; the amine nitrogen is readily protonated by treatment with an acid. The resulting products are called ammonium salts. For example, amphetamine hydrochloride is the ammonium salt formed by treating amphetamine with HCl.

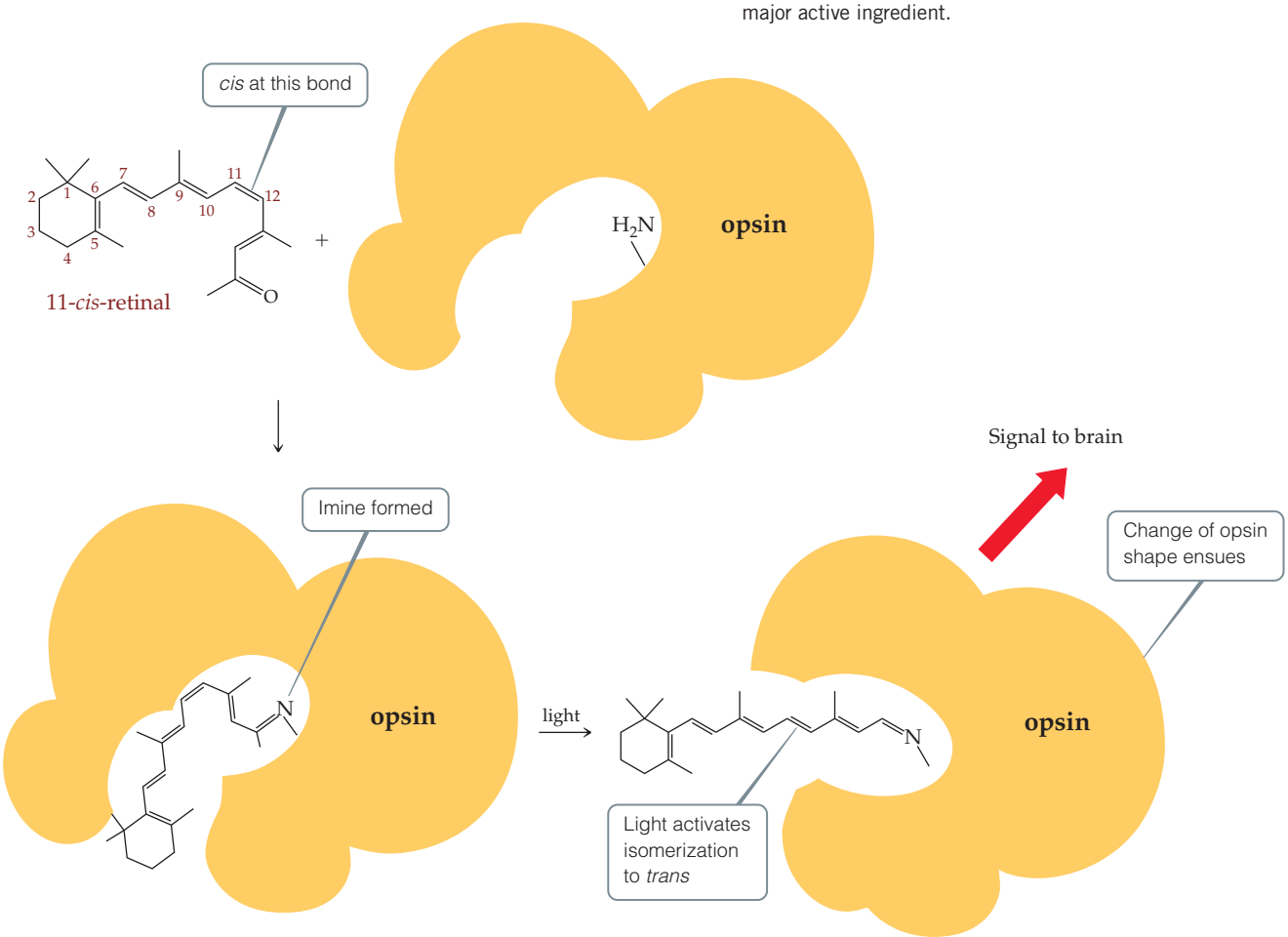


amphetamine amphetamine hydrochloride [31.1]

Such ammonium salts are less volatile, more stable and generally more water soluble than the corresponding neutral amines. Many drugs that are amines are sold and administered as ammonium salts for this very reason. Some examples of over-the-counter medications and cleaning products that contain amine hydrochlorides as active ingredients are shown in **Figure 31.4**.

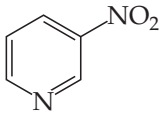


▲ **Figure 31.4 Ammonium salts.** Many commercial products, such as over-the-counter medications and antiseptics, contain amine hydrochlorides as the major active ingredient.

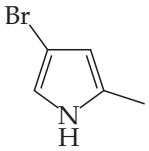


▲ **Figure 31.3 Rhodopsin.** Imine formation between 11-*cis*-retinal and the protein opsin is important for vision.

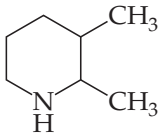
The names of heterocyclic amines are derived from the parent aliphatic or aromatic heterocycle; for example:



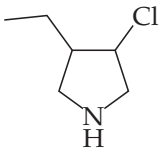
3-nitropyridine



4-bromo-2-methylpyrrole

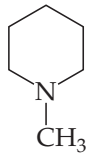


2,3-dimethylpiperidine

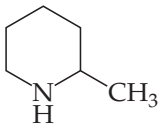


3-chloro-4-ethylpyrrolidine

When more than one type of alkyl group (for example, methyl and ethyl groups) are bonded to nitrogen in the same molecule, the name must also reflect the position of the alkyl groups on nitrogen by using the prefix *N*. For example, the name *N*-methylpiperidine indicates that the methyl substituent is located on the nitrogen of the piperidine ring and not located on the carbon framework (for example, 2-methylpiperidine). The name *N,N*-diethyl-1-butanamine is used to describe both ethyl groups bonded to nitrogen. This compound differs from *N*-ethyl-2-ethyl-1-butanamine and 4-ethyl-3-hexanamine. All three compounds are constitutional isomers.

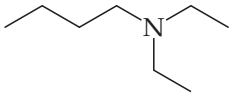


differs from

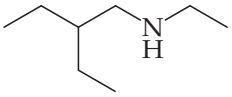


N-methylpiperidine

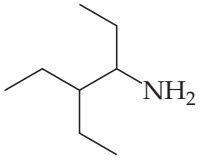
2-methylpiperidine



differs from



differs from



N,N-diethyl-1-butanamine

N-ethyl-2-ethyl-1-butanamine

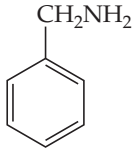
4-ethyl-3-hexanamine

Sample Exercise 31.2

Naming Amines

Write the systematic or IUPAC name for the following amines:

(a) $CH_3CH_2CH_2CH_2CH_2NH_2$ **(b)**



(c) $(CH_3)_3N$

SOLUTION

Analyze We are asked to provide systematic names for three different amines

Plan Use the rules described earlier to structure the names.

Solve

(a) 1-pentanamine—derived from pentane.

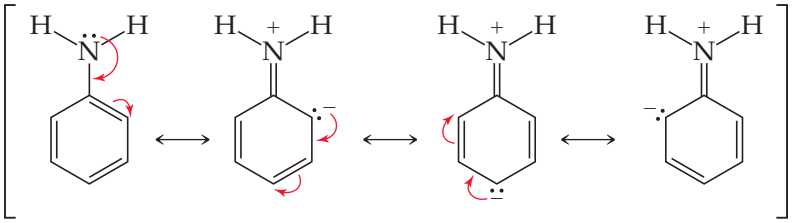
(b) Benzylamine—derived from the benzyl group. This is better than naming the structure phenylmethanamine.

(c) Trimethylamine—derived from the three methyl substituents attached to nitrogen. Note that the prefix *N* is not required.

Practice Exercise

Draw the structures for the following amines:
(a) *tert*-butylamine, (b) 4-nitroaniline,
(c) *N*-methyl-2-hydroxypiperidine

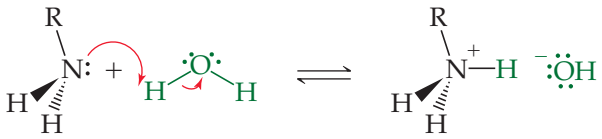
Go Figure Why is cyclohexylamine a stronger base than aniline?



▲ **Figure 31.5 Resonance contributors for aniline.** The electron pair distribution responsible for the mild basicity and nucleophilicity in aromatic amines.

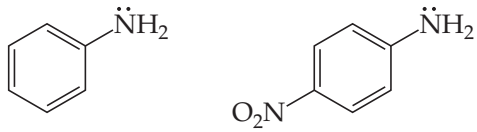
Reactivity of Amines

We introduced the nucleophilic nature of amines in Chapter 28. Along with this nucleophilicity is the ability of primary, secondary and tertiary amines to act as a weak base. The presence of the amine functional group allows for extensive solvation in aqueous media. This means that most amines have some solubility in water and hence can be tested with litmus paper to determine their presence. The acid–base reaction for a primary amine in aqueous solution can be written generally as:



an amine an alkyl ammonium ion [31.2]

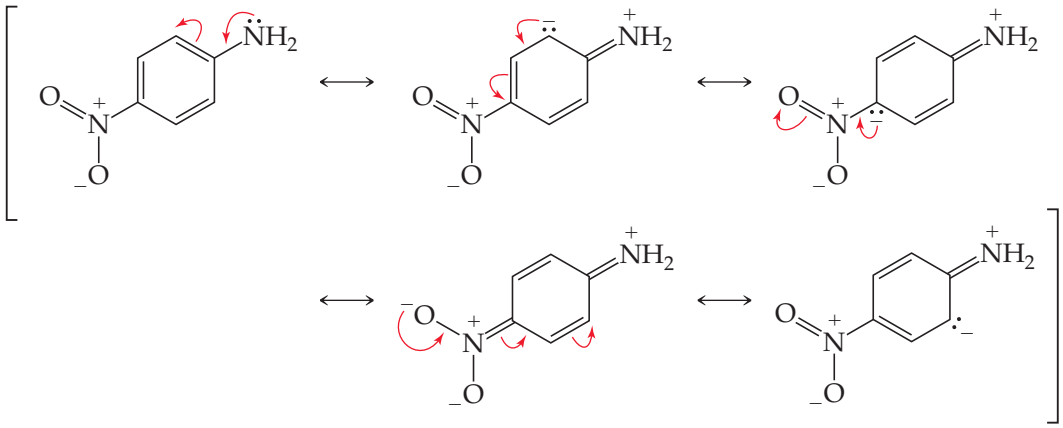
There are a few features to note in this reaction. First, the reaction is an equilibrium reaction, although this equilibrium lies to the left for all amines. Primary, secondary and tertiary alkylamines are over 10^6 times more basic (pK_b = 3–4) than comparable aromatic amines (pK_b = 9–10). The difference in basicity can be attributed to the resonance effects available to aromatic amines, such as shown for aniline in **Figure 31.5**. By distributing electrons around the ring, the nucleophilicity and basicity of aromatic amines is weakened compared with their aliphatic counterparts.



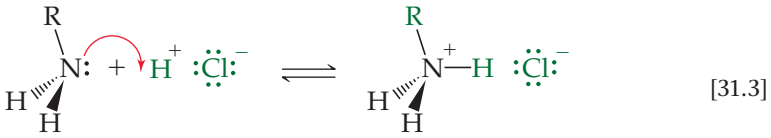
pK_b = 9.4 pK_b = 13.0

The basicity of aromatic amines is also influenced by the substituents on the aromatic ring. For example, 4-nitroaniline (**Figure 31.6**) is a much weaker base than aniline, due to resonance and inductive effects leading to a redistribution of electron density onto the NO_2 group.

The second feature to note is that the acid–base reaction is written so that it involves the lone pair on nitrogen. The two electrons in this lone pair form a new N–H covalent bond. Finally, the product of the reaction is an **alkyl ammonium salt**, also known as a 4° ammonium salt. Such ammonium salts are easily formed in essentially quantitative yield by reaction of an amine with strong acid such as aqueous HCl:

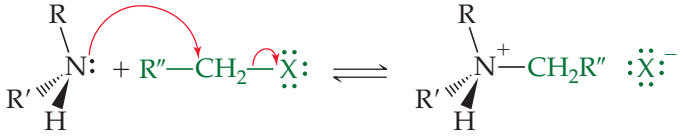


▲ **Figure 31.6 Rationalising the basicity of 4-nitroaniline.** There are more resonance contributors to the structure of 4-nitroaniline when compared to aniline, suggesting the basicity (and nucleophilicity) of the substituted aniline is less. This situation is accentuated by the electron-withdrawing effect of the nitro group, which is inductive throughout the molecule.



a primary amine — an alkyl ammonium salt [31.3]

Such salts are usually highly soluble in water. Alkyl ammonium salts can also be formed by the reaction of amines with haloalkanes. In the following example, a secondary amine is reacted with a haloalkane to form an alkyl ammonium salt:



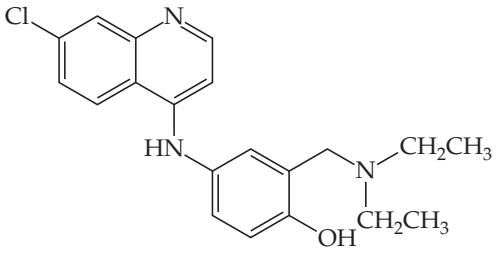
a secondary amine — a trialkyl ammonium salt [31.4]

The alkylation reaction is general but care needs to be taken in stoichiometry of reagents, choice of solvent and choice of haloalkanes in order to limit further alkylation.

Sample Exercise 31.3

Amine Basicity

Amodiaquin is commonly used to treat quinine-resistant malaria. Identify the amine groups within this compound and indicate which of the nitrogen atoms of amodiaquin is the most basic.



amodiaquin

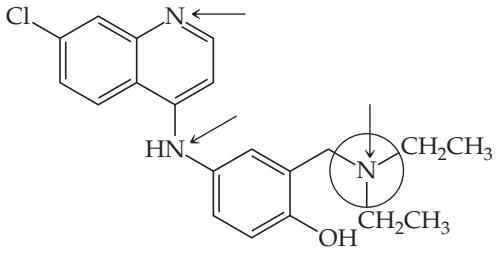
Continued

SOLUTION

Analyze We are asked to classify the amines located within the structure of amodiaquin and from there, which is the most basic.

Plan Identify the amines and look for aliphatic amines as the most basic.

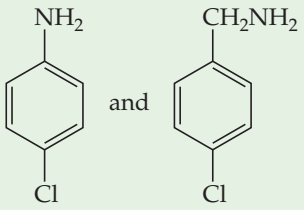
Solve The comparison here is between two aromatic amines and an aliphatic amine (all amine groups indicated by an arrow). The aliphatic amine (circled) is most basic.



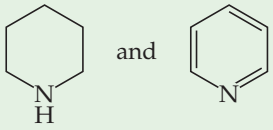
Practice Exercise

Select the stronger base from each amine pair.

(a)

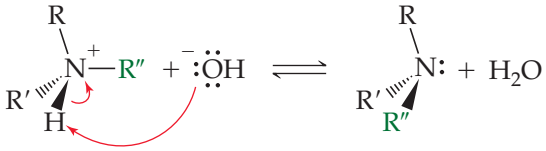


(b)



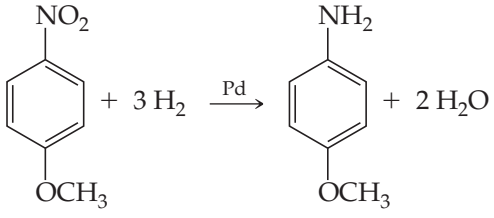
Synthesis of Amines

Amines can be formed in several ways, some simple and some complex. We look at three of the most common ways to form amines. Equation 31.4 illustrates the nucleophilicity of amines and their reactivity towards alkyl halides. The ammonium ion formed in the reaction is a weak acid (pK_a = 9–11), comparable in pK_a to phenols. Addition of an aqueous base during workup (see Equation 31.5) leads in this case to the tertiary amine. Hence, by a simple *alkylation* we have chemically transformed a secondary amine into a tertiary amine.



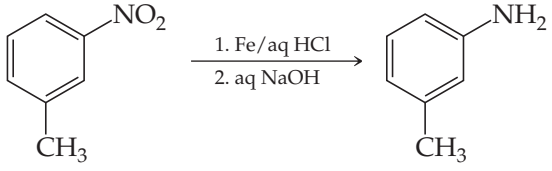
a tertiary amine [31.5]

Aromatic amines such as 4-methoxyaniline are easily prepared by reduction of the corresponding nitro compound. This reduction is usually achieved by catalytic hydrogenation—that is, using H_2 in the presence of a metal catalyst such as Ni, Pd or Pt. Although this reaction is very general, easily accomplished and high yielding, care needs to be taken to ensure that other groups susceptible to hydrogenation, such as double bonds, are not also reduced (recall that benzene does not react like an alkene towards addition type reactions).

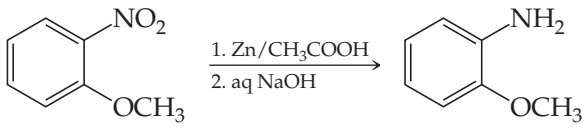


[31.6]

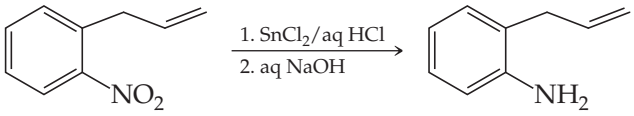
A metal reduction can also be used to effect the same transformation. Metals such as Fe and Zn, and metal salts such as $SnCl_2$, can be used. For example, reduction of the nitro group in Equation 31.6 by hydrogenation (H_2/Pd) would also reduce the alkene group. The use of tin(II) chloride as a reducing agent is more selective for the nitro group, yielding the desired product.



[31.7]

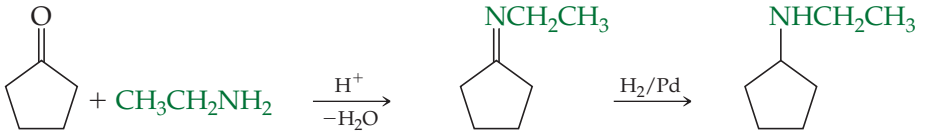


[31.8]



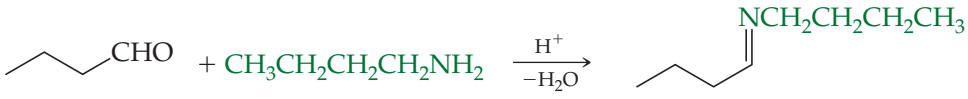
[31.9]

Recall that imines are formed by the reaction of aldehydes and ketones with primary amines. The reactivity of the imine group resembles that of a carbonyl group, meaning that both functional groups are susceptible to hydride reduction and catalytic hydrogenation. This method, known as a **reductive amination**, is an easy way of producing secondary amines from primary amines.



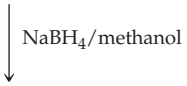
[31.10]

cyclopentanone ethanamine *N*-ethyl-cyclopentanimine, an imine *N*-ethyl-cyclopentanamine



[31.11]

butanal 1-butylamine *N*-butylbutanimine, an imine



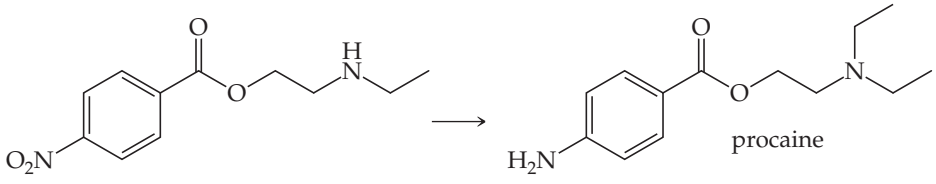
$HN(CH_2CH_2CH_2CH_3)_2$

dibutylamine

Sample Exercise 31.4

Amine Synthesis

Describe a synthesis for procaine, a local anaesthetic, from the suggested starting material. You may choose any reagents and conditions you like that will affect the transformations needed.



SOLUTION

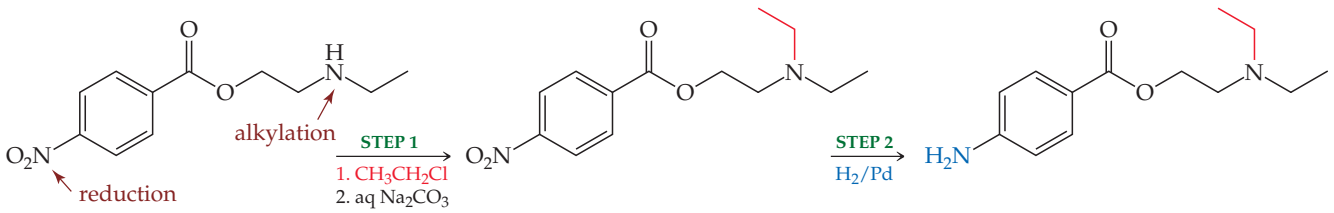
Analyze We are given a compound and asked to devise a synthesis of procaine.

Plan Identify the functional group differences between starting material and product and then a plan of attack to make the necessary interconversions.

Solve In this case, the differences in functional groups can be achieved by an alkylation, introducing the ethyl group, and a reduction of the nitro group to give the amine. *Be very careful with the order of reaction*. In this example, alkylation must occur before reduction in order to yield procaine. Reducing the nitro group to the amino group, followed by alkylation, would be likely to cause a reaction to occur on both nitrogens. The difference in

Continued

nucleophilicity is not significant enough to cause alkylation of just the aliphatic amine.

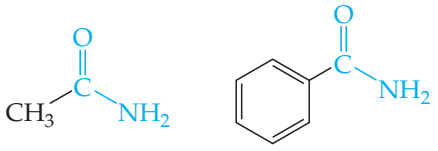


Practice Exercise

Describe a method for separating a mixture of nitrobenzene from aniline in diethyl ether solution.

Amides

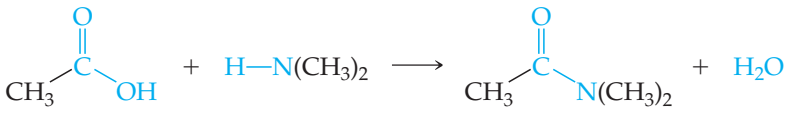
Amides are derivatives of carboxylic acids in which the OH group of the carboxylic acid group has been replaced with a NRR′ group (R, R′ = H, alkyl, aryl), as in these examples:



ethanamide
acetamide

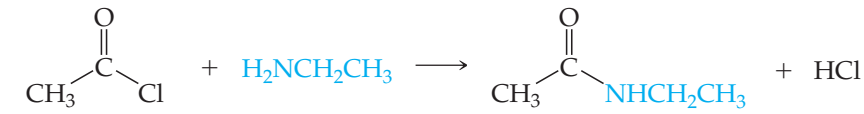
phenylmethanamide
benzamide

An amide can be considered as the condensation product of an amine and a carboxylic acid:

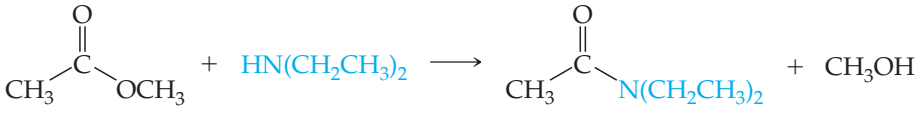


[31.12]

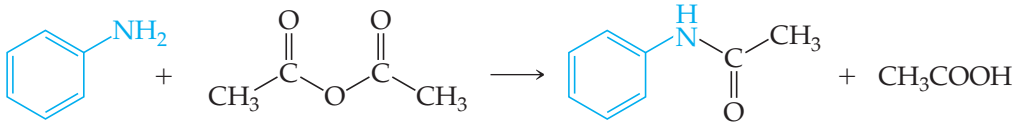
In Section 29.5, we saw that amides can also be formed by reaction of an acid anhydride, acid chloride or ester with ammonia, a primary or secondary amine. Examples of such reactions are:



acetyl chloride (an acid chloride) + ethanamine (a 1° amine) → *N*-ethylacetamide (an amide) + HCl [31.13]



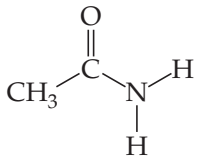
ethyl acetate (an ester) + diethylamine (a 2° amine) → *N,N*-diethylacetamide (an amide) + CH_3OH [31.14]



aniline (an aromatic amine) + acetic anhydride (an acid anhydride) → *N*-phenylacetamide (an amide) + CH_3COOH [31.15]

Amides are classified as primary, secondary or tertiary, depending on their substitution at the amide nitrogen.

- **Primary (1°) amide**: the nitrogen of the amide group is bonded to one carbon atom, which is that of the carbonyl group. For example:

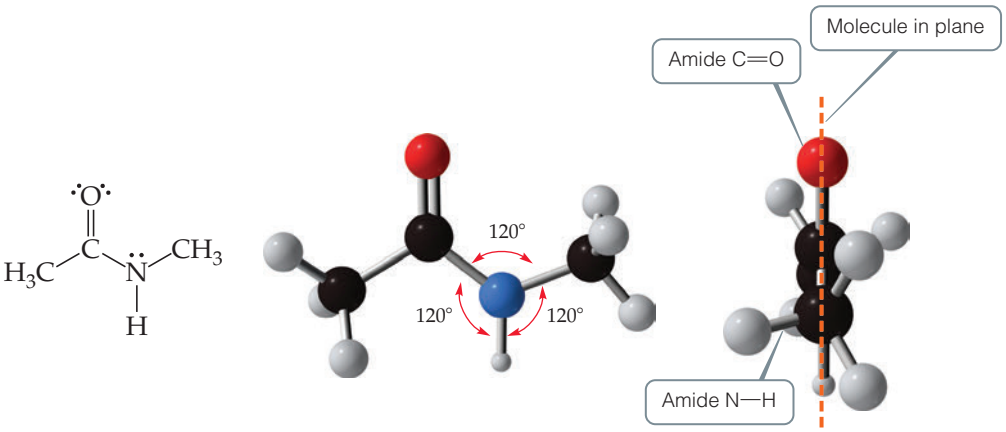


acetamide
1° amide

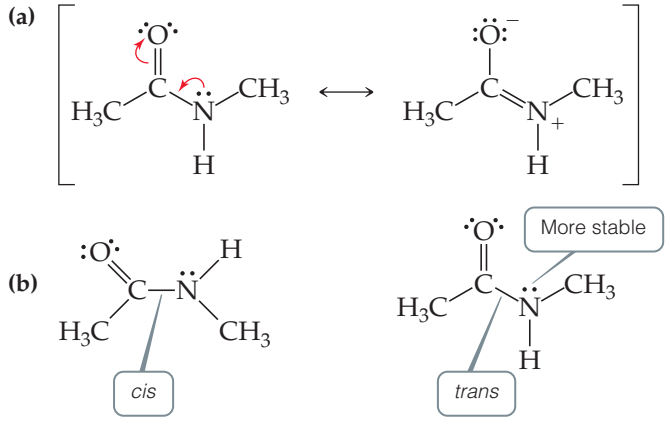
- **Secondary (2°) amide**: the nitrogen of the amide group is bonded to two carbon atoms, one of which is a carbonyl group; for example *N*-phenylacetamide.
- **Tertiary (3°) amide**: the nitrogen of the amide group is bonded to three carbon atoms, one of which is a carbonyl group. The other two carbon atoms usually belong to alkyl or aryl groups; for example *N,N*-diethylacetamide.

The geometry of the amide bond is quite unexpected. At first glance, you would expect the bonding geometry about the nitrogen atom to be a trigonal pyramid, similar to what you would find for an amine. During the 1930s Linus Pauling discovered that an amide is planar through the CONR group (**Figure 31.7**), commensurate with the observed bond angles of approximately 120° about the amide nitrogen.

Pauling rationalized the unusual geometry of the amide bond by describing two resonance hybrid structures (**Figure 31.8(a)**). One structure has a single bond between the carbonyl carbon and nitrogen, whereas the other has a carbon-nitrogen double bond. The overall structure is neither of these, but a hybrid containing a significant amount of carbon-nitrogen double-bond character. It is this double-bond character that makes the six

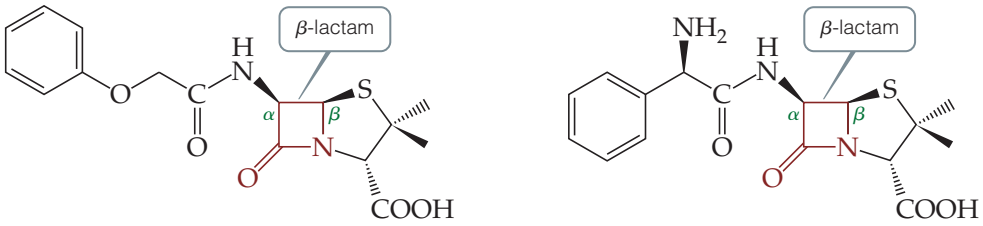


◀ **Figure 31.7 The geometry of the amide bond.** Bond angles of approximately 120° are seen about the amide nitrogen. This trigonal-planar geometry is coplanar with the amide carbonyl group.



◀ **Figure 31.8 Conformation and rationalization.** (a) The planar nature of the amide bond can be rationalized by resonance delocalization. (b) Amides can exist as *cis* or *trans* conformers known as rotamers because there is limited rotation about the C—N bond. The *trans* conformer is favoured because it reduces any steric strain caused by substituents.

▶ **Figure 31.9 Structure of penicillins.** Penicillin V and amoxicillin are two examples of lactams.



penicillin V amoxicillin

atoms about the amide bond planar. As a result of the restricted rotation about the C—N bond, two conformations are possible for the amide bond, *cis* and *trans* (Figure 31.8(b)). The *trans* isomer is favoured because it reduces any steric strain imposed by substituents on either side of the amide bond.

Cyclic amides are called **lactams**. We do not deal with these in any detail except to say that a very potent form of antibiotic, the **penicillins**, all contain a four-membered lactam ring, known as a β-lactam, fused to a five-membered ring containing sulfur (**Figure 31.9**).

Self-Assessment Exercises

31.1 What is the correct name of the following amine?



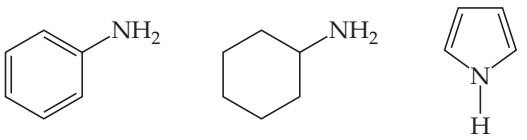
(a) *N*-methyl-*N*-ethyl-1-butanamine
(b) *N*-ethyl-*N*-methyl-1-butanamine
(c) *N*-methyl-3-hexanamine

31.2 What is/are the best reagent(s) to perform the following conversion?



(a) H_2/Pd catalyst
(b) $SnCl_2$/aq HCl
(c) i) $SnCl_2$/aq HCl ii) aq NaOH

31.3 Rank the following amines from the most basic to the least basic.



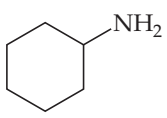
aniline cyclohexylamine pyrrole

(a) aniline > cyclohexylamine > pyrrole
(b) cyclohexylamine > aniline > pyrrole
(c) cyclohexylamine > pyrrole > aniline
(d) pyrrole > aniline > cyclohexylamine

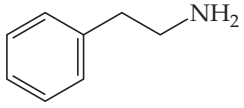
Exercises

31.4 Give names for the following amines:

(a)

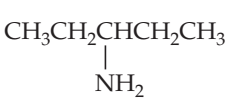


(b)

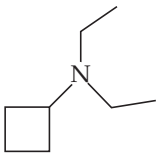


(c) $CH_3CH_2NHCH_3$

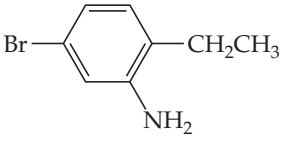
(d)



(e)



(f)

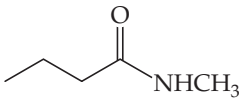


31.5 Provide a structural formula for each of the following compounds:

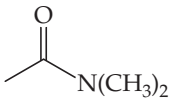
(a) 4-nitropyridine
(b) benzylamine
(c) *N,N*-dimethylpropylamine
(d) 2,4-diaminobenzoic acid
(e) 2-ethyl-1-butanamine

31.6 Give names for the following amides:

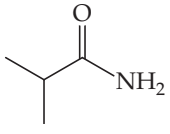
(a)



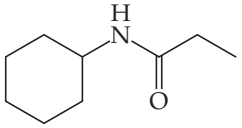
(b)



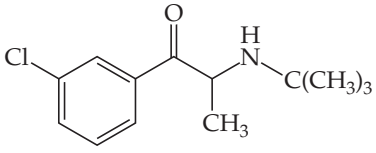
(c)



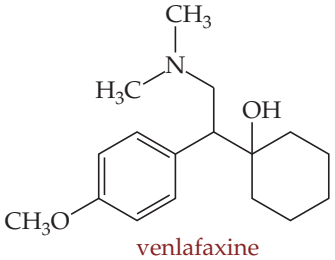
(d)



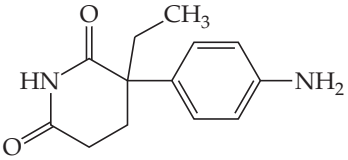
31.7 *Bupropion* is an antidepressant drug also used to treat attention-deficit hyperactivity disorders. *Venlafaxine* (sold under the brand name Effexor®) is an antidepressant drug. *Aminoglutethimide* has been used as an anticonvulsant. Classify bupropion, venlafaxine and aminoglutethimide as primary, secondary or tertiary amines.



bupropion



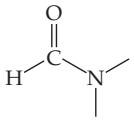
venlafaxine



aminoglutethimide

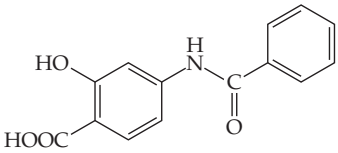
31.8 Define the following amides as primary, secondary or tertiary:

(a)



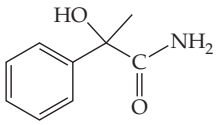
N,N-dimethylformamide
(solvent for organic synthesis)

(b)



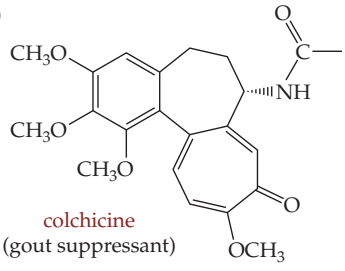
benzoylpas
(an antibacterial)

(c)



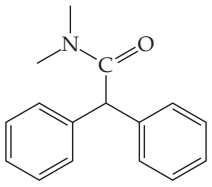
atrolactamide
(an anticonvulsant)

(d)



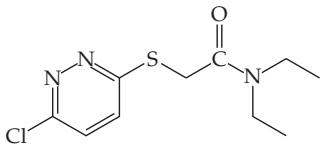
colchicine
(gout suppressant)

(e)



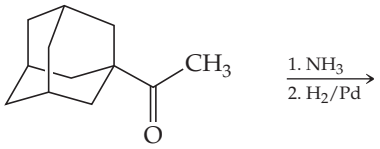
dipenamide
(a herbicide)

(f)

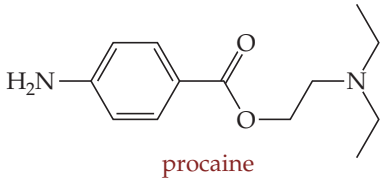


azintamide
(a choleretic)

31.9 *Rimantadine* is effective in preventing infections caused by the influenza A virus. It can be formed from the ketone and the reagents shown. Suggest a structure for rimantadine consistent with the reaction conditions. [*Hint:* The reaction is undertaken in two steps.]



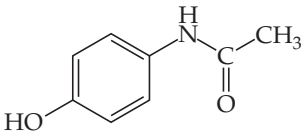
31.10 *Procaine* was one of the first local anaesthetics used. Its hydrochloride salt is marketed as *Novocaine*®.



procaine

(a) Draw the product of the reaction of procaine with 1 mole equivalent of HCl. **(b)** Suggest a synthesis for procaine starting with 4-nitrobenzoic acid.

31.11 Devise a synthesis for *paracetamol* beginning with 4-nitrophenol.



paracetamol

Answers to Self-Assessment Exercises

31.1 (b) 31.2 (c) 31.3 (b)

31.2 Amino Acids



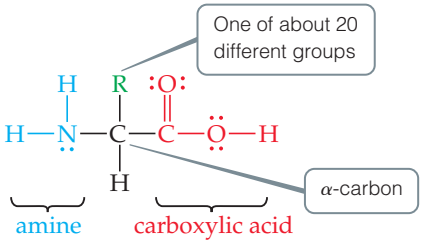
Phenylalanine is one of the two amino acids that make up the sweetener aspartame, an artificial sweetener sold under the trade names "Equal®" and "Nutrasweet®". Phenylalanine also happens to be one of the essential amino acids, which means that we must have it in our diets to survive long term. However, in about one out of 10,000 to 20,000 Caucasian or Asian births, the enzyme that converts phenylalanine to another amino acid, tyrosine, is completely or nearly completely absent because of a genetic defect. The result is that phenylalanine accumulates in the blood and in body tissues. The disease that results is called phenylketonuria (PKU), which causes intellectual disability and seizures. This is why cans of diet soft drink sometimes carry the warning "Phenylketonurics: contains phenylalanine". Newborns are routinely tested for PKU when they are about three days old.

Although biological systems are unimaginably complex, they are nevertheless constructed of molecules of quite modest size. The example here illustrates that, in order to understand biology, we need to understand the chemical behavior of molecules with low molar mass, as well as much larger molecules, which form the basis of *biological chemistry*.

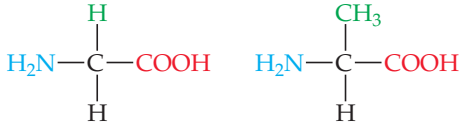
By the end of this section, you should be able to:

- understand the acid-base properties of an amino acid
- know how an amino acid can be made in the laboratory

Amino acids contain both an amino group and a carboxyl group. An **α-amino acid** is an amino acid in which the amino group is bonded to the carbon adjacent to the carboxyl group. α-Amino acids play a large role in biological chemistry as the building blocks of protein, and their properties are dictated somewhat by the nature of the R group.



In *glycine*, which is the simplest amino acid, R is a hydrogen atom; in *alanine*, R is a methyl group.



Because amino acids contain a carboxyl group, they can serve as weak acids. They also contain the NH_2 group, characteristic of amines, and thus they can also act as weak bases.

Amino acids, therefore, are **amphiprotic**. For glycine, we might expect that the acid and the base reactions with water would be as follows:

Acid:

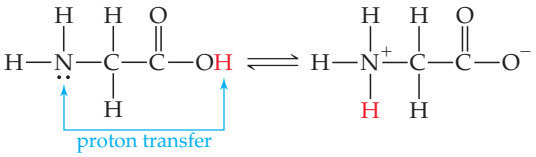
$$H_2NCH_2COOH(aq) + H_2O(l) \rightleftharpoons H_2NCH_2COO^-(aq) + H_3O^+(aq) \quad [31.16]$$

Base:

$$H_2NCH_2COOH(aq) + H_2O(l) \rightleftharpoons {}^+H_3NCH_2COOH(aq) + OH^-(aq) \quad [31.17]$$

The pH of a solution of glycine in water is about 6.0, indicating that it is a slightly stronger acid than a base.

The acid–base chemistry of amino acids is somewhat more complicated than shown in Equations 31.16 and 31.17, however. As a result of the fact that the COOH group can act as an acid and the NH_2 group can act as a base, amino acids undergo a "self-contained" Brønsted–Lowry acid–base reaction in which the proton of the carboxyl group is transferred to the basic nitrogen atom:



[31.18]

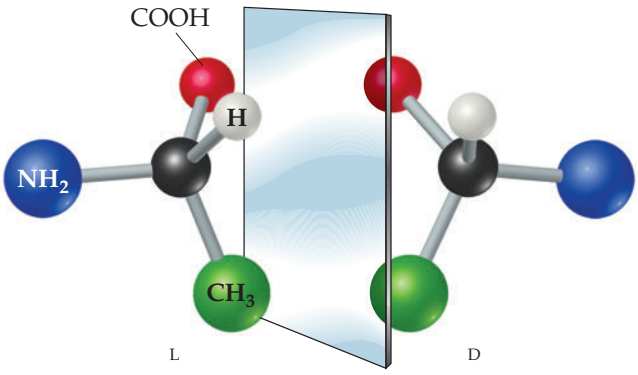
neutral molecule zwitterion

Although the form of the amino acid on the right side of Equation 31.18 is electrically neutral overall, it has a positively charged end and a negatively charged end. A molecule of this type is called a **zwitterion** (German for "hybrid ion"). This doubly ionized form predominates at near-neutral values of pH. Amino acids are more properly written as the zwitterion because of this fact, although there are many instances in science (not necessarily chemistry) where the un-ionized form (left side of Equation 31.18) is commonly written.

Do amino acids exhibit any properties indicating that they behave as zwitterions? If so, they should behave in a similar manner to ionic substances. Crystalline amino acids (**Figure 31.10**) have relatively high melting points, usually above 200 °C, which is characteristic of ionic solids. Amino acids are far more soluble in water than in non-polar solvents. In addition, the dipole moments of amino acids are large, consistent with a large separation of charge in the molecule. Thus the ability of amino acids to act simultaneously as acids and bases has important effects on their properties.

With the exception of glycine, all naturally occurring amino acids have at least one stereocenter, the α-carbon. **Figure 31.11** shows the two enantiomers of the amino acid alanine. For historical reasons, the two enantiomers are distinguished by the labels D and L. All amino acids normally found in proteins have the L configuration at the stereocenter (except for glycine, which is not chiral). In terms of absolute stereochemistry, all naturally occurring α-amino acids have the *S* configuration (Section 25.3). This means that the enantiomer or D-amino acid has R configuration.

Figure 31.12 shows the structural formulas of the 20 most common α-amino acids found in proteins. Our bodies can synthesize 10 of these α-amino acids in sufficient

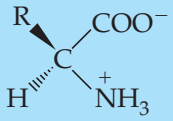


▲ **Figure 31.10 Lysine.** One of the amino acids found in proteins, lysine is available as a dietary supplement. The L in the name L-Lysine refers to a specific configuration of atoms that is found in naturally occurring amino acids.

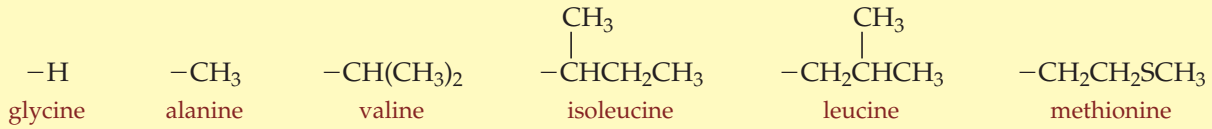
Go Figure Are all α-amino acids chiral?

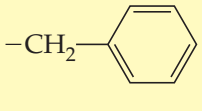
▲ **Figure 31.11 Alanine enantiomers.** The middle carbon of alanine is stereogenic, and therefore there are two enantiomers, which by definition are non-superimposable mirror images of each other.

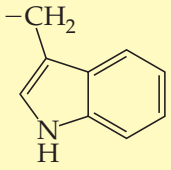
L-amino acid general structure

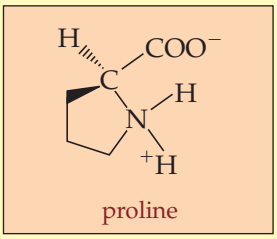


Non-polar side chains (R=)

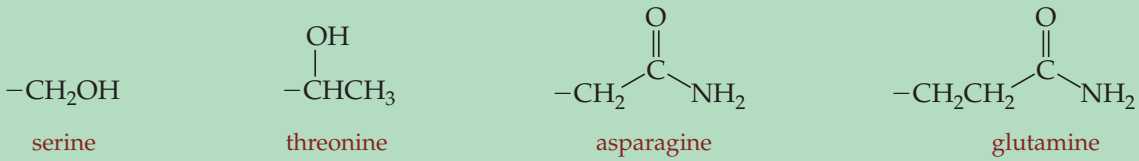




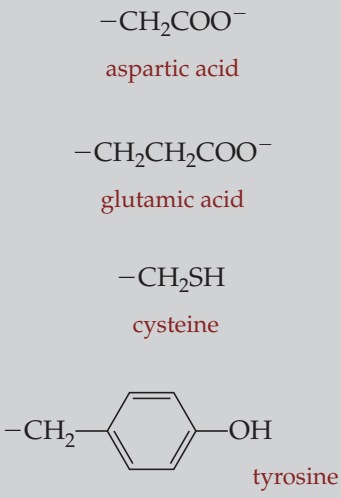




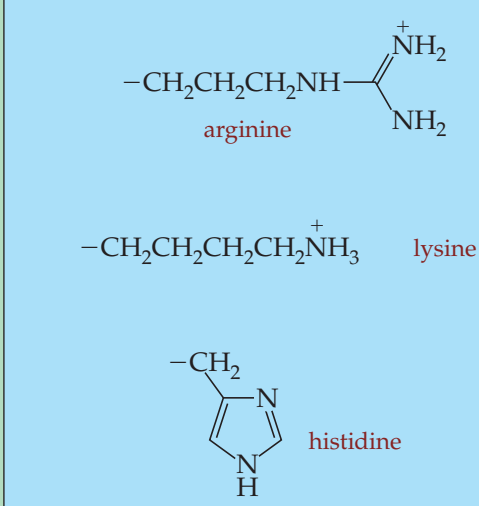
Polar side chains (R=)



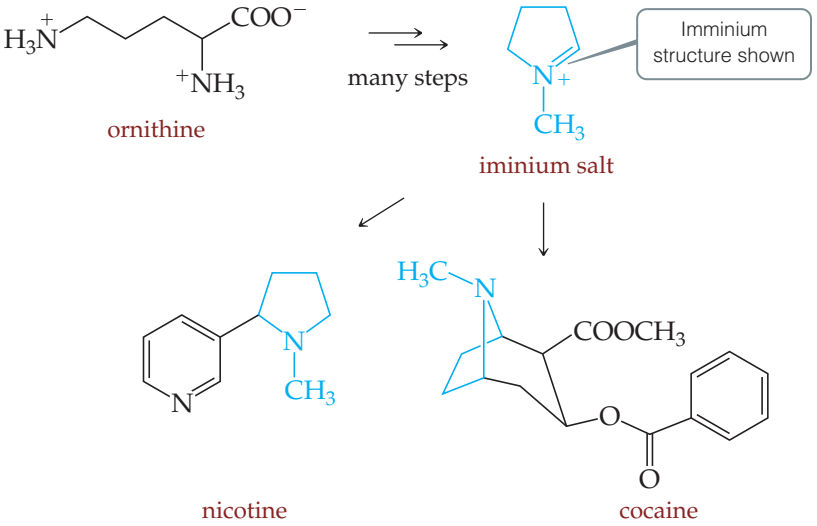
Acidic side chains (R=)



Basic side chains (R=)



▲ **Figure 31.12 The 20 common α-amino acids found in the human body.** Each ionizable group within the acidic and basic classes is shown in the form present in highest concentration at pH = 7.0.



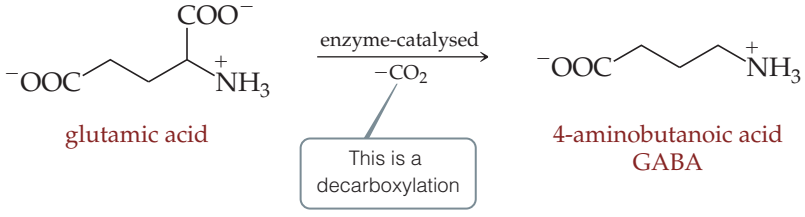
◀ **Figure 31.13 Ornithine.** This amino acid is a relative of lysine but with a shorter side chain.

amounts for our needs. The other 10 must be ingested and are called *essential amino acids* because they are necessary components of our diet.

α-Amino acids, which make up the 20 most common naturally occurring amino acids, can be classified by the nature of their **side chain**, which is bonded to the amino acid's α-carbon. These side chains are used to classify amino acids as polar and non-polar. The polar amino acids can be further classified as ionized (for example, containing acidic and basic side chains) and un-ionized (that is, neutral-polar side chains). Proline is a cyclic amino acid, which differs from the acyclic nature of the other 19 amino acids.

Although all amino acids are chiral, with the exception of glycine, isoleucine and threonine also contain a second stereocenter. Four stereoisomers are possible, but only *one* of the four stereoisomers is found in proteins.

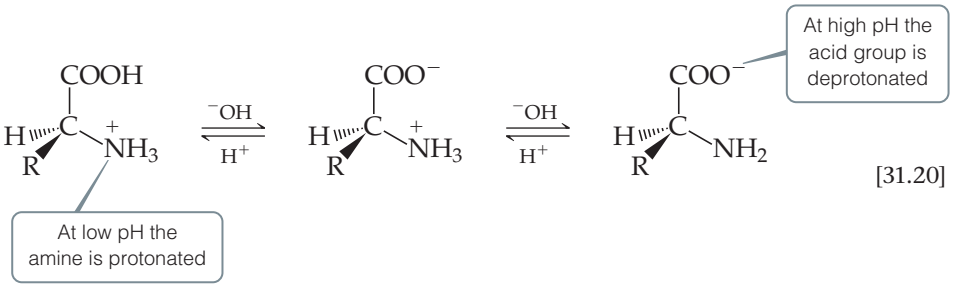
Two amino acids not listed in Figure 31.12 deserve special mention because of their social and medicinal importance. Ornithine is an amino acid found in the liver, with importance in the urea cycle. It is also a precursor for the biosynthesis of nicotine and tropane alkaloids such as cocaine (**Figure 31.13**). GABA (γ-aminobutyric acid) is a neurotransmitter (a substance that transmits nerve impulses across a synapse), found exclusively in the brain and central nervous system (CNS). It has been implicated in several neurodegenerative conditions, including memory loss. GABA is formed within the CNS by the enzyme-catalyzed decarboxylation of glutamic acid. Its systematic name, 4-aminobutanoic acid, is less commonly used than its acronym, GABA.



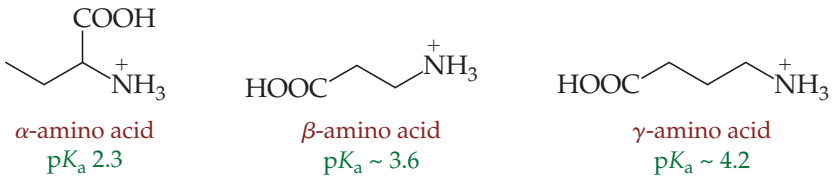
[31.19]

Acid–Base Properties

The amphiprotic nature of α-amino acids can be described by the following equation:



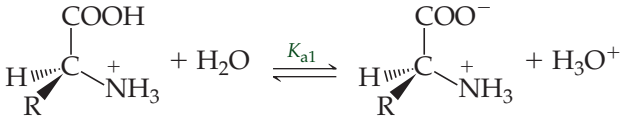
[31.20]



▶ **Figure 31.14 Carboxyl group acidity.** The inductive effect of the ammonium ion changes the pK_a of the COOH of amino acids. The effect of the ammonium group is connectivity dependent and approaches that of a normal carboxylic acid as the number of intervening bonds increase.

At low pH the basic amino group is protonated, forming the ammonium ion. In neutral solution the zwitterion is formed. The pH at which the zwitterion concentration is the highest is called the **isoelectric point**. In basic solution, the carboxylic acid group is ionized to form the carboxylate group. Notice that amino acids are ionic at all pHs, which makes them highly water soluble and difficult to purify by the normal procedures used in organic chemistry.

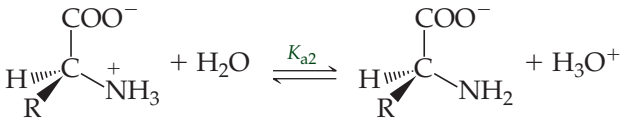
Consider the following reaction:



[31.21]

The average pK_a value (pK_{a1}) for the carboxyl group of an α-amino acid is ~2. This value is considerably lower than that for acetic acid (pK_a = 4.76), which implies that α-amino acids are stronger acids than acetic acid. The reason for this difference in pK_a can be attributed to the inductive electron-withdrawing effect of the ammonium group, which draws electron density out of the O—H bond, making it weaker relative to the same bond in acetic acid. **Figure 31.14** shows how this inductive effect weakens as the number of intervening bonds increases.

The ammonium group of an α-amino acid is a stronger acid than a comparable aliphatic ammonium ion due to the weak inductive effect of the carboxyl group. The average pK_a for an α-amino acid (pK_{a2}) is ~9.5, compared with pK_a ~10.5 for an aliphatic amine. This implies that the amine of an α-amino acid is generally a weaker base than a 1° aliphatic amine.

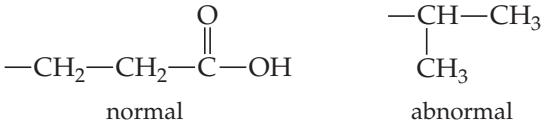


[31.22]

A CLOSER LOOK Sickle-Cell Anemia

Our blood contains a complex protein called hemoglobin, which carries oxygen from the lungs to other parts of the body. In the genetic disease known as sickle-cell anemia, hemoglobin molecules are abnormal and have a lower solubility, especially in their unoxygenated form. Consequently, as much as 85% of the hemoglobin in red blood cells crystallizes from solution.

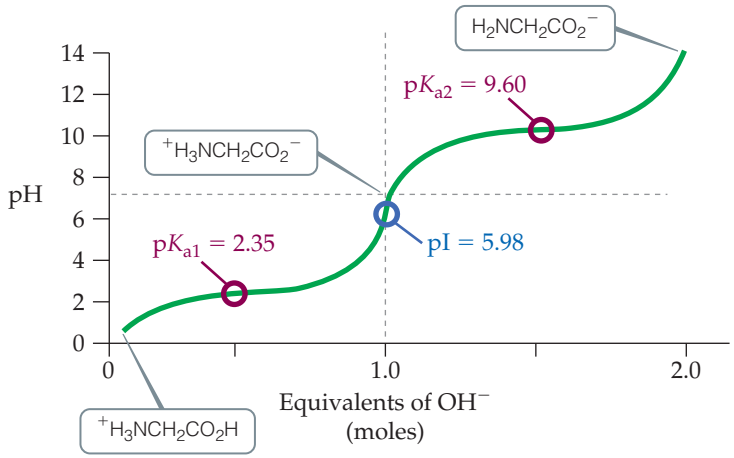
The reason for the insolubility of hemoglobin in sickle-cell anemia can be traced to a structural change in one part of an amino acid side chain. Normal hemoglobin molecules contain glutamic acid, which contributes to the solubility of the hemoglobin molecule in water. In the hemoglobin molecules of people suffering from sickle-cell anemia, the glutamic acid residue is replaced by valine:



Valine is non-polar (hydrophobic), and its presence leads to the aggregation of the defective form of hemoglobin into particles too large to remain suspended in biological fluids. It also causes the cells to distort into a sickle shape, as shown in **Figure 31.15**. The sickled cells tend to clog the capillaries, causing severe pain, physical weakness and gradual deterioration of the vital organs. The disease is hereditary and, if both parents carry the defective genes, it is likely that their children will possess only abnormal hemoglobin.



▲ **Figure 31.15 Normal and sickled red blood cells.** Normal red blood cells are about 1 μm in diameter.



◀ **Figure 31.16 Titration of glycine with aqueous NaOH solution.** pK_{a1} relates to the pK_a of the carboxylic acid, while pK_{a2} relates to the pK_a of the ammonium ion.

Let us now investigate what the pK_a value of an α-amino acid means and what information it provides. To do this, we need to consider the pH titration of a simple amino acid, such as glycine, with aqueous sodium hydroxide solution (**Figure 31.16**).

At low pH, glycine is in its fully protonated form, $^+H_3NCH_2CO_2H$. The addition of OH^- sees a gradual rise in pH until a plateau is reached (also described as a *point of inflexion* on the titration curve). At this point, which corresponds to the addition of 0.5 mol of OH^-, the pH = pK_{a1}. This is the point at which the concentration of the zwitterion equals that of the ammonium ion:

$$\text{when pH} = pK_{a1},\ [^+H_3NCH_2CO_2H] = [^+H_3NCH_2CO_2^-]$$

A pH value *lower* than pK_{a1} means that the ammonium ion predominates. A pH value *higher* than pK_{a1} means the zwitterion predominates in solution.

The endpoint of this first reaction is reached when 1 mole equivalent of OH^- is added. This point, known as the *isoelectric point*, is where the zwitterion $^+H_3NCH_2CO_2^-$ is at its maximum concentration. At the isoelectric point, pI, the amino acid has no net charge. The pI of an amino acid usually lies at the midpoint of pK_{a1} and pK_{a2}. We can represent this mathematically by:

$$\text{pI} = \tfrac{1}{2}(pK_{a1} + pK_{a2}) \qquad [31.23]$$

$$\text{for glycine,} \qquad \text{pI} = \tfrac{1}{2}(2.35 + 9.60) = 5.98$$

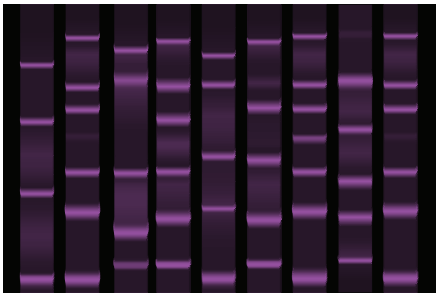
The addition of another 0.5 molar equivalents of OH^- causes the pH to rise, then plateau. This point of inflexion indicates pK_{a2}, the pK_a value associated with the ammonium group. This is the point at which the concentration of the zwitterion equals that of the carboxylate ion:

$$\text{when pH} = pK_{a2},\ [^+H_3NCH_2CO_2^-] = [H_2NCH_2CO_2^-]$$

A value of pH *lower* than pK_{a2} means that the zwitterion ion predominates. A value for the pH *higher* than pK_{a2} means that the amine and carboxylate groups predominate in solution.

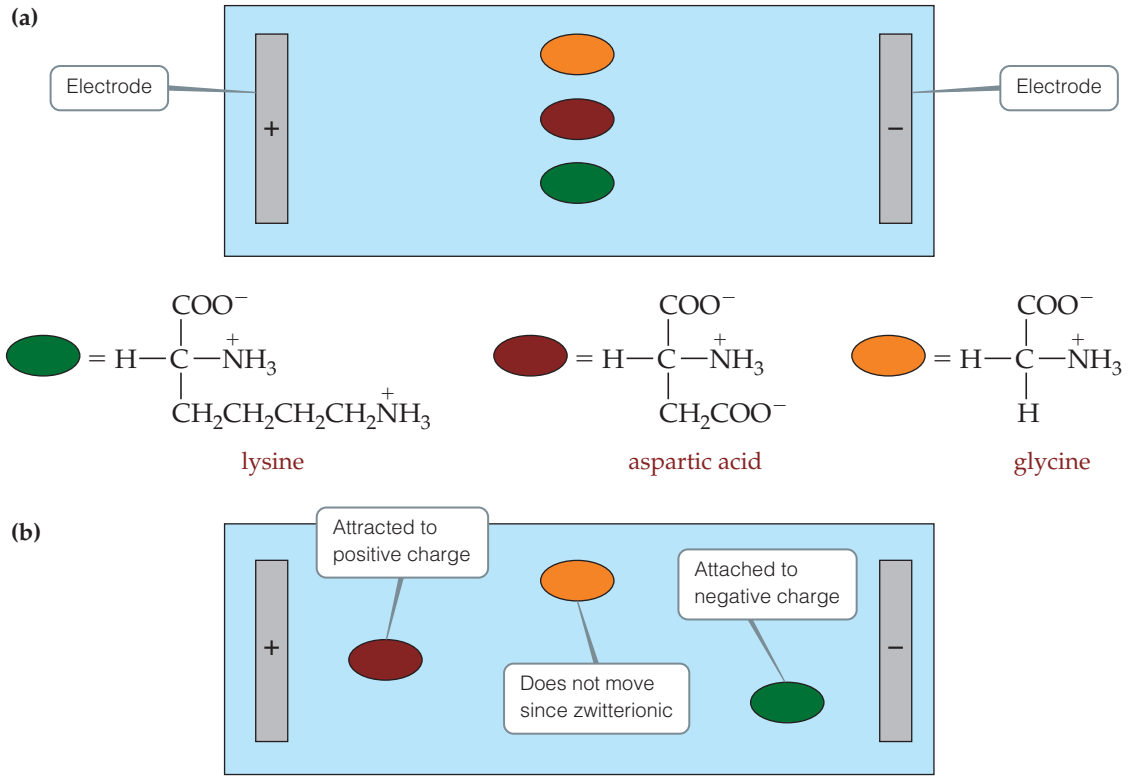
The net charge of an amino acid is easily estimated using the pI value. As pH values fall below pI, the amino acid exists more and more as the ammonium ion, which is positively charged. At pH values higher than the pI, the amino acid exists as the carboxylate ion, which is negatively charged.

Knowledge about the pI of an amino acid is also useful for purification by **electrophoresis**, a process used to separate molecules based on charge (**Figure 31.17**). This useful technique uses either paper or gel as a separating medium and electric charge to separate amino acids, proteins and other charged molecules (**Figure 31.18**). You will learn more about this technique in courses devoted to biochemistry and cellular biology, where the separation of amino acids (and proteins) by this technique is a fundamental tool in the laboratory.



▲ **Figure 31.17 A typical electrophoresis result.** The bands highlighted under UV light represent different amino acids, peptides or proteins that have been separated in a gel matrix. Each species can be isolated and then identified.

Go Figure How would tyrosine, pI = 5.66, act at pH 5.66 in electrophoresis? Would this change at pH 9?



▲ **Figure 31.18 Separation of amino acids by electrophoresis.** By running an electrophoresis experiment at pH 5.98, we can separate three amino acids, based on their pI values. At pH 5.98, glycine has no net overall charge because of its zwitterionic state. Aspartic acid (pI 2.77) is deprotonated at pH 5.98 and is attracted to the positive electrode. Lysine (pI 9.74) is protonated at pH 5.98 and is attracted to the negative electrode. (a) At time = 0, (b) at time > 0.

Sample Exercise 31.5

Acid–Base Properties of Amino Acids

Draw structural formulas for the predominant form of glycine (pK_a 2.35, 9.60) in aqueous solution at pH 1, 6 and 12.

SOLUTION

Analyze We are asked to draw the form of an amino acid at a given pH knowing the pK_a.

Plan When working through a problem like this, it is important to identify the relationship between the pH and the closest pK_a value.

Solve At pH 1, glycine is predominantly in the fully protonated form:

$$^{+}H_3NCH_2CO_2H$$

The reason is that pH < pK_{a1}.

pH 6 is between the two given pK_a values, so the zwitterion is the major form:

$$^{+}H_3NCH_2CO_2^{-}$$

At pH 12, the carboxylate form predominates:

$$H_2NCH_2CO_2^{-}$$

The reason is that pH > pK_{a2}.

To verify the answer to this problem, you could use Figure 31.16.

Practice Exercise

Draw structural formulas for the predominant forms of serine (pK_a 2.21, 9.15) in aqueous solution at pH 2, 7 and 10.

We can predict which species predominates at a certain pH in a much more quantitative way. For example, the equation for the acid-dissociation constant K_{a1}, shown in Equation 31.21, can be written as follows:

$$K_{a1} = \frac{[H_3O^+][R'-CO_2^-]}{[R'-COOH]} \qquad [31.24]$$

$$\text{where } R' = RCH\overset{+}{N}H_3$$

Rearrangement gives

$$\frac{K_{a1}}{[H_3O^+]} = \frac{[R'-CO_2^-]}{[R'-COOH]} \qquad [31.25]$$

Knowing the value of pK_{a1} and the pH of the solution (which determines the value of $[H_3O^+]$), we can calculate the exact ratio of the fully protonated and zwitterion forms at values between pH = 0 and the pI, as well as the net charge on the α-carboxyl group at that pH.

In a similar way, the equation for the acid-dissociation constant K_{a2}, shown in Equation 31.22, can be written as follows:

$$K_{a2} = \frac{[H_3O^+][R'-NH_2]}{[R'-NH_3^+]} \qquad [31.26]$$

$$\text{where } R' = RCHCO_2^-$$

Rearrangement gives

$$\frac{K_{a2}}{[H_3O^+]} = \frac{[R'-NH_2]}{[R'-NH_3^+]} \qquad [31.27]$$

Knowing the value of pK_{a2} and the pH of the solution, we can calculate the exact ratio of the amine and zwitterion forms at values between pI and pH = 14, as well as the net charge on the α-amino group at that pH.

These calculations are similar to those used for buffer solutions using the Henderson–Hasselbalch equation for weak acid/conjugate base pairs:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \qquad [31.28]$$

Sample Exercise 31.6

Estimating Net Charge

Let's reconsider the question posed in Practice Exercise 31.5. Estimate the net charge on serine at pH = 2.

SOLUTION

Analyze We are asked to determine the percentage of each species in solution to determine the net charge at a given pH.

Plan Use the Henderson–Hasselbalch equation to determine the ratio of acid to conjugate base, hence the percentage of each in solution.

Solve Using Equation 31.28 and substituting in values:

$$pH = 2 \text{ and } pK_a = 2.21$$

gives

$$2 = 2.21 + \log \frac{[R'CO_2^-]}{[R'CO_2H]}$$

$$\frac{[R'CO_2^-]}{[R'CO_2H]} = 0.62$$

Continued

This ratio concludes that the amino acid exists as 38% $R'CO_2^-$ and can be calculated using:

$$\frac{x}{100-x} = 0.62$$

where x = the percentage of $R'CO_2^-$

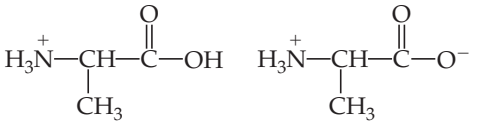
A similar calculation for the amino group gives

$$2 = 9.15 + \log \frac{[R'NH_2]}{[R'NH_3^+]}$$

$$\frac{[R'NH_2]}{[R'NH_3^+]} = 7.1 \times 10^{-8}$$

which indicates that the amino group is > 99.9% protonated at pH 2.

The average charge of the amino acid in solution can be calculated from the contributions of each charged species at pH 2. That is, at pH 2 the following two species exist:



62% 38%

Their respective charges are +1 and 0.

Therefore, based on their relative proportions in solution,

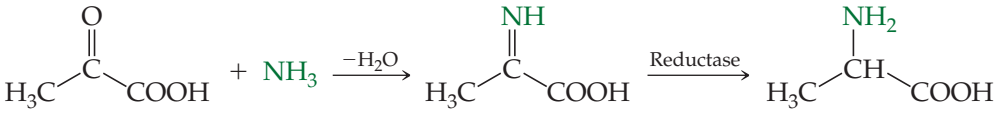
$$\text{Average charge} = 0.62 \times 1.0 + 0.38 \times 0 = +0.62$$

Practice Exercise

Estimate the net charge on serine at pH = 7 and pH = 10.

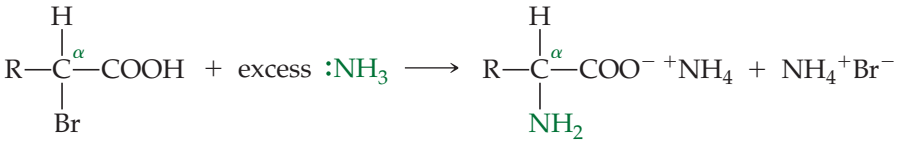
Reactions Involving Amino Acids

There are several biological pathways for synthesising amino acids. For example, the bacterium *Bacillus subtilis* synthesizes alanine from pyruvic acid in the following way:



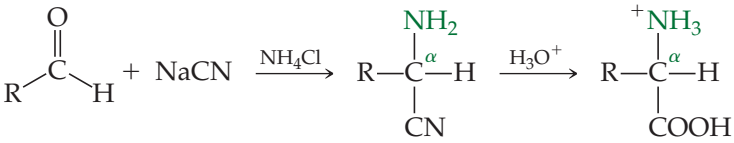
pyruvic acid an imine alanine [31.29]

In a laboratory, there are two main ways of synthesising α-amino acids. The first method involves nucleophilic substitution of an α-halo carboxylic acid with ammonia:



α-halo carboxylic acid α-amino acid salt [31.30]

The second method is called **Strecker synthesis** of α-amino acids. This three-step reaction converts aldehydes to α-amino acids in the presence of cyanide ion.

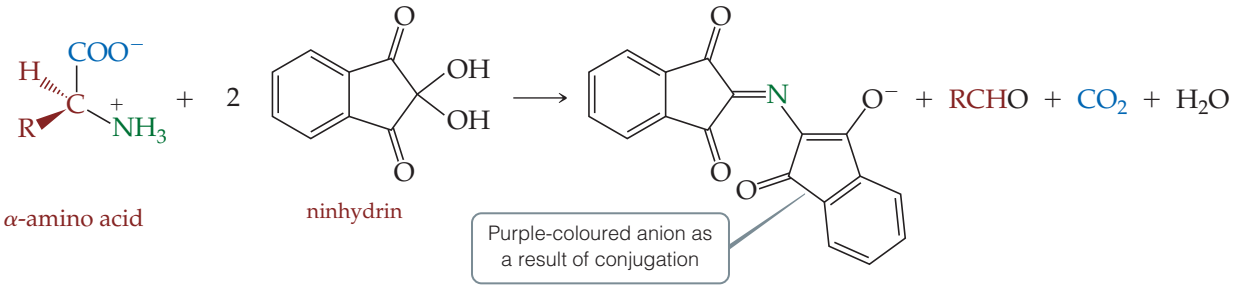


aldehyde amino nitrile α-amino acid [31.31]

Treatment of the aldehyde with cyanide ion in the presence of ammonium chloride yields the intermediate amino nitrile. This reaction is twofold: reaction of the aldehyde with ammonium chloride yields an imine, which undergoes addition of the cyanide ion to form the amino nitrile; the nitrile group is then hydrolyzed to the carboxylic acid in the presence of aqueous acid.

The methods described in Equations 31.30 and 31.31 are not ideal because the products are typically formed as racemates, which need to be separated to form the enantiomerically pure compounds. In some instances, separation is easily achieved by chiral resolution techniques. In other cases, more complicated and expensive techniques are required.

Since most amino acids are neither colored nor fluorescent, their detection requires the use of a dye. The most common dye used, called ninhydrin, reacts specifically with α-amino acids to produce a purple-colored anion, an aldehyde, CO_2 and water.



[31.32]

The fact that a purple-colored solution is formed from colorless starting materials is important for the use of ninhydrin in quantifying the amount of α-amino acid present in a sample using absorption spectroscopy at 580 nm. Note that only α-amino acids containing a primary amino group react to form the purple-colored anion. Proline, which has a secondary amino group, does not react in the same way.

Self-Assessment Exercises

31.12 Methionine has pK_a values of 2.28 and 9.21. At what pH do you get the maximum concentration of the zwitterionic form of methionine?

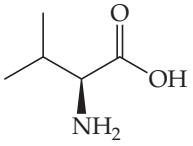
(a) 2.28

(b) 5.75

(c) 7.00

(d) 9.21

31.13 In the Strecker synthesis of valine, what is the starting aldehyde?



valine

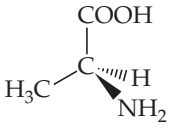
(a) 3-methylbutanoic acid

(b) 3-methylbutanal

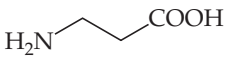
(c) methylpropanal

Exercises

31.14 Describe the relationship between β-alanine and L-α-alanine.



L-α-alanine



β-alanine

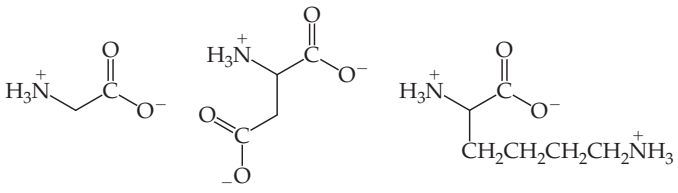
31.15 Alanine can exist in water in several ionic forms. **(a)** Suggest the form of alanine at low pH and at high pH. **(b)** Amino acids are reported to have two pK_a values, one in the range of 2 to 3 and the other in the range of 9 to 10. Alanine, for example, has pK_a values of about 2.3 and 9.6. Suggest the origin of the two pK_a values.

31.16 Glutamic acid has pK_a values of 2.19, 4.25 and 9.67. **(a)** What would be the predominant species in solution at pH 2? **(b)** What would be the predominant species in solution at pH 8? **(c)** Estimate the isoelectric point, pI, for glutamic acid.

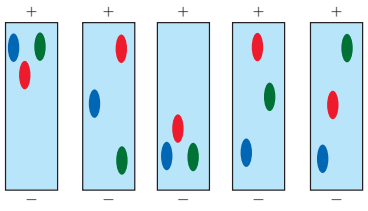
31.17 Using Equation 31.28, estimate the average charge on glutamine **(a)** at pH 3, **(b)** at pH 7. Glutamine has pK_a values of 2.17 and 9.13.

31.18 Why is the average pK_a value (pK_{a1}) for the carboxyl group of an α-amino acid ~2 when that for acetic acid is about 4.8?

31.19 Which of the following electrophoresis results could represent the separation of the following three compounds if a mixture is applied to the center of the strip? Explain.



amino acid A amino acid B amino acid C

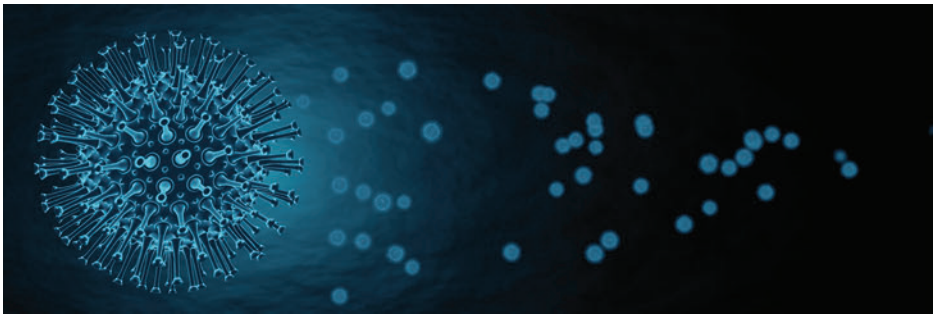


31.20 Outline a synthesis of phenylalanine **(a)** from 2-bromo-3-phenylpropanoic acid and **(b)** by the Strecker synthesis from 2-phenylethanal.

Answers to Self-Assessment Exercises

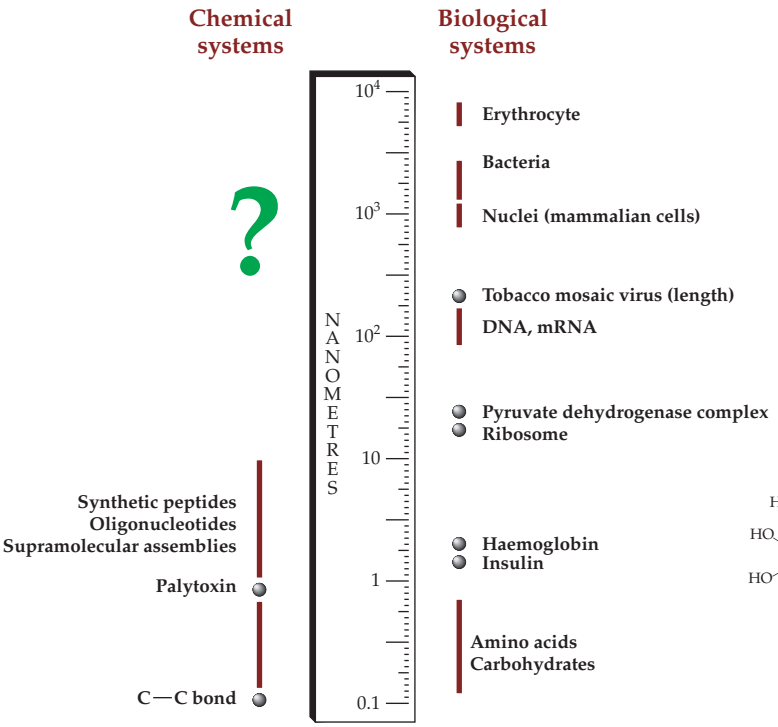
31.12 (b) 31.13 (c)

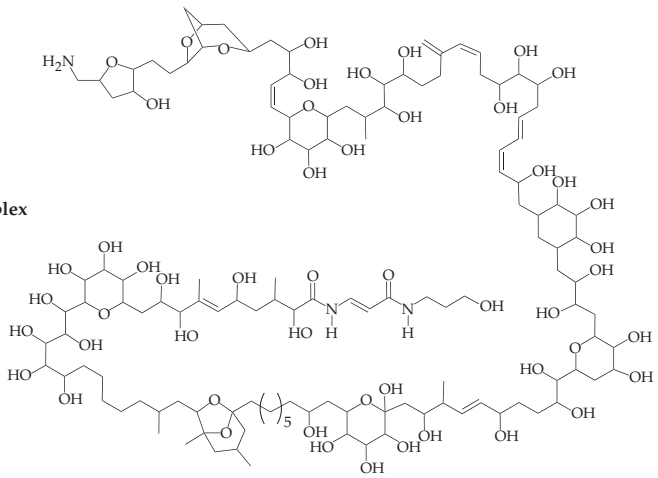
31.3 | Proteins, Peptides, and Enzymes



Research at the interface of chemistry and biology, termed *biological chemistry*, is an exciting and dynamic area for scientists in both disciplines. Biological chemists apply the principles of chemistry to understand the molecular basis of biological processes relevant to medicine, biotechnology, and other life sciences, such as structural biology, biochemistry, genetics, pharmacology, and physiology. They then apply this knowledge to new chemical transformations, in materials science, or in the area of medicinal chemistry. This differs from the area of science known as *biochemistry*, which aims to understand life in terms of its processes and reactions, but not necessarily on a molecular scale. In the next two sections, we present a brief overview of some of the elementary aspects of biological chemistry—proteins, vitamins, and nucleic acids—from a molecular point of view and discuss the importance of nitrogen in each case.

Many biologically important molecules are very large. Nevertheless, they may be understood by first breaking them down into their component parts, each containing the functional groups that we have studied in the last five chapters. The synthesis of large molecules is remarkable and one that places large demands on the chemical systems in





Palytoxin

living organisms. Organisms build complex biomolecules (as, for example, in the coronavirus disease COVID-19) from much smaller and simpler substances that are readily available in the biosphere. The synthesis of large molecules requires energy because most of the reactions required are endothermic and also represent a decrease in entropy as a random mix of raw materials is assembled into an ordered structure. The ultimate source of this energy is the sun. Mammals and other animals have no capacity for using solar energy directly; rather, they depend on plant photosynthesis to supply the bulk of their energy needs.

By the end of this section, you should be able to:

- Understand the components of protein structure
- Know how a protein sequence may be determined

We have introduced some important biochemical applications of fundamental chemical ideas in the Chemistry and Life boxes that appear throughout this text. Hydrogen bonding, for example, is critical to the function of many biological systems. The geometry of, and functional groups within, molecules can govern their biological activity. Many of the large molecules in living systems are polymers of much smaller molecules. These polymers, called *biopolymers*, can be classified into three broad categories: proteins, polysaccharides (carbohydrates) and nucleic acids.

Proteins are macromolecular substances present in all living cells and viruses. About 50% of your body's dry weight is protein. Proteins serve as the major structural components in animal tissues; they are a key part of skin, nails, cartilage and muscles. Other proteins catalyze reactions, transport oxygen, serve as hormones to regulate specific body processes and perform other tasks. Whatever their function, all proteins are chemically similar, being composed of the same basic building blocks—amino acids.

Proteins can be classified in two ways, as simple or conjugated proteins or as globular and fibrous proteins. **Simple proteins** are those that yield only amino acids upon hydrolysis; for example, blood serum albumin. **Conjugated proteins** yield other compounds, such as carbohydrates, lipids or metal complexes, as well as amino acids on hydrolysis. Examples include myoglobin and ferrichrome. In fact, conjugated proteins are more common in the body than simple proteins. **Globular proteins** are tightly bundled proteins that are named because of their globular or spherical shape. These proteins, which include albumins, enzymes, immunoglobulins and insulin, are water soluble and typically mobile within cells. They have non-structural functions, such as combating the invasion of foreign objects, transporting and storing oxygen and acting as catalysts. **Fibrous proteins**, such as collagen and keratins, are arranged like filaments or fibers. In these substances the long coils align themselves in a more or less parallel fashion to form long, water insoluble fibers. Fibrous proteins provide structural integrity and strength to many kinds of tissue and are the main components of muscle, tendons and hair. **Table 31.1** summarizes some common protein classes and their functions.

Peptide is the name given to a short polymer (oligomer) of amino acids joined by *peptide amide bonds*. Peptides are classified by the number of amino acids in the chain. For example, a *dipeptide* is a molecule containing two amino acids joined by a peptide bond. A *tripeptide* is a molecule containing three amino acids joined by peptide bonds. **Polypeptides** are formed when many amino acids are linked together by peptide bonds. They are classed as *macromolecules* or *biopolymers*.

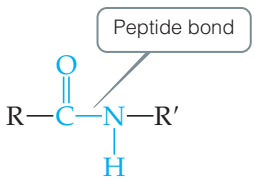
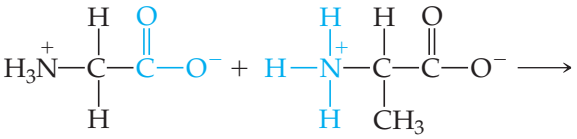


TABLE 31.1 Some common protein classes and their function

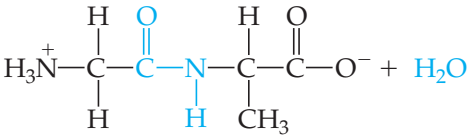
Name of class	Composition examples	Definition and functions
Glycoproteins	Contain carbohydrates, e.g. ovalbumin (egg white)	A ubiquitous family of proteins containing oligosaccharides (carbohydrates), which impart properties of solubility, ligand affinity, cellular targeting and stability. Many proteins released by cells to the blood and other fluids are glycoproteins. For example, Antarctic fish survive near-freezing water temperatures as a result of freezing-point depression of their blood serum by a globular glycoprotein.
Lipoproteins	Contain fats, oils or steroids (lipids), e.g. low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs)	Lipoproteins serve as carriers of hydrophobic ligands through solubility barriers such as aqueous body fluids. LDLs are the main transport for cholesterol through the body. HDLs carry excess cholesterol to the liver for processing.
Metalloproteins	Contain coordinated metal ions, e.g. hemoglobin, ferredoxin, NADH dehydrogenase, coenzyme Q, cytochrome c reductase	Metalloproteins are proteins that contain a metal cofactor. The metal may be an isolated ion or may be coordinated with a non-proteinaceous organic compound, such as the porphyrin found in hemoproteins. In some cases, the metal is coordinated with a side chain of the protein and an inorganic non-metallic ion.
Nucleoproteins	Contain nucleic acids, e.g. chromatin, RNA binding proteins, ribosomes	Nucleoproteins are any supramolecular complex of protein and nucleic acid; or any protein usually found closely associated with nucleic acid. They contain a diverse group of viral and genetic regulatory proteins which bind in a sequence-specific manner to DNA.
Phosphoproteins	Contain a phosphate group, e.g. synapsins, caesins (milk)	Phosphoproteins are any of a group of proteins containing chemically bound phosphoric acid. Protein phosphorylation is probably the most ubiquitous and diverse molecular mechanism of biological signaling and regulation.

Coding Peptides

A **peptide bond** is formed by a condensation reaction between the carboxyl group of one amino acid and the amino group of another amino acid. Alanine and glycine, for example, can react to form the dipeptide glycylalanine:



Glycine (Gly) Alanine (Ala)



[31.33]

Glycylalanine (Gly-Ala)

The amino acid that furnishes the carboxyl group for peptide bond formation is named first, with a *-yl* ending; then the amino acid furnishing the amino group is named second. To make the naming of peptides easier, especially those that are more than 25 amino acids long, series of three-letter and single-letter codes have been devised (**Table 31.2**). Based on the three-letter codes for the amino acids from Table 31.2, glycylalanine can be abbreviated Gly-Ala. In this notation it is understood that the unreacted amino group is on the left and the unreacted carboxyl group on the right. The artificial sweetener *aspartame* (**Figure 31.19**) is the methyl ester of the dipeptide of aspartic acid and phenylalanine, Asp-Phe:

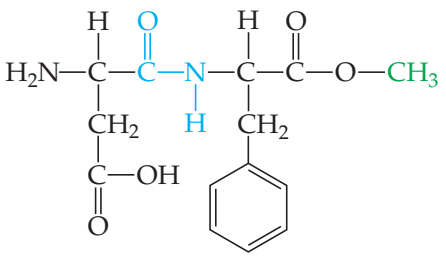


TABLE 31.2 Amino acid codes for proteins and peptides

Amino acid	Three-letter code	Single-letter code
Glycine	Gly	G
Alanine	Ala	A
Valine	Val	V
Leucine	Leu	L
Isoleucine	Ile	I
Methionine	Met	M
Phenylalanine	Phe	F
Tryptophan	Trp	W
Proline	Pro	P
Asparagine	Asn	N
Glutamine	Gln	Q
Serine	Ser	S
Threonine	Thr	T
Aspartic acid	Asp	D
Glutamic acid	Glu	E
Cysteine	Cys	C
Tyrosine	Tyr	Y
Arginine	Arg	R
Histidine	His	H
Lysine	Lys	K



▲ **Figure 31.19 Sweet stuff.** The artificial sweetener aspartame is the methyl ester of the dipeptide Asp-Phe.

Proteins are linear (that is, unbranched) polypeptide molecules with molecular weights ranging from about 5000 to over 50 million u. Proteins differ from polypeptides in that proteins are capable of some function, whether chemical or structural, as a result of their three-dimensional structure. Because 20 different amino acids are commonly linked together in proteins and because proteins consist of hundreds of amino acids, the number of possible arrangements of amino acids within proteins is virtually limitless.

Sample Exercise 31.7

Drawing the Structural Formula of a Tripeptide

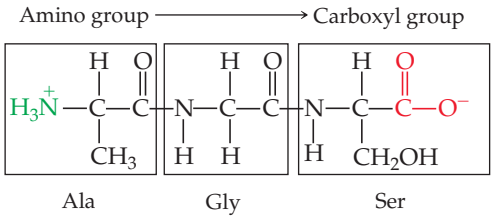
Draw the full structural formula for alanylglycylserine.

SOLUTION

Analyze We are asked to draw a tripeptide.

Plan The name of this substance suggests that three amino acids—alanine, glycine and serine—have been linked together, forming a *tripeptide*. Note that the ending *-yl* has been added to each amino acid except for the last one, serine. By convention, the first-named amino acid (alanine, in this case) has a free amino group and the lastnamed one (serine) has a free carboxyl group. Thus, we can construct the structural formula of the tripeptide from its amino acid building blocks.

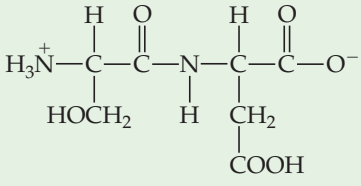
Solve We first combine the carboxyl group of alanine with the amino group of glycine to form a peptide bond and then the carboxyl group of glycine with the amino group of serine to form another peptide bond. The resulting tripeptide consists of three "building blocks" connected by peptide bonds:



We can abbreviate this tripeptide as Ala-Gly-Ser, or AGS.

Practice Exercise

Name the dipeptide that has the following structure and give its abbreviation:

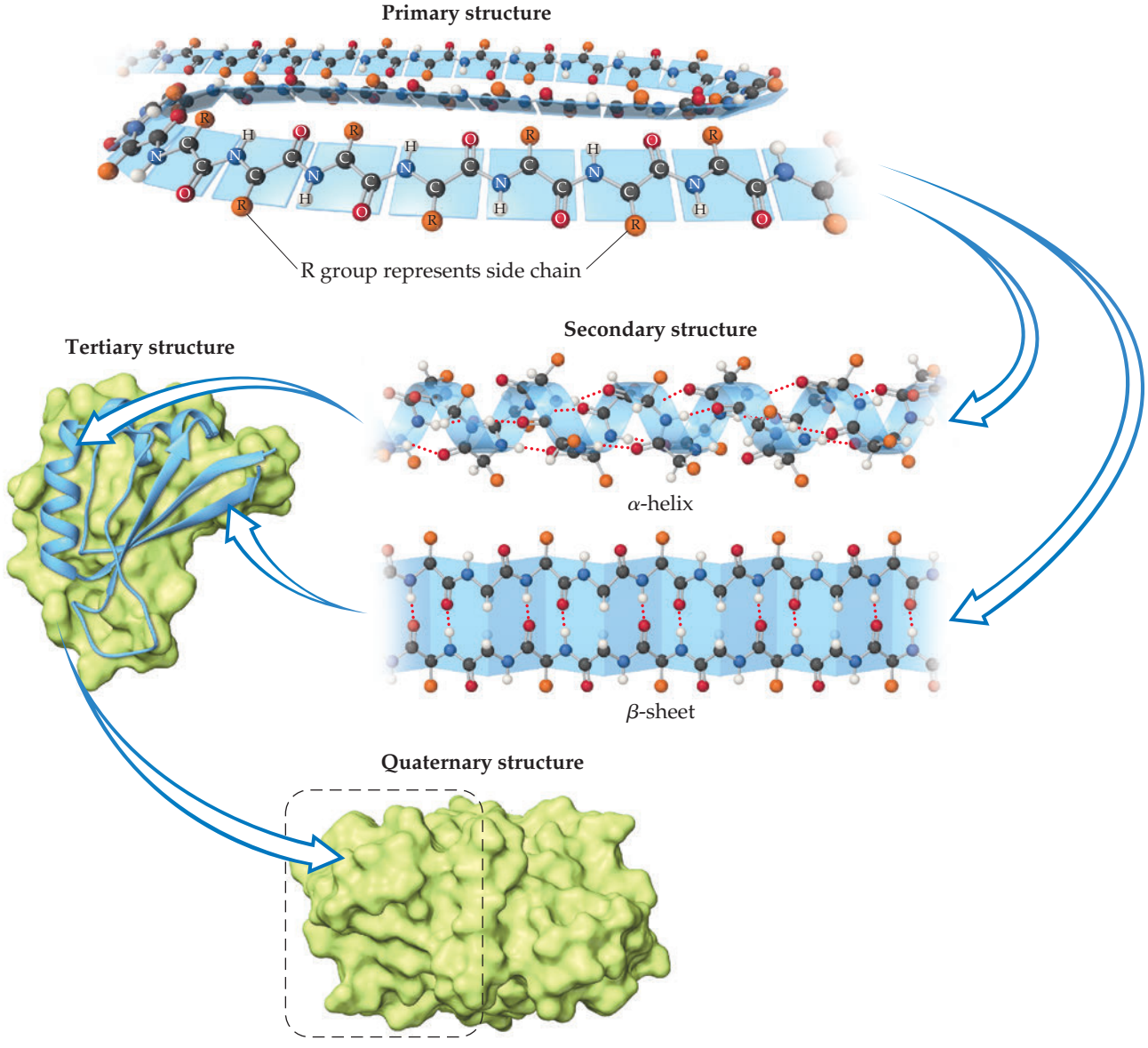


Protein Structure

The arrangement, or sequence, of amino acids along a protein chain is called its **primary structure**. The primary structure gives the protein its unique identity. A change in even one amino acid can alter the biochemical and physiological characteristics of the protein. For example, sickle-cell anemia is a genetic disorder resulting from a single replacement in a protein chain in hemoglobin. The chain that is affected contains 146 amino acids. The substitution of a single amino acid with an acidic functional group for one that has a hydrocarbon side chain alters the solubility properties of the hemoglobin, and normal blood flow is impeded (see the A Closer Look box in Section 31.2).

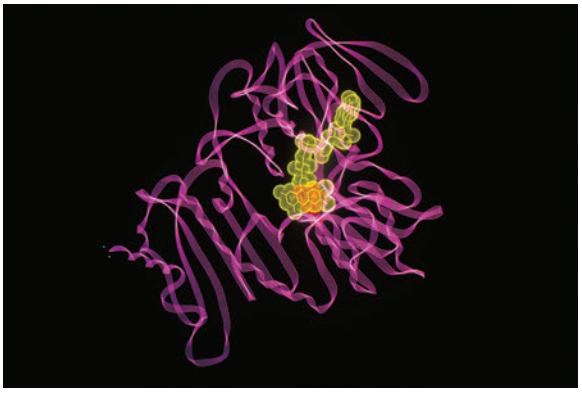
Another example occurs within the free-radical scavenging Zn/Cu enzyme, superoxide dismutase (SOD1). A single mutation in the primary structure of SOD1—for example, by replacing Gly with Ala at the 93rd position of the peptide sequence—is enough to implicate this mutant enzyme as a contributor to motor neuron disease (MND).

Proteins in living organisms are not simply long, flexible chains with random shapes. Rather, the chains coil and stretch in particular ways. The **secondary structure** of a protein refers to how segments of the protein chain are orientated in a regular pattern as seen in Figure 31.20.



▲ Figure 31.20 The four levels of structure of proteins.

One of the most important and common secondary-structure arrangements is the **α-helix** (Figure 31.20), first proposed by Linus Pauling and Robert B. Corey (1897–1971). Imagine winding a long protein chain in a helical fashion around a long cylinder. The helix is held in position by hydrogen bond interactions between N—H bonds and the oxygen atoms of nearby carbonyl groups. The pitch of the helix and the diameter of the cylinder must be such that (1) no bond angles are strained and (2) the N—H and C═O functional groups on adjacent turns are in a proper position for hydrogen bonding. In fact, each C═O group is hydrogen bonded to an N—H group four amino acid units away from it. An arrangement of this kind is possible for some amino acids along the chain, but not for others. Large protein molecules may contain segments of the chain that have the α-helical arrangement, interspersed with sections in which the chain is in a random coil. Typically, the α-helix has 3.6 amino acids per turn. The N—H groups of the amino acid point along the axis of the helix and all orientate themselves in the same direction. The C═O groups of the amino acids also point along the axis but in the opposite direction to the N—H groups, as a result of the *trans* arrangement of the peptide bond. All R groups point away from the helix structure.

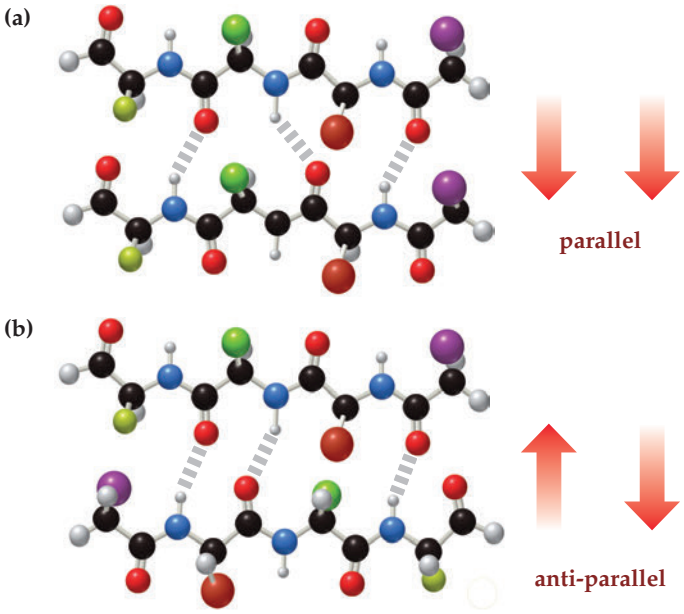


▲ **Figure 31.21 An enzyme containing a substrate.** A computer-generated model of an enzyme showing the amino acid backbone as a green ribbon. The substrate (violet) is shown to interact with a specific part of the protein called the active site.

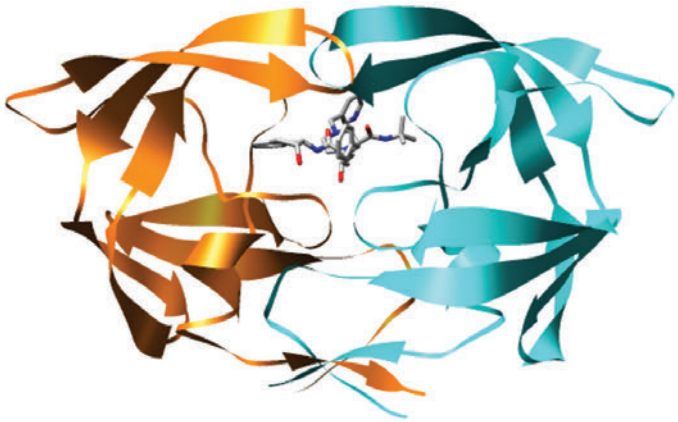
Figure 31.21 shows the structure of an enzyme containing a small molecular substrate. The important aspect of this protein is the highly coiled nature of the amino acid backbone (depicted as a ribbon). These coils are α-helices, which help give rise to the overall three-dimensional structure of the protein.

Another form of secondary structure that is often seen in proteins is the **β-pleated sheet**. This structure is not restricted to *intramolecular* hydrogen bonding structure, as is the α-helix, but may also form an intermolecular hydrogen bonding arrangement with another peptide chain (**Figure 31.22**). Since the peptide backbone contains only the α-carbon, NH and carbonyl carbon in an alternating manner from the *N*- to *C*-terminus, the two peptide chains can hydrogen bond in one of two orientations: parallel or anti-parallel. Both orientations are seen in natural proteins, although anti-parallel is the most common form. **Figure 31.23** shows an example of a protein with extensive β-sheets. These β-sheets are formed by the interaction of two or more peptide chains in an anti-parallel manner (as indicated by the direction of the arrows). Note that it is not necessary for all the peptide chains contributing to the sheet structure to be of the same size.

Proteins are not active biologically unless they are in a particular form in solution. The process by which the protein adopts the biologically active form is called **folding**.



◀ **Figure 31.22 β-sheet form of a protein.** F, Cl, Br and I are used along the peptide backbone to describe the two orientations possible for a β-sheet formation. (a) A parallel sheet, in which the two peptides orientate in the same direction from *N*- to *C*-terminus. (b) An anti-parallel sheet in which the two halide trends (F to I) occur in opposite directions.



▶ **Figure 31.23 A dimeric protein containing β-sheets.** The arrowed ribbons represent the directions of peptide chains that undergo intermolecular hydrogen bonding, forming β-sheet structures. The substrate in the middle fits nicely into the void made by the two halves of this protein dimer.

The overall shape of a protein in its folded form, determined by all the bends, kinks and sections of rod-like α-helical and flat β-sheet structures, is called the **tertiary structure**.

The tertiary structure of a protein is maintained by many different interactions. Certain folding of the protein chain leads to lower-energy (more stable) arrangements than other folding patterns. For example, a globular protein dissolved in aqueous solution folds in such a way that the non-polar hydrocarbon portions are tucked within the molecule, away from the polar water molecules. Most of the more polar acidic and basic side chains, however, project into the solution, where they can interact with water molecules through ion–dipole, dipole–dipole or hydrogen bonding interactions. The result of a mis-folding based on the change of a polar group was seen clearly in the example of sickle-cell anemia.

Some proteins are more complicated and have a fourth level of structure known as the **quaternary structure**. This level of structure involves the aggregation of two or more protein substructures into a larger macromolecular assembly. For example, the protein shown in Figure 31.23 has a quaternary structure, made up of two identical protein substructures that interact non-covalently with each other. The function the protein exhibits is only possible due to the quaternary (dimeric) structure and not by either substructure separately.

Enzymes

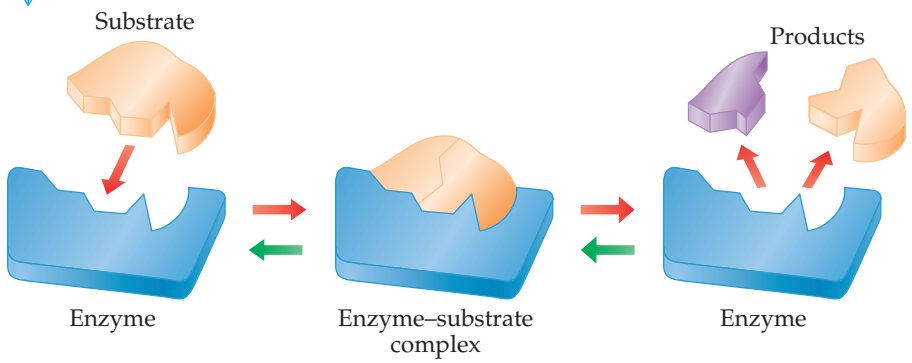
One of the most important classes of proteins are the **enzymes**, large protein molecules that serve as catalysts. Enzymes usually catalyze only very specific reactions. Their tertiary and quaternary structures generally dictate that only certain substrate molecules can interact with the enzyme (Figures 31.21 and 31.23).

Many of the most interesting and important examples of catalysis involve reactions within living systems. The human body is characterized by an extremely complex system of interrelated chemical reactions. All these reactions must occur at carefully controlled rates and at 37 °C in order to maintain life. Enzymes enable these reactions to take place in the proper order and at the correct rate. Most enzymes are proteins with molecular weights ranging from about 10 000 to about 1 million u. They are very selective in the reactions they catalyze, and some are absolutely specific, operating for only one substance in only one reaction. The decomposition of hydrogen peroxide, for example, is an important biological process. Because hydrogen peroxide is strongly oxidizing, it can be physiologically harmful. For this reason, the blood and livers of mammals contain an enzyme, *catalase*, which catalyzes the decomposition of hydrogen peroxide into water and oxygen (Equation 15.33). **Figure 31.24** shows the dramatic acceleration of this chemical reaction by the catalase in beef liver.



▲ **Figure 31.24 Effect of an enzyme.** Ground-up beef liver causes hydrogen peroxide to decompose rapidly into water and oxygen. The decomposition is catalyzed by the enzyme *catalase*. Grinding the liver breaks open the cells, so that the reaction takes place more rapidly. The frothing is due to escape of oxygen gas from the reaction mixture.

Go Figure Why might this be called a lock-and-key model?

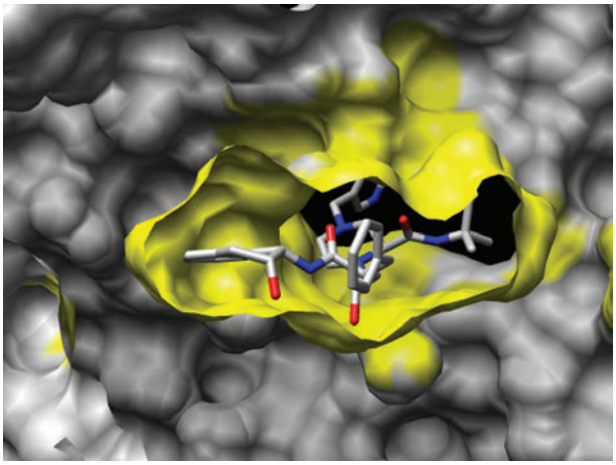


▲ **Figure 31.25 The lock-and-key model for enzyme action.** The correct substrate is recognized by its ability to fit the active site of the enzyme, forming the enzyme–substrate complex. After the reaction of the substrate is complete, the products separate from the enzyme. The reaction is just as suited to forming covalent bonds (right to left) as it is in breaking them (left to right).

Although an enzyme is a large molecule, the reaction is catalyzed at a very specific location in the enzyme, called the **active site**. The substances that undergo reaction at this site are called **substrates**. A simple explanation for the specificity demonstrated by enzymes is provided by the **lock-and-key model** illustrated in Figure 31.25. The substrate is pictured as fitting neatly into a special place on the enzyme (the active site), much like a specific key fitting into a lock. The active site is created by the coiling and folding of long protein chains to form a space, something like a pocket, into which the substrate molecule fits. Figure 31.26 shows a model of an enzyme's active site (cross-sectioned) with a bound substrate molecule.

The combination of the enzyme and the substrate is called the enzyme–substrate complex. Although Figure 31.25 shows both the active site and its complementary substrate as having rigid shapes, there is often a fair amount of flexibility in the active site. Thus, the active site may change shape as it binds the substrate. The binding between the substrate and the active site involves intermolecular forces such as dipole–dipole attractions, hydrogen bonds and London dispersion forces.

As the substrate molecules enter the active site, they are activated so that they are capable of extremely rapid reaction at mild (for example, 37 °C) temperatures. This activation may result from the enzyme withdrawing or donating electron density at a particular bond. In addition, in the process of fitting into the active site, the substrate molecule may be distorted and thus made more reactive. Once the reaction occurs, the products then depart, allowing another substrate molecule to enter. This means that the products must



◀ **Figure 31.26 Molecular model of an active site.** The active site (shown in yellow) has been cut away to show how well the substrate fits into the different depressions and pockets, like a hand in a glove. Compare this representation to that in Figure 31.23 of the same protein.

bind more weakly to the active site than does the substrate. If the reverse were true, inhibition of the enzyme's activity would be observed.

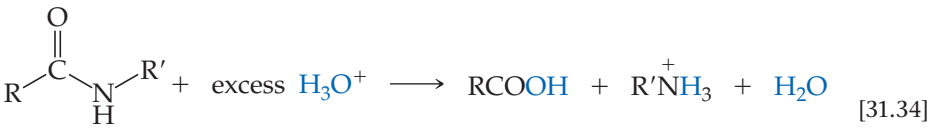
The activity of an enzyme is also destroyed if some molecule in the solution is able to bind strongly to the active site and block the entry of the substrate. Such substances are called *enzyme inhibitors*. Nerve poisons and some toxic metal ions, such as lead and mercury, are believed to act in this way to inhibit enzyme activity. Other poisons act by attaching elsewhere on the enzyme, thereby distorting the active site so that the substrate no longer fits.

Enzymes are typically more efficient than human-made catalysts. The number of individual catalyzed reaction events occurring at a particular active site, called the *turnover number*, is generally in the range of 10^3 to 10^7 per second. Such large turnover numbers correspond to very low activation energies. This is an area of chemistry of intense study because of its benefits associated with (a) mild reaction conditions, (b) high turnover numbers, (c) the sustainability of using microbes, bacteria and other organisms to promote reaction and (d) the removal of hazardous chemicals and solvents. Remember, most biological processes occur in water.

Sequencing of Peptides and Proteins

As a result of the almost endless permutations of amino acid sequences and the very specific nature of a protein's function, chemists and biochemists have come up with some clever ways of determining the precise structure of a protein. Let's consider the problem. There are three aspects of sequencing that need to be elucidated: (1) which amino acids are present; (2) what amounts of each amino acid are present; and (3) what order do these amino acids take in the primary structure of the protein.

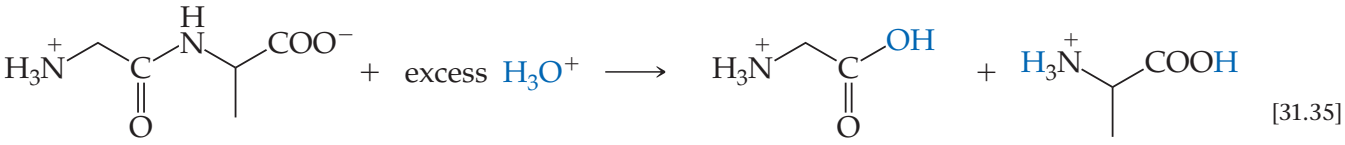
The first two of these questions are easily answered provided the protein is pure. Amide bonds are hydrolyzed in excess aqueous 6M HCl to yield the ammonium salt and carboxylic acid:



amide — carboxylic acid — ammonium salt

[31.34]

For a simple dipeptide such as Gly-Ala, the products are the ammonium salts of glycine and alanine:

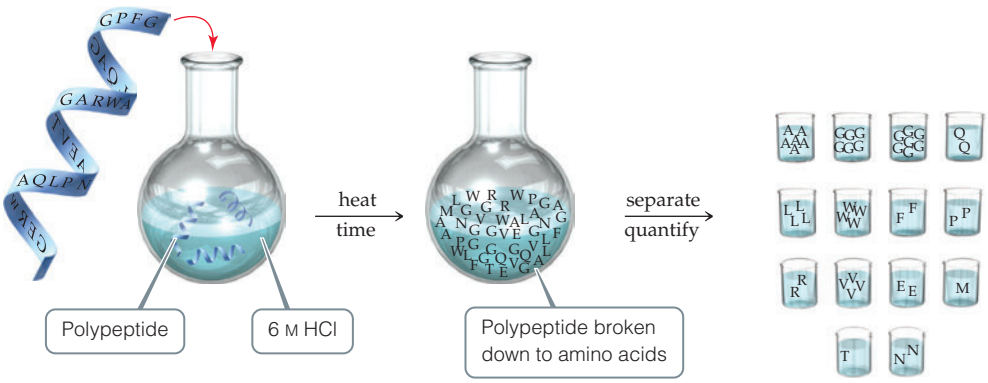


Gly-Ala — Gly — Ala

[31.35]

Amino acids can be separated from each other by electrophoresis (Figure 31.18) and other separating methods such as chromatography. The amount of each amino acid is then quantified using ninhydrin by the reaction shown in Equation 31.32. **Figure 31.27** summarizes this entire process using a general protein.

Knowing which amino acids are present, as well as their relative amounts, is only the beginning. The specific sequence of amino acids within the protein, which gives rise to the protein's function, is critical. Even, the simple dipeptide Gly-Ala is different from Ala-Gly. The processes required to sequence a protein need to be very specific and efficient. Two approaches are possible. Either the whole protein can be sequenced, or the protein can be cleaved at specific points to make smaller peptides, which are then sequenced. Both approaches have their advantages, although the latter is more practical. **Table 31.3** lists three common methods of undertaking the cleavage of peptide bonds at specific amino acid sites.

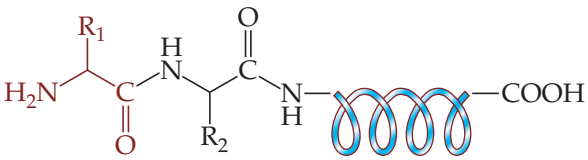


◀ **Figure 31.27 Amino acid analysis.** Note that the single-letter codes for the amino acids (Table 31.2) have been used in this example.

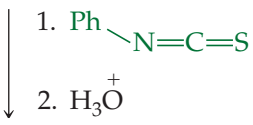
TABLE 31.3 Useful reagents for protein cleavage

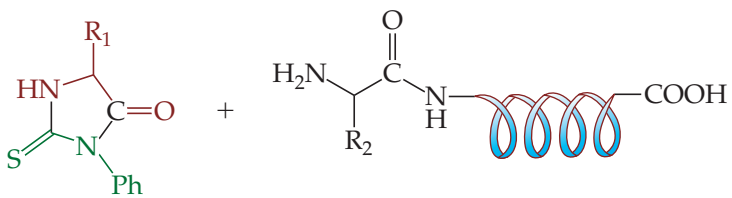
Reagent	Cleavage point(s) at the carboxyl group of
Cyanogen bromide (BrCN)	Methionine
Trypsin	Arginine and lysine
Chymotrypsin	Phenylalanine, tryptophan and tyrosine
6 M HCl (partial hydrolysis)	Indiscriminant

The most widely used method of sequencing proteins was developed by Pehr Edman (1916–1977) in the 1950s. The process is a laborious one and has been automated to save time and sample amounts. Modern instruments can sequence as little as 0.1 μg of a protein. The general idea of his approach, called the **Edman degradation**, is to cleave and identify one amino acid at a time from the *N*-terminus of the peptide chain. The process is repeated until the entire sequence is known. The Edman degradation requires treatment of the peptide with phenyl isothiocyanate (Ph—N=C=S), followed by mild acid hydrolysis. The product of this reaction, a phenylthiohydantoin, is collected and compared with known phenylthiohydantoin derivatives of the 20 common amino acids to identify which amino acid is cleaved. The new peptide (which is now one residue shorter) is also subjected to the same conditions to characterize the second amino acid residue and so on.



peptide





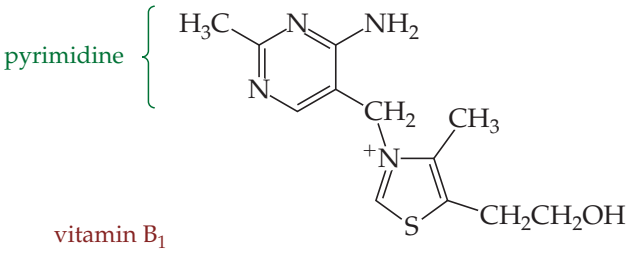
[31.36]

a phenylthiohydantoin

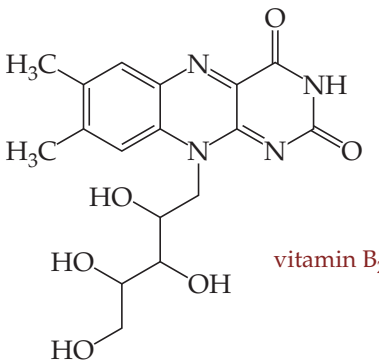
CHEMISTRY AND LIFE B Group Vitamins

Vitamins are small organic molecules that must be obtained through diet. They are usually required in trace amounts for proper growth. Many vitamins are used as coenzymes by the body; that is, they are required for the catalytic function of certain enzymes. All of the major B-group vitamins are nitrogen-containing compounds.

Vitamin B_1 is also known as thiamin, a water soluble heterocyclic structure made up of a substituted pyrimidine and a thiazole ring coupled by a methylene (CH_2) bridge. Thiamin is converted to its active form, thiamin pyrophosphate (TPP), in the brain and liver. In this form, thiamin acts as a cofactor for reductase enzymes responsible for, among other things, the reduction of pyruvate (Equation 31.29). A deficiency in thiamin may lead to *fatigue* and *depression*. Riboflavin, or vitamin B_2, is employed as a coenzyme for flavoproteins, which have a wide range of redox roles within the body. Riboflavin is found in useful quantities in eggs, milk, meat and cereal. A deficiency in vitamin B_2 leads, among other things, to *cracked lips* and *scaly skin*.

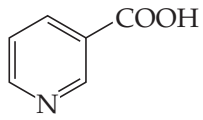


vitamin B_1

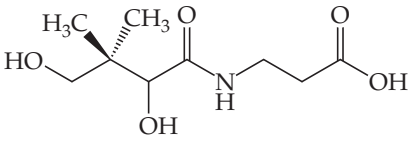


vitamin B_2

Nicotinic acid is the most common source of Vitamin B_3, also known as niacin. The human body uses vitamin B_3 in the form of NAD^+ (nicotinamide adenine dinucleotide) and $NADP^+$ (nicotinamide adenine dinucleotide phosphate) as a coenzyme in more than 50 enzyme-based reactions. Vitamin B_3 is instrumental in the release of energy from carbohydrates. It is necessary for proper brain function and is also involved in fat and cholesterol metabolism. A deficiency in vitamin B_3 may lead to *dermatitis, diarrhoea* and *dementia*. Vitamin B_5, also known as pantothenic acid, is found in abundance in whole-grain cereals, legumes and meat, and is usually formed from β-alanine and pantoic acid. Vitamin B_5 is required for the synthesis of coenzyme A (CoA), an acyltransferase, and for the metabolism of carbohydrates, fats and proteins. A deficiency in vitamin B_5 leads to *weight loss* and *irritability*.

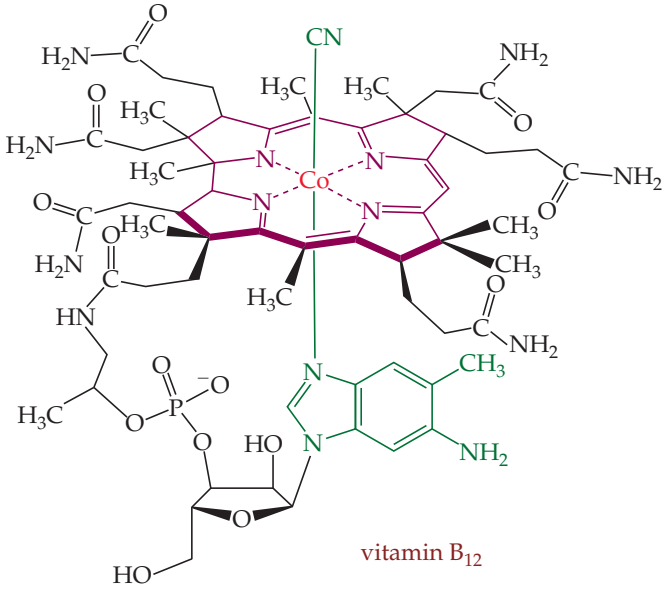


nicotinic acid



vitamin B_5

One of the most complicated and essential of the vitamins is vitamin B_{12}. Vitamin B_{12} is unusual as it is the only metal-ion-containing vitamin. The tetrapyrrole macrocycle (purple) of vitamin B_{12} is called a *corrin*, which is related to the porphyrin structure found in myoglobin, hemoglobin and chlorophyll. Centrally coordinated to the corrin macrocycle is a cobalt(II) ion with an octahedral geometry (red). The cyano (CN) and benzimidazole ligands (green) bind axially to the metal ion.



vitamin B_{12}

Vitamin B_{12} is synthesized exclusively by microorganisms and is found in the liver of animals. The liver can store up to six years' supply of vitamin B_{12}, so deficiencies in this vitamin are rare. Vitamin B_{12} helps to protect nerves and is involved in the formation of red blood cells in bone marrow which prevents anemia. Vitamin B_{12} is necessary in the catabolism of fatty acids.

Sample Exercise 31.8

Sequencing Peptides

An unknown pentapeptide was subjected to a range of different experiments to ascertain its structure. The following results were obtained:

Experiment	Fragment result
Total hydrolysis	Arg, Glu, His, Phe, Ser
Edman degradation	Glu
Chymotrypsin hydrolysis	Glu-His-Phe, Arg-Ser
Trypsin hydrolysis	Glu-His-Phe-Arg, Ser

What is the pentapeptide sequence?

SOLUTION

Analyze We are asked to sequence a small peptide based on the fragments obtained by different chemical reactions.

Plan Identify the reactions and what type of fragment each leads to. Determine the number of different amino acids listed through the hydrolysis products. Construct the peptide one fragment at a time.

Solve Total hydrolysis yields five amino acids, which is the total required for the pentapeptide. Hence, each amino acid occurs only once in the sequence. Peptides are always written from the *N*- to *C*-terminus. The Edman degradation yields the *N*-terminus residue, Glu. Chymotrypsin hydrolyzes at the carboxyl end of Phe, which indicates the first three residues are Glu-His-Phe. At this point, the sequence can be only one of two possibilities: Glu-His-Phe-Arg-Ser or Glu-His-Phe-Ser-Arg. Since trypsin cleaves at the carboxyl group of Arg, leaving the single amino acid residue, Ser, the pentapeptide sequence was:

Glu-His-Phe-Arg-Ser

Practice Exercise

The partial hydrolysis of an unknown hexapeptide gave the following fragments: Gly-Ala-Phe, Phe-Tyr-His, Tyr-His-Glu. What is the sequence of the hexapeptide?

Self-Assessment Exercises

31.21 Does Gly-Ala have the same structure as Ala-Gly?

(a) Yes

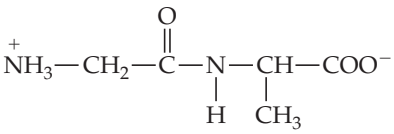
(b) No

31.22 What information does the acid hydrolysis of a peptide provide on its composition or structure?

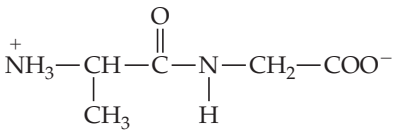
(a) The amino acids present

(b) The primary structure of the peptide

(c) The secondary structure of the peptide



gly-ala



ala-gly

Exercises

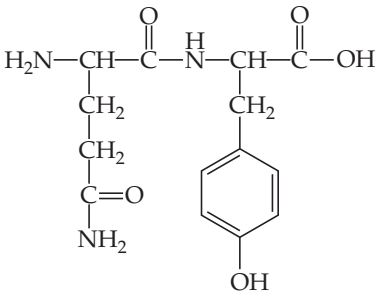
31.23 **(a)** Draw the two possible dipeptides formed by the condensation reaction between serine and lysine. **(b)** If a racemic mixture of both amino acids is used, how many stereoisomers will result?

31.24 **(a)** Draw the condensed structure of the tripeptide Ile-Ala-Cys. **(b)** How many different tripeptides can be made from the amino acids serine, threonine and phenylalanine? Give the abbreviations for each of these tripeptides, using the three-letter and one-letter codes for amino acids.

31.25 Describe what is meant by the primary, secondary and tertiary structures of proteins. Give examples to illustrate your answer.

31.26 Glutathione is a tripeptide found in most living cells. Partial hydrolysis yields Cys-Gly and Glu-Cys. What is the structure of glutathione?

31.27 Name the dipeptide that has the following structure, and give its one-letter and three-letter abbreviations:



31.28 Bradykinin is a small peptide containing nine amino acids. Partial hydrolysis gave the following fragments:

Arg-Pro-Pro, Ser-Pro, Pro-Phe-Arg, Gly-Phe-Ser, Pro-Pro-Gly

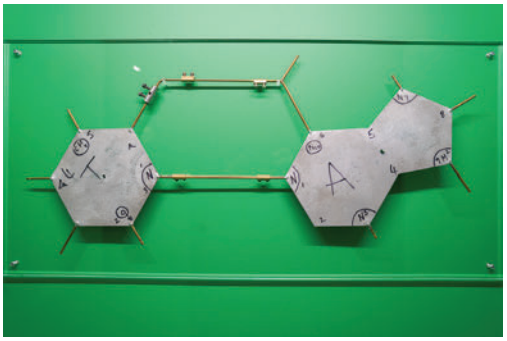
What is the primary structure of bradykinin?

31.29 The abbreviation for a peptide is VAKG. **(a)** Draw the structural formula for this peptide. **(b)** Is this peptide neutral, acidic or basic? **(c)** What would be the products of a trypsin digestion? **(d)** Which amino acid would be identified in VAKG by the Edman degradation?

Answers to Self-Assessment Exercises

31.21 (b) **31.22** (a)

31.4 Nucleic Acids and DNA





Gregor Mendel, who made a careful study of 8000 pea plants, was the first to recognize that there were some specific characteristics passed from one generation to the next. He published his findings in 1866, but it was not until forty years later that the term "gene" was coined. At this time, proteins were thought to be the repository of inherited information until the 1940's when experiments concluded that DNA was fundamental to the process. There were many people contributing vital information that eventually led James Watson and Francis Crick to propose the structure of DNA in 1953. DNA was discovered in 1869 by Friedrich Miescher, while the Russian born biochemist Phoebus Levene, working in the early twentieth century in America, determined the component parts that made up this biopolymer—a sugar, a phosphate group, and four nitrogen heterocyclic compounds, referred to as "bases". Erwin Chargaff studied these bases and found that, irrespective of the organism the DNA was extracted from, the amount of adenine (A) present was always similar to the amount of thymine (T) present and amount of guanine (G) similar to the amount of cytosine (C). This became known as Chargaff's rule. This, together with the pioneering work of Rosalind Franklin and Maurice Wilkins on the X-ray crystallographic analysis of DNA, led Watson and Crick to believe the paring of "bases" A+T and G+C was central to the structure of DNA. They used cardboard cutout models of the bases to determine the patten. At first, nothing seemed to fit, but after Jerry Donohue suggested a more likely tautomeric form of the bases, the jigsaw fell into place. Watson and Crick proposed the now famous double-stranded helix held together

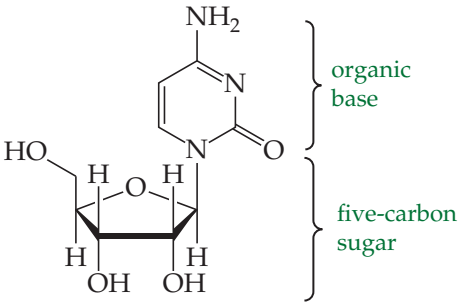
by hydrogen bonding between pairs of bases. They celebrated their discovery with a beer in "The Eagle", Cambridge, where a plaque commemorates the place where they first announced their discovery to the public.

In this section, we introduce one of the most remarkable known biopolymers. By the end of section, you should:

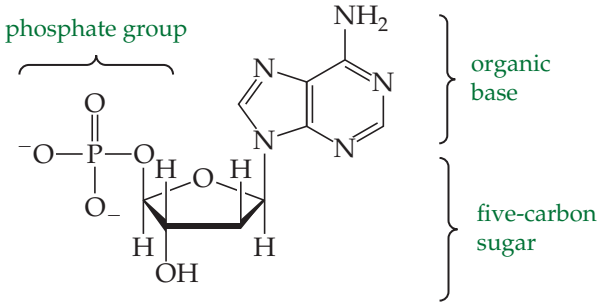
- Understand the components and functioning of DNA.

Nucleic acids make up a class of biopolymers that are the chemical carriers of an organism's genetic information. **Deoxyribonucleic acids (DNA)** are huge molecules whose molecular weights may range from 6 million to 16 million u. **Ribonucleic acids (RNA)** are smaller molecules, with molecular weights in the range of 20000 to 40000 u. DNA is found primarily in the nucleus of the cell, whereas RNA is found mostly outside the nucleus in the *cytoplasm*, the non-nuclear soup enclosed within the cell membrane. DNA stores the genetic information of the cell and specifies which proteins the cell can synthesize. RNA carries the information stored by DNA out of the nucleus of the cell into the cytoplasm as part of the *transcription* process. Once in the cytoplasm, the information, transcribed into messenger RNA (mRNA), is used in protein synthesis. The process of protein synthesis from genetic material, known as *translation*, also involves two other forms of RNA, called ribosomal RNA (rRNA) and transfer RNA (tRNA), which bring together the programmed amino acids in the correct sequence for polypeptide synthesis.

The monomers of nucleic acids can come in two forms. **Nucleosides** are compounds containing a five-carbon sugar and a nitrogen-containing organic base. **Nucleotides** are nucleosides containing an additional phosphate group.

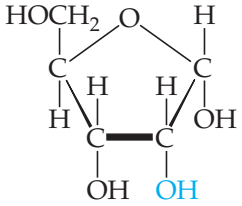


cytidine
a ribonucleoside

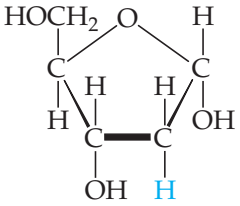


deoxyadenine monophosphate
a deoxyribonucleotide

The sugar component of RNA is *ribose*, whereas that in DNA is *deoxyribose*. *Deoxy*ribose differs from ribose only in that it lacks the OH group at carbon 2:



ribose

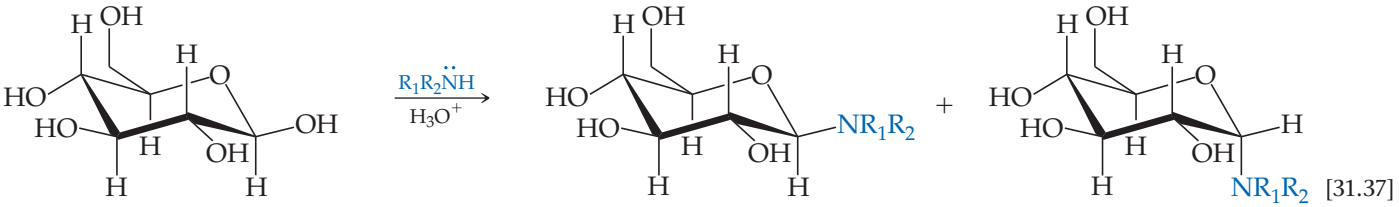


deoxyribose

Hence, nucleosides and nucleotides can be either ribose or deoxyribose based. For example, a nucleoside derived from ribose is called a *ribonucleoside* and is found in RNA.

A nucleotide derived from deoxyribose is called a *deoxyribonucleotide* and is found in DNA.

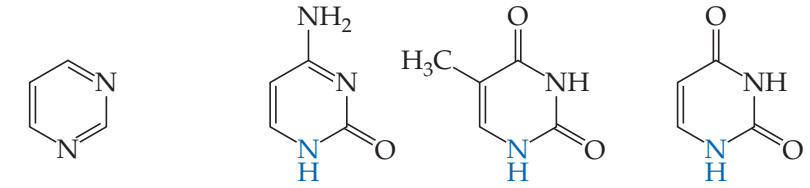
Nucleosides are also known generally as ***N*-glycosides**. An *N*-glycoside is formed when a monosaccharide reacts with an amine in the presence of acid. A general reaction for the formation of an *N*-glycoside is



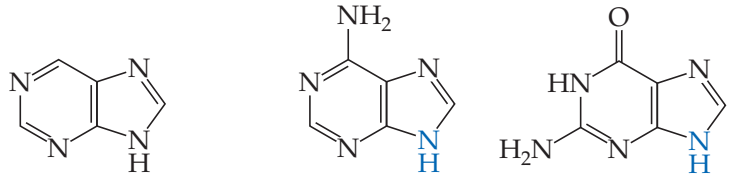
[31.37]

β-*N*-glycoside *α*-*N*-glycoside

In the case of DNA and RNA, the amines used are derived from the aromatic heterocycles **pyrimidine** and **purine**. The heterocycles adenine (A), thymine (T), cytosine (C) and guanine (G) form the four bases of DNA used to store the genetic code.



pyrimidine cytosine **C** thymine **T** uracil **U**



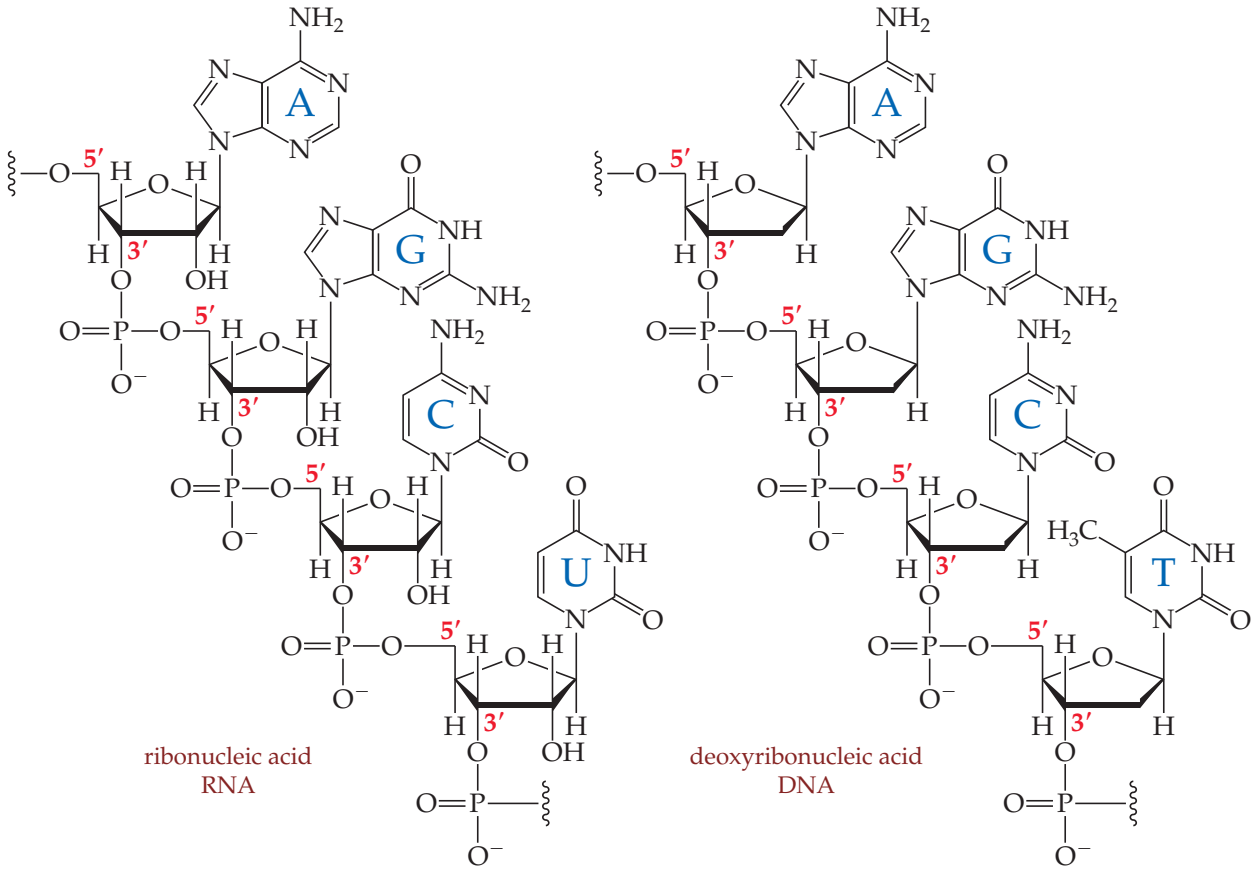
purine adenine **A** guanine **G**

RNA differs from DNA not only in the monosaccharide used, ribose or deoxyribose, but also in the replacement of thymine (T) by uracil (U) within the base code.

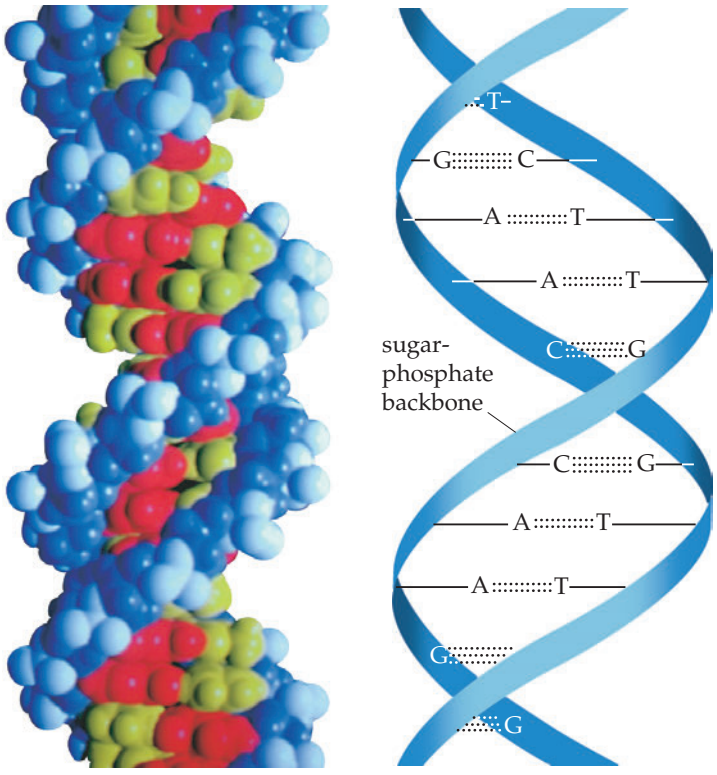
Nucleic acids are polynucleotides formed by condensation reactions between an OH group of the phosphoric acid unit at the 5′ position on one nucleotide with the OH group at the 3′ position of another nucleotide. **Figure 31.28** shows a portion of the polymeric chain of DNA and RNA, illustrating the 3′–5′ linkage and the different bases employed by each nucleic acid.

DNA molecules consist of two deoxyribonucleic acid chains or strands that are wound together in the form of a **double helix**, as shown in **Figure 31.29**. The drawing in Figure 31.31(b) has been simplified to show the essential features of the structure. The sugar and phosphate groups form the backbone of each strand. The bases (represented by the letters A, T, C, and G) are attached to the sugars. The two strands are held together by attractions between the bases in one strand and those in the other strand. These attractions involve both London dispersion interactions and hydrogen bonds.

Go Figure Is DNA positively charged, negatively charged, or neutral in aqueous solution at pH 7?

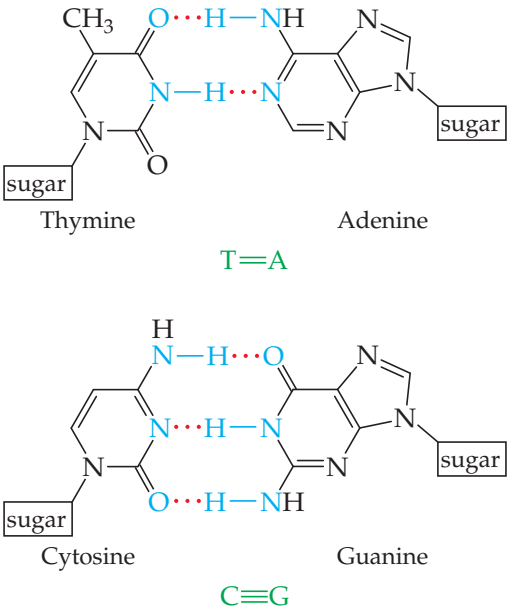


▲ **Figure 31.28 Structure of a polynucleotide.** The general structure of DNA and RNA is shown, demonstrating the differences between the two types of nucleic acids.



◀ **Figure 31.29 Two views of DNA.** (a) A computer-generated model of a DNA double helix. The dark blue and light blue atoms represent the sugar-phosphate chains that wrap around the outside. Inside the chains are the bases, shown in red and yellow-green. (b) A schematic illustration of the double helix showing the hydrogen bond interactions between complementary base pairs.

Go Figure Which pair of complementary bases, A—T or G—C, would you expect to bind more strongly?



▲ **Figure 31.30 Hydrogen bonding between complementary base pairs.** The hydrogen bonds are responsible for the formation and stability of the double-stranded helical structure of DNA, shown in Figure 31.29(b).



▲ **Figure 31.31 James Watson (1928–) and Francis Crick (1916–2004).** Nobel laureates 1962, along with Maurice Wilkins (1916–2004), for their role in the determination of the structure of nucleic acids.

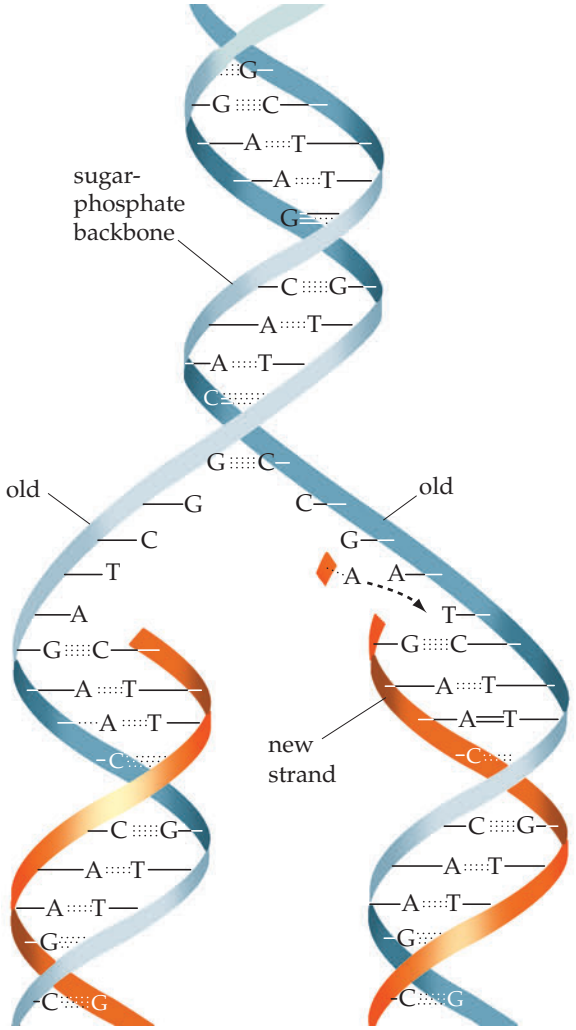
As shown in **Figure 31.30**, the structures of thymine (T) and adenine (A) make them perfect partners for hydrogen bonding. Likewise, cytosine (C) and guanine (G) form ideal hydrogen bonding partners. In the double-helix structure, therefore, each thymine on one strand is opposite an adenine on the other strand. Likewise, each cytosine is opposite a guanine. This *base-pairing* of C—G and A—T is called **Watson–Crick pairing**, after two of the scientists who were instrumental in solving the structure of DNA (**Figure 31.31**). The double-helix structure with complementary bases on the two strands is the key to understanding how DNA functions.

The two strands of DNA unwind during cell division, and new complementary strands are constructed on the unravelling strands (**Figure 31.32**). This enzyme-catalyzed process results in two identical double-helix DNA structures, each containing one strand from the original structure and one newly synthesized strand. This replication process allows genetic information to be transmitted when cells divide.

The structure of RNA and its relationship to DNA is also the key to understanding protein synthesis, the means by which viruses infect cells, and many other problems of central importance to modern biology and medicine. The basis of taking the information stored in DNA and processing it to form proteins is shown in **Figure 31.33**. The mechanism for protein biosynthesis takes place within a *ribosome*, a complex piece of biological machinery composed of protein and rRNA, which reads the code contained within the mRNA to be translated. This code determines the order of the amino acid sequence within the polypeptide being synthesized.

So how is it possible for just four bases to code for all 20 naturally occurring amino acids? The answer is by using the ribonucleotides, A, C, G and U, in a triplet coding called a **codon**. Each codon is specific for a given amino acid (**Table 31.4**). For example, the codon CAU on mRNA codes for histidine to be incorporated into the growing peptide chain, whereas the codon GCA on mRNA codes for alanine to be incorporated into the growing peptide chain.

The reason why translation uses a triplet code is very easy to understand. Using a triplet code based on the four ribonucleotides means that there are $4^3 = 64$ possible triplet



◀ **Figure 31.32 DNA replication.** The original DNA double helix partially unwinds, and new nucleotides line up on each strand in complementary fashion. Hydrogen bonds help align the new nucleotides with the original DNA chain. When the new nucleotides are joined by condensation reactions, two identical double-helix DNA molecules result.



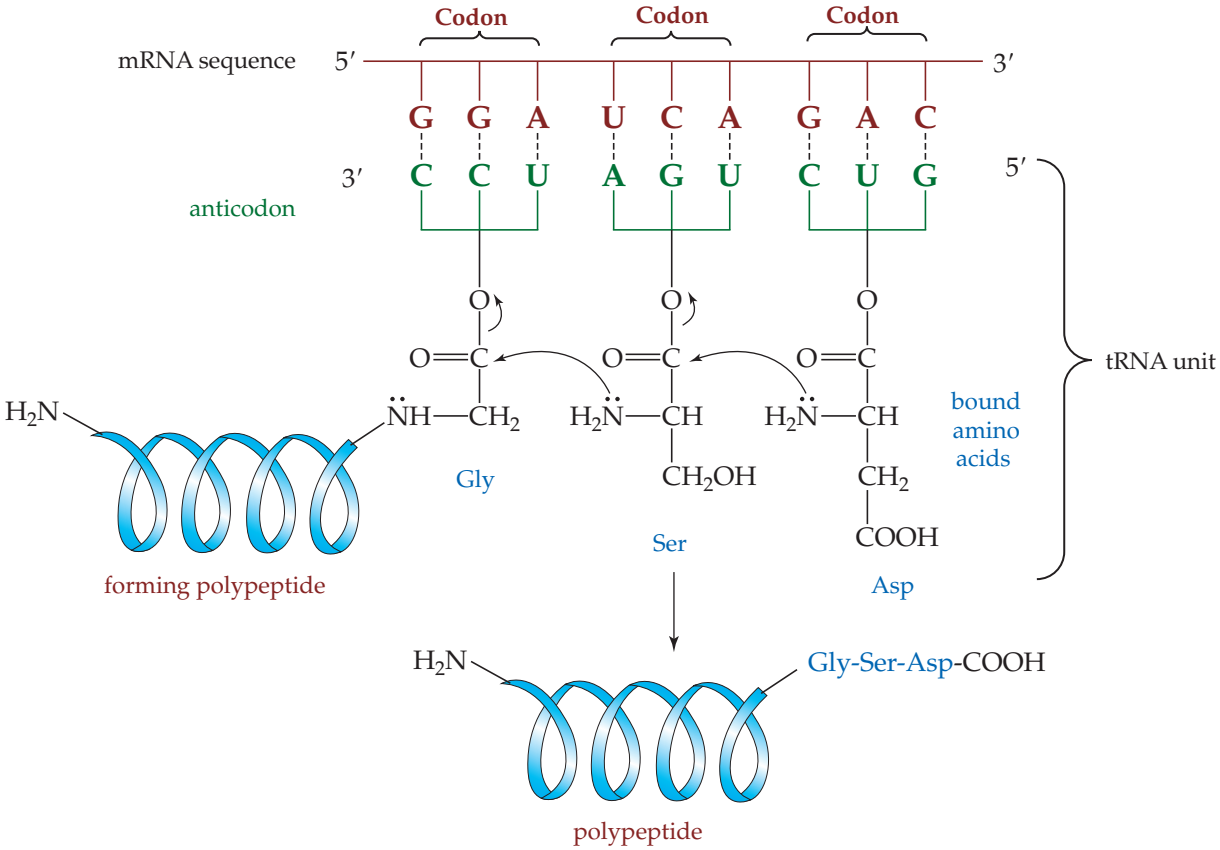
◀ **Figure 31.33 From DNA to protein.**

codes, which is the smallest number of permutations possible greater than 20, which counts for the 20 naturally occurring amino acids. Of the possible 64 permutations for the codons, 61 are used for specific amino acids. Most amino acids are specified by more than one codon, with the exception of methionine (Met) and tryptophan (Trp). The amino acids serine, leucine and arginine are all specified by any one of six codons. The three remaining codons are used to terminate the synthesis of the polypeptide and release it from the ribosome. These codons are called *stop codons*.

The construction of the polypeptide using the 61 codons sequenced on mRNA requires complementary sequence codons, called *anticodons*, on tRNA. For example, the codon series, 5′-UCA GAC, sequenced on mRNA requires a serine-bound tRNA with the complementary sequence, 3′-AGU-5′, as well as an aspartic acid-bound tRNA with the complementary sequence, 3′-CUG-5′. Once bound in the correct orientation, the two units are added to the growing peptide chain by an enzymatic process that cleaves the amino acid from the tRNA anticodon. **Figure 31.34** illustrates the process schematically.

TABLE 31.4 Codon assignments

First base 5′ end	Second base	Third base 3′ end: U	C	A	G
U	U	UUU = **Phe**	UUC = **Phe**	UUA = **Leu**	UUG = **Leu**
	C	UCU = **Ser**	UCC = **Ser**	UCA = **Ser**	UCG = **Ser**
	A	UAU = **Tyr**	UAC = **Tyr**	UAA = Stop	UAG = Stop
	G	UGU = **Cys**	UGC = **Cys**	UGA = Stop	UGG = **Trp**
C	U	CUU = **Leu**	CUC = **Leu**	CUA = **Leu**	CUG = **Leu**
	C	CCU = **Pro**	CCC = **Pro**	CCA = **Pro**	CCG = **Pro**
	A	CAU = **His**	CAC = **His**	CAA = **Gln**	CAG = **Gln**
	G	CGU = **Arg**	CGC = **Arg**	CGA = **Arg**	CGG = **Arg**
A	U	AUU = **Ile**	AUC = **Ile**	AUA = **Ile**	AUG = **Met**
	C	ACU = **Thr**	ACC = **Thr**	ACA = **Thr**	ACG = **Thr**
	A	AAU = **Asn**	AAC = **Asn**	AAA = **Lys**	AAG = **Lys**
	G	AGU = **Ser**	AGC = **Ser**	AGA = **Arg**	AGG = **Arg**
G	U	GUU = **Val**	GUC = **Val**	GUA = **Val**	GUG = **Val**
	C	GCU = **Ala**	GCC = **Ala**	GCA = **Ala**	GCG = **Ala**
	A	GAU = **Asp**	GAC = **Asp**	GAA = **Glu**	GAG = **Glu**
	G	GGU = **Gly**	GGC = **Gly**	GGA = **Gly**	GGG = **Gly**



▲ **Figure 31.34 Translation.** The codons on mRNA orientate the tRNA anticodons bearing amino acid residues. Once bound, enzyme-mediated processes cause the amino acid to be cleaved from the anticodon and covalently bound to the growing peptide chain.

Sample Integrative Problem

Putting Concepts Together

Glycine, NH_2CH_2COOH, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. **(a)** Draw a Lewis structure that indicates the charges on the molecule at the physiological pH of 7.4. **(b)** Use your structure to illustrate the concept of resonance. **(c)** Describe the hybridization of the two carbon atoms and the nitrogen atom in glycine and the geometry of the atoms surrounding these three atoms. **(d)** Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

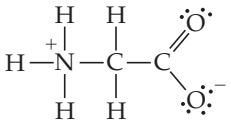
SOLUTION

Analyze We are asked about the structure of a simple amino acid at a particular pH. This includes considering the hybridization and molecular geometry of some of the atoms and commenting on a physical property.

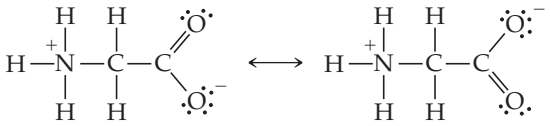
Plan First draw the Lewis structure of glycine and determine the ionization state of the amine and the carboxylic acid groups.

Solve

(a) A pH of 7.4 is several units on the base side of 2.35, consequently the carboxylic acid ($pK_a = 2.35$) will exist in the conjugate base form. Conversely physiological pH is more than two units on the acid side of 9.78 and so the amine will exist in the conjugate acid form ($pK_a = 9.78$). The Lewis structure will be:



(b)



(c) N: sp^3 hybridized, tetrahedral geometry, CH_2: sp^3 hybridized, tetrahedral geometry, COO^-: sp^2 hybridized, trigonal-planar geometry

(d) Glycine exists as a zwitterion and strong electrostatic attraction between molecules results in some ionic-like characteristics such as a relatively high melting point.

Self-Assessment Exercise

31.30 What codon sequence on mRNA would give the tripeptide: Val-Gly-Gly?

(a) GUU GGC GGA

(b) UUG GGG GGC

(c) GUC GAA GAG

(d) UGC AGU CAG

Exercises

31.31 Describe a nucleotide. Draw the structural formula for the nucleotide deoxycytidine monophosphate, which contains cytosine in the organic base.

31.32 Imagine a single DNA strand containing a section with the following base sequence: ACTCGA. What is the base sequence of the complementary strand?

31.33 An mRNA strand has the following sequence: GUCAG-GAAUCUU. What would be the sequence of the parent DNA strand that led to this transcription?

31.34 *Chargaff's rule* states that DNA contains equimolar amounts of guanine and cytosine and also equal amounts of adenine and thymine. **(a)** Does this imply that there are equimolar amounts of purine and pyrimidine bases in DNA? **(b)** Does Chargaff's rule apply only to double-stranded DNA or is it also applicable to single-stranded DNA? Explain.

31.35 Poly U added to a cell-free system containing all the necessary materials for biosynthesis yields a polypeptide comprising a single amino acid. **(a)** What is that amino acid? **(b)** What synthetic addition polymer might have similar properties to the one formed by translating poly U?

31.36 The motion picture *GATTACA* (1997) is set around a society that strives for human perfection through genetic selection. Its name is a play on the genetic code, comprising the bases A, T, C and G. **(a)** What is the complementary DNA sequence for GATTACA? **(b)** Transcribe this sequence into mRNA.

31.37 What amino acid sequence is encoded by the following mRNA sequence?

UUU CCA GUG GAU CCG AUC UAA

Answers to Self-Assessment Exercise

31.30 (a)

Chapter Summary and Key Terms

SECTION 31.1 **Amines** are hydrocarbon derivatives containing one or more basic nitrogen atoms. **Aliphatic amines** contain alkyl chains. **Heterocycles** containing a basic nitrogen atom are classed as either **cyclic** or **aromatic amines**. **Alkaloids** are amines found in the bark, leaves and roots of plants, for example cocaine, nicotine and morphine. The **amino group** of a primary (RNH_2), secondary (RR′NH) or tertiary (RR′R″N) amine can be converted to an **alkyl ammonium salt** by the addition of acid or alkyl halide. Amines can be synthesized by the **reductive amination** of aldehydes and ketones. The condensation of an amine with a carboxylic acid yields an amide. Amides can be **primary**, **secondary** or **tertiary** based on the number of hydrogen atoms bonded to the amide nitrogen. The amide bond is highly planar due to resonance. **Lactams**, such as those found in the **penicillins**, are cyclic amides.

SECTION 31.2 Compounds containing both carboxylic acid and amine functional groups are called **amino acids**. **α-Amino acids** are chiral substances, with only the L enantiomers found naturally. Since both acidic and basic groups are found within the same molecule, amino acids are said to be **amphiprotic**. At neutral pH, amino acids exist as **zwitterions**. The **isoelectric point** of an amino acid is the pH where the neutral zwitterion predominates in solution. The 20 common naturally occurring amino acids are classed as α-amino acids. They differ only in the identity of their **side chains**. These side chains give the α-amino acids their different physical properties and allow their separation from each other by techniques such as **electrophoresis**. Amino acids can be formed by the **Strecker synthesis**, which converts aldehydes to α-amino acids in the presence of cyanide ion.

SECTION 31.3 **Proteins** are functional polymers of amino acids. The amino acids within proteins are linked by **peptide** (amide) **bonds**. A **polypeptide** is a polymer formed by linking many amino acids by peptide bonds. A **peptide** is the name given to a short sequence of amino acids. Proteins are classed as either **simple** or **conjugated** based on their constituents. They can be classed also as **fibrous** or **globular** based on their macromolecular shape. Protein structure is determined by the sequence of amino acids in the chain (its **primary structure**), the coiling or stretching of the chain (its **secondary structure**), the overall shape of the complete molecule (its **tertiary structure**) or its interaction with other proteins (its **quaternary structure**). The most important secondary structure arrangements are the **α-helix** and **β-pleated sheet**. The process by which a protein assumes its biologically active tertiary structure is called **folding**. The primary structure of a peptide or protein can be elucidated using the **Edman degradation**. Some proteins, called **enzymes**, function as catalysts. Enzymes contain an **active site**, which is the area of reactivity for a **substrate**. The active site and substrate form a very specific and functioning complex, much like a **lock and key**.

SECTION 31.4 **Nucleic acids** are biopolymers that carry the genetic information necessary for cell reproduction and development through control of protein synthesis. The building blocks of these biopolymers are **nucleosides** and phosphoric acid, which react to form **nucleotides**. Nucleosides are also generally known as ***N*-glycosides**. There are two types of nucleic acids: the **ribonucleic acids (RNA)** and the **deoxyribonucleic acids (DNA)**. These substances consist of a polymeric backbone of alternating phosphate and sugar groups, with **pyrimidine-** or **purine**-derived organic bases attached to the sugars. The DNA forms a **double helix** held together by hydrogen bonding between matching organic bases on the two strands. The specific nature of **Watson–Crick pairing** is the key to gene replication and protein synthesis. Each set of three nucleotides, or **codon**, within messenger RNA (mRNA) codes for a particular amino acid. This process, called translation, converts the genetic code into protein.

Key Skills

- Be able to name and classify amines and amides. (Section 31.1)
- Recall that amines are both bases and nucleophiles and appreciate relative pK_a values. (Section 31.1)
- Prepare amines and amides from other functional groups. (Section 31.1)
- Know the 20 most common amino acids and their three-letter codes. Expand this to describe small peptides. (Section 31.2)
- Be able to use the Henderson–Hasselbalch equation. (Section 31.2)
- Have an understanding of the importance to biological processes of nitrogen-containing compounds. (Sections 31.3 and 31.4)
- Know the general classes of proteins and describe what is meant by primary, secondary, tertiary and quaternary structure of a protein. (Section 31.3)
- Be able to sequence a peptide through the fragment approach. (Section 31.3)
- Identify the purine and pyrimidine bases used in nucleic acids. (Section 31.4)
- Be able to show A/T and C/G complementarity in a DNA/DNA or RNA/DNA sequence. (Section 31.4)
- Have an understanding of the process of translation and transcription. (Section 31.4)

Key Equations

- Isoelectric point

$$\mathrm{pI} = \tfrac{1}{2}(\mathrm{p}K_{a1} + \mathrm{p}K_{a2}) \qquad [31.23]$$

- Henderson–Hasselbalch equation

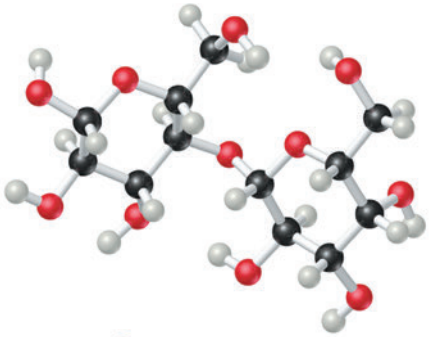
$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \qquad [31.28]$$

Exercises

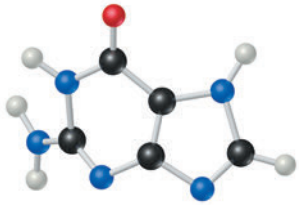
Visualizing Concepts

31.38 From examination of the following ball-and-stick molecular models, choose the substance that **(a)** can be hydrolyzed to form a solution containing glucose, **(b)** is capable of forming a zwitterion, **(c)** is one of the four bases present in DNA. [Sections 31.2 and 31.4]

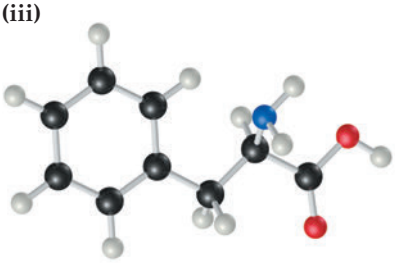
(i)



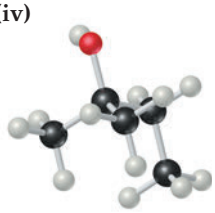
(ii)



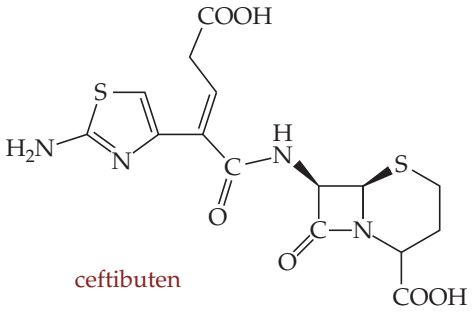
(iii)



(iv)

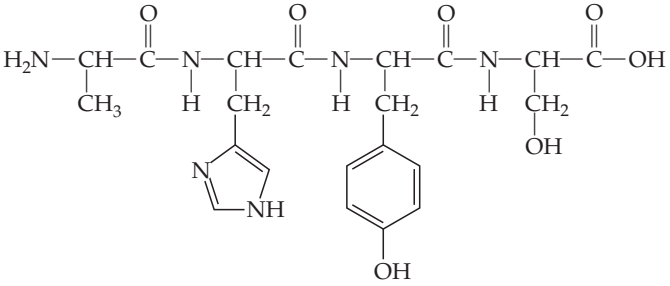


31.39 Ceftibuten is an orally active cephalosporin antibiotic. Identify the β-lactam, secondary amide, primary amine and heterocyclic amine in this structure. [Section 31.1]

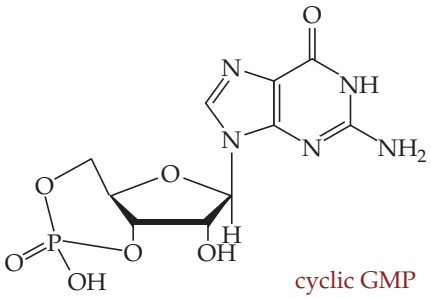


ceftibuten

31.40 What are the three-letter and one-letter codes for the following tetrapeptide? [Section 31.3]

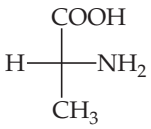


31.41 Cyclic GMP is a cellular regulatory agent found in animal and bacteria cells in concentrations of 10^{-6} moles kg^{-1}. Cyclic GMP is also implicated in the action and potency of Viagra. **(a)** Can you suggest what GMP might stand for? **(b)** What is the name given to the monosaccharide central to the structure of cyclic GMP? **(c)** Can cyclic GMP be classified as a glycoside? If so, what type of glycoside? [Section 31.4]



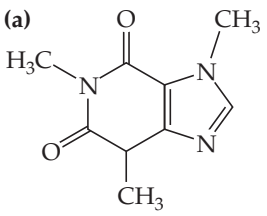
cyclic GMP

31.42 The configuration of an amino acid is drawn here as a Fischer projection. **(a)** Name the amino acid. **(b)** Assign its absolute stereochemistry as *R* or *S*. [Section 31.2]

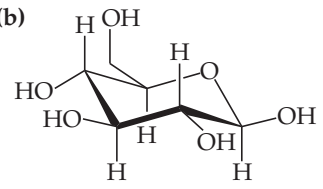


31.43 Classify the following compounds as an alkaloid, amino acid, nucleoside, or carbohydrate. [Sections 31.1, 31.2 and 31.4]

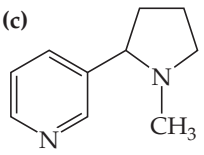
(a)



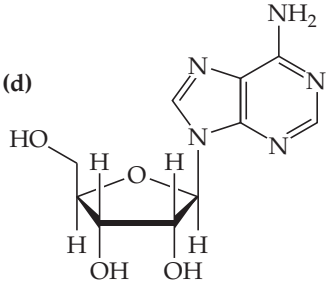
(b)



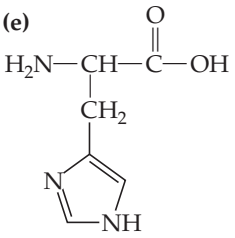
(c)



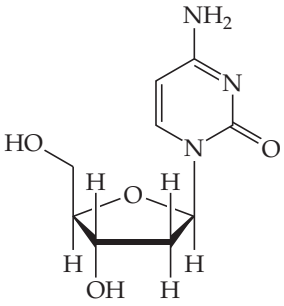
(d)



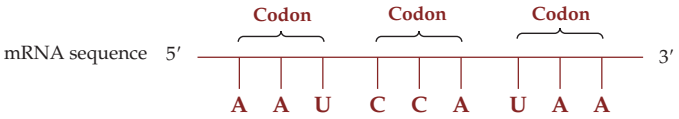
(e)



(f)



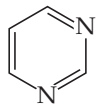
31.44 Identify the peptide formed by the mRNA sequence following translation. [Section 31.4]



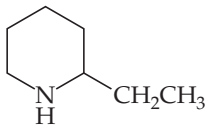
Amines and the Amide bond (Section 31.1)

31.45 Give names for the following amines:

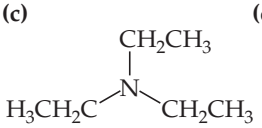
(a)



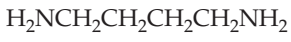
(b)



(c)



(d)



31.46 Provide a structural formula for each of the following compounds:

(a) 2-propanamine

(b) 2-aminobutanoic acid

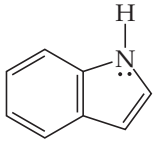
(c) *N,N*-dimethylcyclopentanamine

(d) 2-methylcyclohexylamine

(e) 2-methyl-3-ethylpyrrole

31.47 **(a)** Draw a primary, secondary, and tertiary amine with the molecular formula $C_6H_{15}N$. What relationship exists between the three compounds you have drawn? **(b)** How would you expect the boiling points of these three amines to vary, and why? **(c)** Propylamine is entirely miscible with water; trimethylamine has reasonably high solubility in water. What accounts for these data, considering that isobutane ($(CH_3)_3CH$) is considerably less soluble than trimethylamine?

31.48 Indole smells rather terrible in high concentrations but has a pleasant floral odor when highly diluted. It has the following structure:



Indole is a planar molecule. The nitrogen is a very weak base, with a K_b of 2×10^{-12}. Explain how the K_b indicates that the indole molecule is aromatic in character.

31.49 Aniline is prepared by catalytic hydrogenation of nitrobenzene. **(a)** Write an equation for this reaction including reagents and catalyst. **(b)** Devise a chemical procedure based on the basicity of aniline to separate it from any unreacted nitrobenzene. [*Hint:* Both compounds are soluble in diethyl ether and insoluble in water.]

31.50 Provide a structural formula for each of the following compounds:

(a) 2-methylpropanamide

(b) acetamide

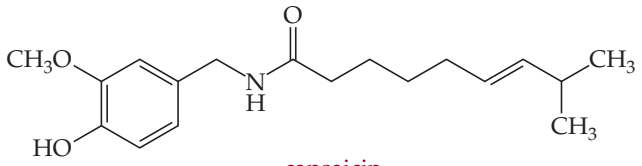
(c) *N*-phenylacetamide

(d) *N,N*-dimethyl-1-pentanamide

(e) *N*-ethylbenzamide

31.51 Draw a primary, secondary and tertiary amide with the molecular formula $C_5H_{11}NO$. What isomeric relationship exists between the three compounds you have drawn?

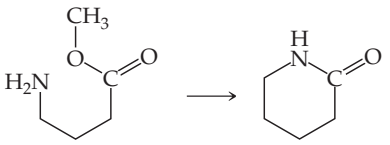
31.52 *Capsaicin*, shown in the accompanying figure, is the compound responsible for the sensation felt when chillis are eaten. It is often used as a tool in neurobiological research and has application as a topical analgesic. **(a)** Draw the structure of the carboxylic acid and amine that lead to capsaicin. **(b)** What is the general name given to this type of reaction?



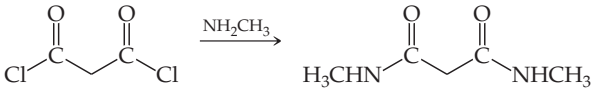
capsaicin

31.53 Propose a mechanism for the following reactions:

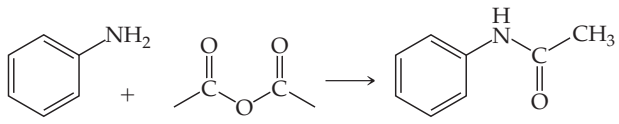
(a)



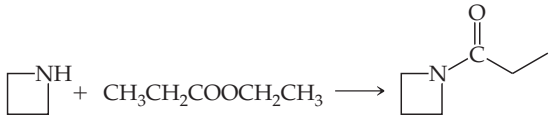
(b)



(c)



(d)

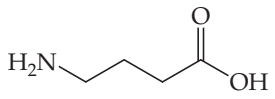


Amino Acids, Proteins, and Peptides (Sections 31.2 and 31.3)

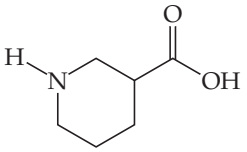
31.54 What properties of the side chains (R groups) of amino acids are important in affecting the amino acid's overall biochemical behaviour? Give examples to illustrate your answer.

31.55 Classify the following five molecules as α-, β-, γ- or δ-amino acids:

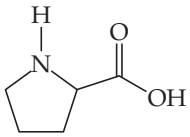
(a)



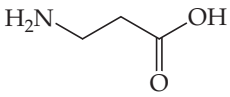
(b)



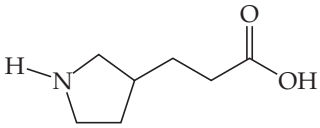
(c)



(d)



(e)



31.56 Aspartic acid is reported to have three pK_a values, one in the range of 2 to 3, another in the range 3 to 4, and the last in the range of 9 to 10. Suggest the origin of the three pK_a values.

31.57 **(a)** What is meant by the term *isoelectric point*? **(b)** Valine has pK_a values of 2.32 and 9.69. Determine the isoelectric point, pI, for valine.

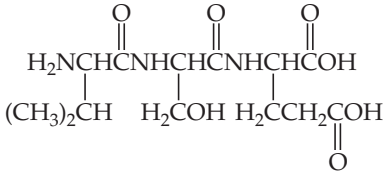
31.58 Using Equation 31.28, estimate the average charge on phenylalanine **(a)** at pH 1, **(b)** at pH 5.5, **(c)** at pH 8. Phenylalanine has pK_a values of 2.58 and 9.24.

31.59 **(a)** Draw leucine and lysine in their zwitterionic forms. **(b)** The pI for leucine and lysine are 5.98 and 9.74, respectively. How could you use this information to separate a mixture of the two amino acids by electrophoresis?

31.60 Outline a synthesis of isoleucine **(a)** from 2-bromo-3-methylpentanoic acid and **(b)** by the Strecker synthesis.

31.61 **(a)** Write a chemical equation for the formation of methionyl glycine from its constituent amino acids. **(b)** If a racemic mix of both amino acids is used, how many stereoisomers will result?

31.62 **(a)** What amino acids would be obtained by hydrolysis of the following tripeptide?



(b) How many different tripeptides can be made from the amino acids glycine, serine and glutamic acid? Give the abbreviation for each of these tripeptides, using the three-letter codes for amino acids.

31.63 **(a)** Describe the role of hydrogen bonding in determining the α-helical structure of a protein. **(b)** Suggest a reason why proline is never found within a protein α-helix.

31.64 **(a)** Draw the condensed structural formula of each of these tripeptides: Val-Gly-Asp, Phe-Ser-Ala. **(b)** What general properties would you expect each tripeptide to have based on their side chains—for example, are they hydrophobic or hydrophilic, acidic or basic?

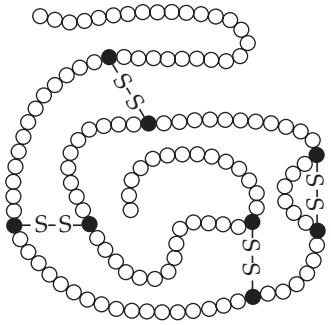
31.65 Draw the full structural formula for alanylglycylserine.

31.66 A new cyclic pentapeptide has been isolated from a marine sponge. Total hydrolysis of the cyclic peptide yielded the following amino acid composition:

Lys Gly Phe Cys

(a) What experimental conditions and reagents could be used to perform this hydrolysis? **(b)** What techniques could be used to cleave the cyclic peptide at specific sites to help identify the structure?

31.67 The protein ribonuclease A in its native, or most stable, form is folded into a compact globular shape. **(a)** Does the native form have a lower or higher free energy than the denatured form, in which the protein is an extended chain? **(b)** What is the sign of the entropy change in going from the denatured to the folded form? **(c)** In its folded form, the ribonuclease A has four –S–S– bonds that bridge parts of the chain, as shown in the diagram here. What effect do you predict that these four linkages have on the free energy and entropy of the folded form as compared with a hypothetical folded structure that does not possess the four –S–S– linkages? Explain. **(d)** A gentle reducing agent converts the four –S–S– linkages to eight –S–H bonds. What effect do you predict this would have on the tertiary structure of the protein?



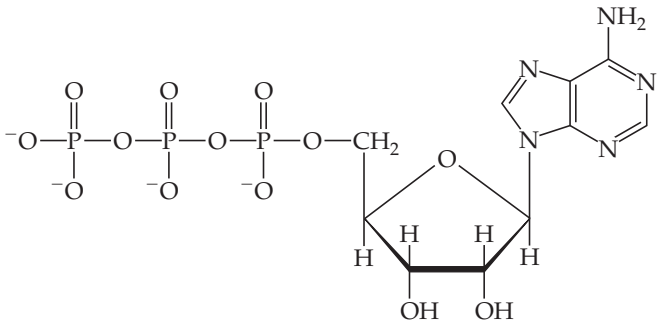
native ribonuclease A

Nucleic Acids and DNA (Section 31.4)

31.68 A nucleoside consists of an organic base of the kind shown in Section 31.4, bound to ribose or deoxyribose. Draw the structure for deoxyguanosine, formed from guanine and deoxyribose.

31.69 When samples of double-stranded DNA are analysed, the molar quantity of adenine present equals that of thymine. Similarly, the molar quantity of guanine equals that of cytosine. Explain the significance of these observations.

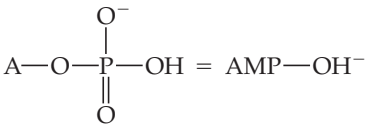
31.70 One of the most important molecules in biochemical systems is adenosine triphosphate (ATP), for which the structure is:



ATP

ATP is the principal carrier of biochemical energy. It is considered an energy-rich compound because the hydrolysis of ATP to yield adenosine diphosphate (ADP) and inorganic phosphate is spontaneous under aqueous biochemical conditions. **(a)** Write a balanced equation for the reaction of ATP with water to yield ADP and inorganic phosphate ion. **(b)** What would you expect for the sign of the free energy change for this reaction? **(c)** ADP can undergo further hydrolysis. What would you expect for the product of that reaction?

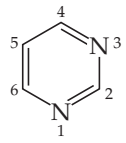
31.71 The monoanion of adenosine monophosphate (AMP) is an intermediate in phosphate metabolism:



where A = adenosine. If the pK_a for this anion is 7.21, what is the ratio of [AMP—OH^-] to [AMP—O^{2-}] in blood at pH 7.4?

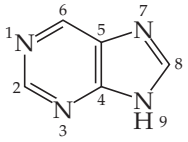
31.72 **(a)** Draw the structure of adenine and thymine and indicate how they interact through Watson–Crick base pairing. **(b)** Draw the structure of cytosine and guanine and indicate how they interact through Watson–Crick base pairing. **(c)** Why doesn't guanine base-pair with thymine? Explain.

31.73 *Broxuridine* is used to replace thymine during replication to cause radiosensitivity. Its systematic name is 5-bromo-2′-deoxyuridine or 5-bromouracil deoxyriboside. Draw the structural formula for broxuridine.



pyrimidine

31.74 *Cladribine* is a substituted purine nucleoside with antileukaemic activity. Its systematic name is 2-chloro-2′-deoxyadenosine. Draw the structural formula for cladribine.



purine

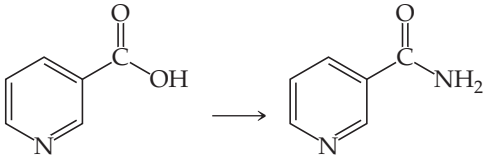
31.75 **(a)** What amino acid sequence is encoded by the following mRNA sequence?

AGG ACU GCA UCG CAA

(b) What anticodon sequence of tRNAs is needed for the synthesis of this peptide?

Integrative Exercises

31.76 Devise a synthesis for nicotinamide starting from nicotinic acid.



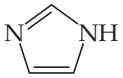
nicotinic acid nicotinamide

31.77 **(a)** How many amide groups are there in vitamin B_{12}? See page 1436. **(b)** What type of glycoside is found in vitamin B_{12}? **(c)** Is the sugar component a furanose or pyranose form?

31.78 What general features of a vitamin allow you to predict whether it is a hydrophilic or a lipophilic vitamin?

31.79 Quinine is a natural product that has anti-malarial properties. It was originally extracted for therapeutic use from the bark of the cinchona tree, but is now synthesized by the pharmaceutical industry. Quinine is generally administered as the hydrochloride salt ($C_{20}H_{24}N_2O_2$•HCl). The pK_a of this salt is 4.32. **(a)** What are the advantages of using the hydrochloride salt of quinine in medicine? **(b)** What is the pH of a 0.053 *M* solution of quinine hydrochloride?

31.80 Imidazole is a cyclic amine with the following structure.



(a) Draw a tautomer of imidazole. **(b)** Imidazole is a highly polar molecule; draw a resonance structure that demonstrates this polarity. **(c)** Imidazole is aromatic with six π-electrons; identify the π-electrons involved. **(d)** Protonation of imidazole occurs on only one of the nitrogen atoms. Which nitrogen atom is protonated and explain why this is so? Imidazole forms part of the side chain of the amino acid histidine and coordinates to iron in the oxygen transport protein, hemoglobin. **(e)** What part of the imidazole molecule acts as a donor in this coordination?

Design an Experiment

You are tasked with identifying the sequence of a peptide in the most efficient way possible. You conduct a series of experiments and collect the following data:

- Edman degradation on the peptide yields Cys.
- Chymotrypsin hydrolysis gives two fragments; one fragment contains the amino acids Cys and Lys and the other fragment contains Cys, Gly, and Phe.
- Trypsin hydrolysis also gives two fragments; one containing the amino acids Cys, Gly, Lys, and Phe and another composed of just Cys.

What is the sequence of the peptide? If you had repeated the Edman degradation until you had identified each of the amino acids present, how many experiments would this have involved? If you had conducted an acid hydrolysis to release all of the amino acids in a single experiment, can you think of a way to quantify the amino acids present?

WHAT'S AHEAD

32.1 ▶ The Electromagnetic Spectrum

32.2 ▶ Infrared (IR) Spectroscopy

32.3 ▶ Nuclear Magnetic Resonance (NMR) Spectroscopy

32.4 ▶ Mass Spectrometry

32.5 ▶ Compound Identification Using Spectra

32

SOLVING MOLECULAR STRUCTURE

32.1 The Electromagnetic Spectrum



In 1666, Isaac Newton used a prism to disperse white light into the colors of the rainbow. He observed that a round beam of white light would produce an oblong image of colors. From this, he concluded that different colors are bent by the prism at different angles. This indicated that color was a property of light rather than of an object that the light illuminates. We now recognize that the electromagnetic spectrum is far more extensive than the visible portion that

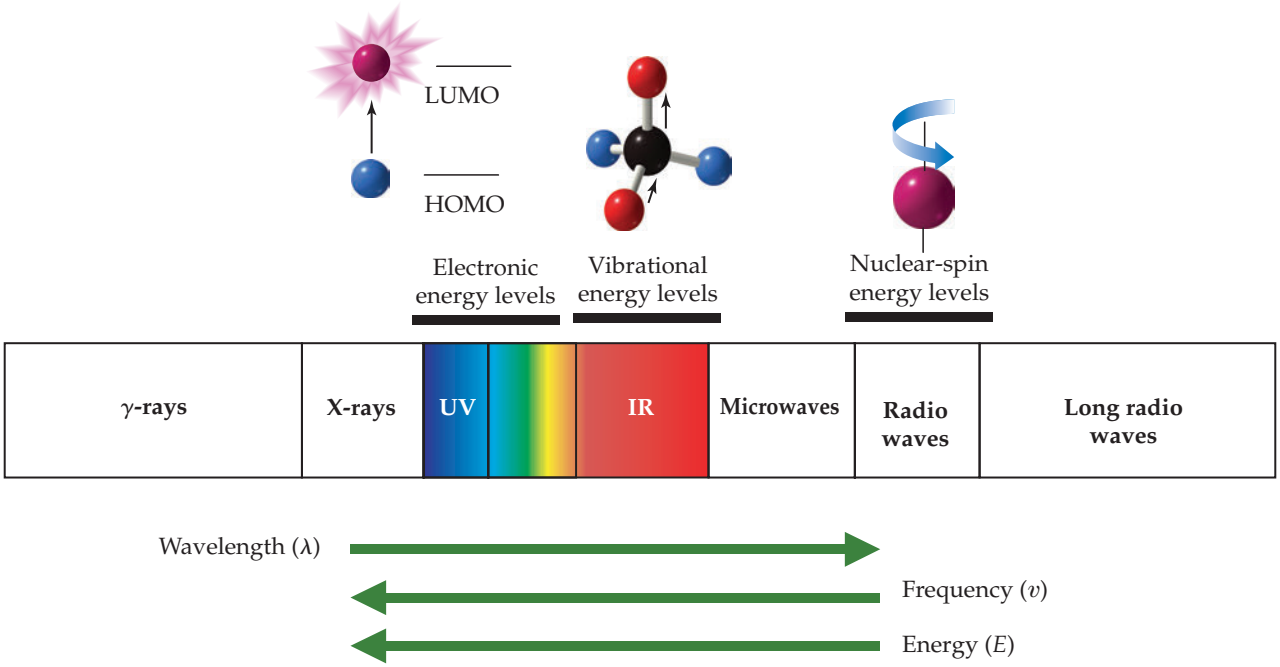
we see and different parts of it correspond to different physical processes that may occur within a molecule. By the end of this section, you should:

- Understand the parts of the spectrum that are used in the analysis of molecules

In Chapter 6, we introduced the electromagnetic spectrum and the concepts of wavelength (λ) and frequency (υ).

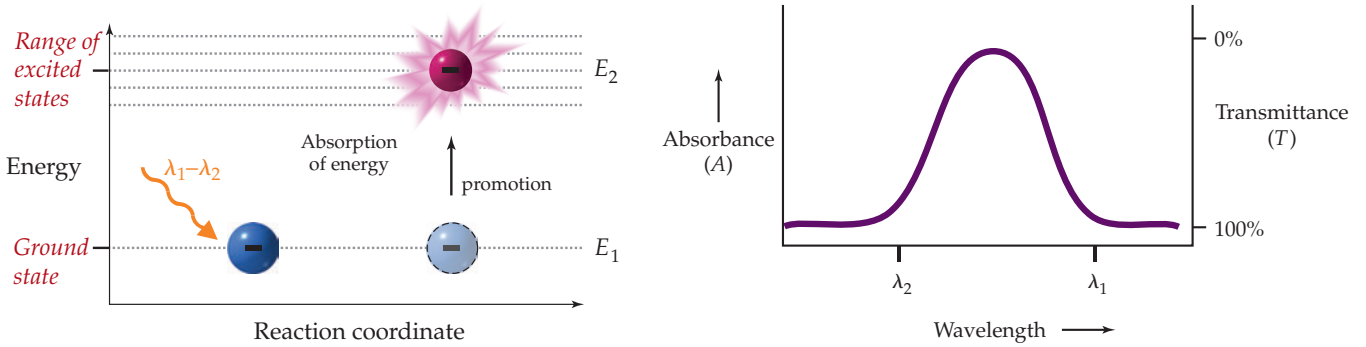
Three regions of the electromagnetic spectrum are particularly important to the organic chemist (**Figure 32.1**). The UV (ultraviolet) and visible region of the spectrum is of an energy that equates to the transition of electrons between electronic energy levels within a molecule (**Figure 32.2**). The technique, aptly named **UV-visible spectroscopy**, is particularly useful for aromatic and π-conjugated compounds. The infrared (IR) region of the spectrum corresponds to transitions between the vibrational energy levels within a molecule. This region of the electromagnetic spectrum is lower in energy than that required to excite an electron from the ground state using ultraviolet radiation, and provides unique information on the types of functional groups present in a molecule. The third region of importance is found at the frequency of radio waves. In this region, the energies relate to transitions between nuclear-spin energy levels. The energies required here are much lower than for either IR- or UV-visible spectroscopy.

When an organic molecule is exposed to a spectrum of electromagnetic radiation, it absorbs energy at certain wavelengths in the ultraviolet and visible region and allows other wavelengths to pass through. Figure 32.2 illustrates the process. A molecule initially in the lower-energy E_1 state, referred to as the *ground state*, can undergo a transition to E_2, the *excited state*, only by absorption of electromagnetic energy of wavelength λ. This wavelength is related to the difference between E_1 and E_2 by Equations 6.1 and 6.2, so $\lambda = hc/(E_2 - E_1)$. In atoms, the absorptions occur at very defined energies giving a spectrum of sharp lines. In molecules, each electronic energy level has a stack of much smaller vibrational energy levels associated with it and this results in a broader absorption. The UV-visible absorption spectrum of a molecule is characteristic for each different substance.



▲ **Figure 32.1 The electromagnetic spectrum.** Energy depends upon wavelength. The regions are described in terms of atomic transitions and the type of related spectroscopy.

Go Figure The absorption characteristics displayed by molecules have an analogy in everyday life. Why do dark-colored cars get hotter inside than light-colored cars?



▲ **Figure 32.2 An absorption spectrum** is generated when a molecule absorbs electromagnetic radiation of a particular wavelength range ($\lambda_1 - \lambda_2$).

UV-visible spectroscopy is one of several spectroscopic techniques in which energy interacts with a molecule to give a characteristic absorption spectrum. Modern spectroscopic techniques use only minute amounts of material, which in most cases may be recovered unchanged after the analysis. These are called *non-destructive* techniques. Other methods of analysis do destroy the compound and are sometimes unavoidable, for example, mass spectrometry.

In this chapter, we deal with three powerful and complementary techniques that form the cornerstone of modern synthetic organic chemistry. Each technique is useful because it provides a vital piece of evidence, using very small amounts of sample. The chemical detective can draw a logical conclusion to the structural problem by combining two, but usually more, pieces of evidence. The techniques are:

- *infrared (IR) spectroscopy*, which observes the vibrations of covalent bonds and provides useful evidence for the presence of functional groups;

A CLOSER LOOK Using Spectroscopic Methods to Measure Reaction Rates

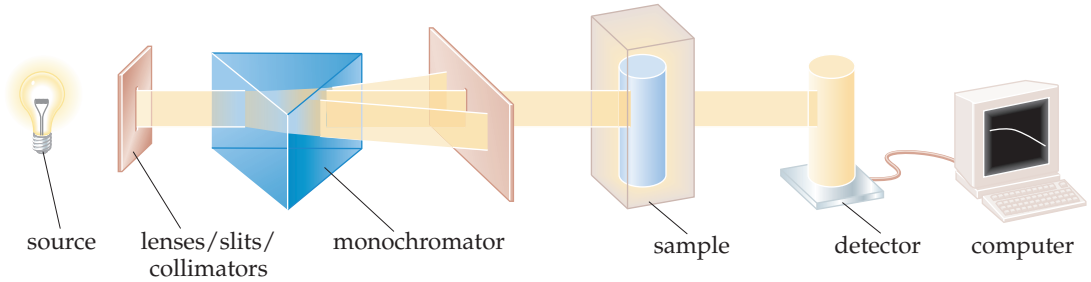
A variety of techniques can be used to monitor the concentration of a reactant or product during a reaction. Spectroscopic methods, which rely on the ability of substances to absorb (or emit) electromagnetic radiation, are some of the most useful. Spectroscopic kinetic studies are often performed with the reaction mixture in the sample compartment of a spectrometer. The spectrometer is set to measure the light absorbed at a wavelength characteristic of one of the reactants or products. In the decomposition of HI(g) into H_2(g) and I_2(g), for example, both HI and H_2 are colorless, whereas I_2 is violet. During the course of the reaction, the color increases in intensity as I_2 forms. As the concentration of I_2 increases and its color becomes more intense, the amount of light absorbed by the reaction mixture increases, causing less light to reach the detector.

Figure 32.3 shows the basic components of a spectrometer. The spectrometer measures the amount of light absorbed by the sample by comparing the intensity of the light emitted from the light source with the intensity of the light that emerges from the sample.

Beer–Lambert's law relates the amount of light being absorbed to the concentration of the substance absorbing the light:

$$A = \varepsilon c l \qquad [32.1]$$

In this equation, A is the measured absorbance, ε is the molar extinction coefficient (a characteristic of the substance being monitored at a particular wavelength), l is the path length through which the radiation must pass, and c is the molar concentration of the absorbing substance. Thus, for a constant path length, the concentration is directly proportional to absorbance.



▲ **Figure 32.3 Basic components of a spectrometer.**

- *nuclear magnetic resonance (NMR) spectroscopy*, the technique of choice for the organic chemist. This method observes nuclear transitions within a strong magnetic field and yields information on the connectivity of atoms;
- *mass spectrometry (MS)*, which typically bombards a very small amount of sample with electrons to ionize the molecules. Analysis of the mass of these ions gives the molecular mass. Mass spectrometry often provides clues to the structure and functional groups within a molecule, through either fragmentation or isotopic patterns. This technique is often used routinely because it needs only μg amounts of sample.

Self-Assessment Exercise

32.1 What portion of the electromagnetic spectrum corresponds to the energy difference between vibrational energy levels?

(a) UV-visible light
(b) Infrared radiation
(c) Radio waves

Answers to Self-Assessment Exercises

32.1 (b)

32.2 | Infrared (IR) Spectroscopy



A high body temperature is usually an indicator that the body is fighting an infection. In times of epidemics, such as COVID-19, temperature measuring devices are frequently employed at the entrance to hospitals, at transport hubs and even large shopping centers to screen the general public for the first signs of an infection. It is important these devices do not touch the skin to prevent the risk of transmitting any possible infection from one person to another. Infrared thermometers are often used in these situations and provide a lightweight, robust, and relatively cheap device that is easy for the operator to hold in their hands. The heat we radiate is directly related to our body temperature and is detected as infrared radiation.

In this section, we use infrared radiation in the non-destructive analysis of molecules to determine if they contain some common functional groups. By the end of this section, you should be able

- To recognize if an analyte contains certain functional groups from their characteristic IR frequency of absorption.

Infrared photons (*infra*, Latin, meaning below or beneath) do not have enough energy to cause electronic transitions, but they can cause groups of atoms to vibrate about their respective bonds. These vibration transitions correspond to distinct energy levels. Molecules and, more importantly, the different functional groups contained within them, absorb IR radiation at specific wavelengths to induce the different vibrational modes within a covalent bond (that is, single, double, triple bonds). **Infrared spectroscopy** is the technique that records the absorption of infrared energy of a molecule as a function of energy. It identifies functional groups, but gives little structural information.

The position of an infrared band in an *IR spectrum* is defined by a **wavenumber** value (abscissa) and the band's percentage transmittance (%T) (ordinate), as shown in **Figure 32.4**. The wavenumber has traditionally been the most common method of specifying IR absorption, although sometimes the wavelength value (in microns) is also employed. The wavenumber is a type of frequency unit and is the true frequency divided by the speed of light. It corresponds to the number of waves per unit distance, chosen to be centimeters in IR spectroscopy (and, therefore, written in terms of cm^{-1}).

The absorbance of a sample is related to the **transmittance** by the equation:

$$\text{Absorbance} = -\log_{10}(\text{transmittance})$$

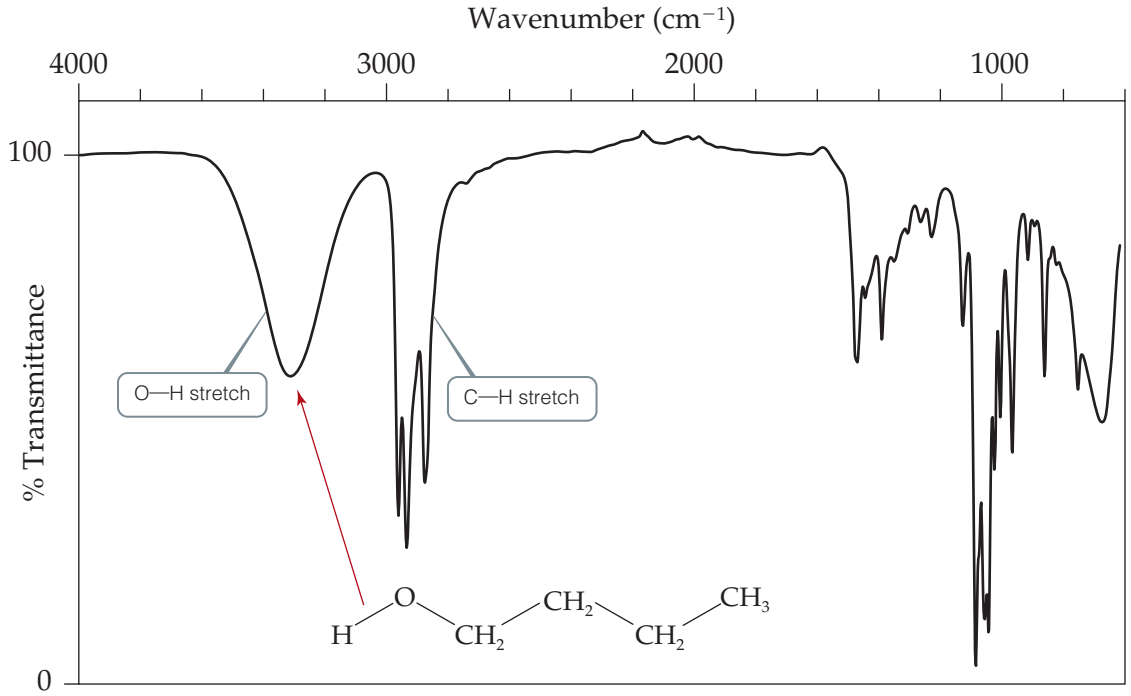
or

$$A = -\log_{10} T \qquad [32.2]$$

The value of transmittance (T) always lies between the values of 0 and 1 and the %T between 0 and 100.

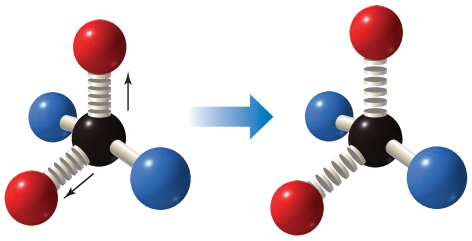
The Spring Model

Before discussing the characteristics of IR absorptions, it is helpful to understand some theory on molecular vibrations. To do this, let's consider the covalent bond between two atoms as a spring (**Figure 32.5**). This spring can be stretched (shown), compressed, bent or twisted, and then released from the input leading to the distortion. The output, which can be observed as a band within the IR spectrum, is in fact a vibration. The force needed

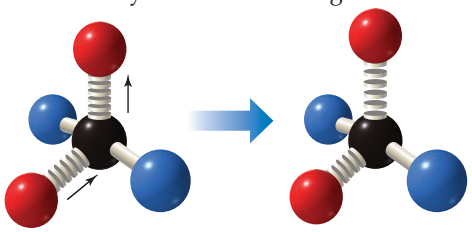


▲ **Figure 32.4 IR spectrum of butan-1-ol.** This IR spectrum is measured as a function of wavenumber (cm^{-1}). The ordinate describes the intensity, measured as percentage transmission (%T). In this spectrum of butan-1-ol, the broad, strong absorption at 3300 cm^{-1} is due to the strong O—H stretching vibrations that occur at this frequency.

Go Figure Do loose springs oscillate with a higher or lower frequency than tight springs?



Symmetric stretching



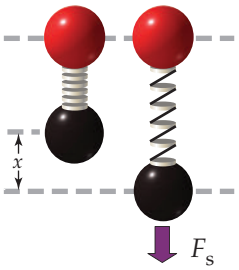
Asymmetric stretching

▲ **Figure 32.5 Spring model.** IR spectroscopy can be more easily understood by thinking of covalent bonds as springs. The stretching, bending or torsion of the spring leads to vibrations of a particular frequency. The vibrations can be modelled using Hooke's law.

to cause the vibration follows **Hooke's law**, which states that the elongation of a spring is proportional to the load applied. Mathematically:

$$F_s = -kx \qquad [32.3]$$

where F_s is the applied force (which equals the force exerted by the spring, only opposite in sign) in units of newtons (N), k is the spring constant (N m^{-1}) and x is the deformation of the spring (for example, stretching, with units m) from an equilibrium position (Figure 32.6). The strain in the spring is directly proportional to the load. In any system that can be described by Hooke's law, there exists a fundamental frequency of vibration, $\upsilon = \frac{1}{2}\pi\left(\frac{k}{m}\right)^{\frac{1}{2}}$. This is also true for molecules, so the frequency of vibration of any chemical bond depends on the mass (m) of atoms at the moving end of the bond and the stiffness (k) of the bond.



▲ **Figure 32.6 Hooke's law** of elasticity applied to a spring system states that the elongation of a spring is proportional to the load applied.

In a group of bonds with similar bond energies, the frequency decreases with an increase in atomic weight of the atoms. Of more interest to the organic chemist is the fact that stronger bonds (for example, double bonds) are generally "stiffer" than single bonds and require more force to stretch or compress them. As a result, stronger bonds usually vibrate faster than weaker bonds. For example, O—H bonds (D(O—H = 463 kJ/mol) are stronger than C—H bonds (D(C—H = 413 kJ/mol), so O—H bonds vibrate at higher wavenumber. Carbon–carbon triple bonds are stronger than carbon-carbon double bonds, so triple bonds vibrate at higher wavenumbers than do double bonds. In a group of bonds with atoms of similar masses, the frequency increases with increasing bond energy.

The absorption of energy into molecular vibrations is recorded in an IR spectrum. This spectrum gives a record of the energy absorbed as a function of the energy of radiation. An IR spectrum is recorded on an IR spectrophotometer. In the context of this course, we consider only certain vibrations: O—H stretching, C—H stretching, C=C stretching, C—C stretching, N—H stretching and C=O stretching. These stretching vibrations give rise to the easy identification of the most common functional groups in organic chemistry. The low-wavenumber region within the IR spectrum contains most of the complex vibrations and is commonly called the **fingerprint region** of the spectrum (300–1400 cm^{-1}). Although it is useful to know of this region, its use in identifying organic molecules is limited because of the complexity of the spectrum in this region. Inorganic chemists

find this region useful for the identification of metal–ligand (M—L) interactions. Organic chemists use the fingerprint region primarily to confirm the identity of a sample, by comparing it with an authentic spectrum of a known compound thought to be the same as the sample under investigation.

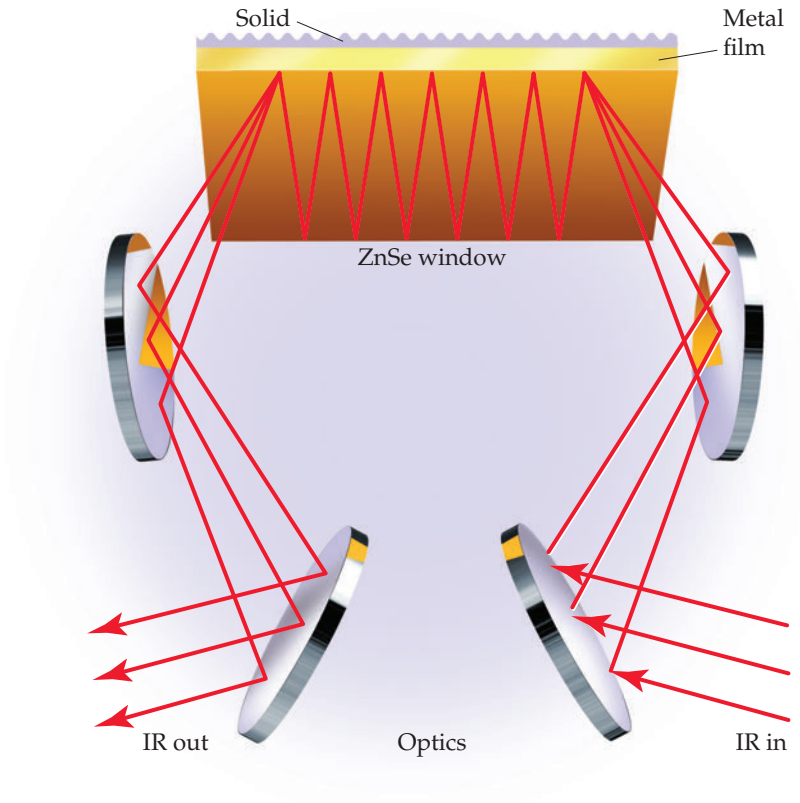
Stretching vibrations in the region 1550–3800 cm^{-1} are the most characteristic and predictable.

At this point, we should also recognize that not all molecular vibrations absorb IR radiation. Generally, only bonds with dipole moments (for example, O—H, C═O, N—H bonds) are IR active and hence result in IR absorptions. A dipole moment between two covalently bonded atoms is achieved when the two atoms differ significantly in their electronegativity.

If the molecule is placed in an electromagnetic field, its bonds interact with the field, usually leading to a change in the vibration of the covalent bond, and a change in the dipole moment of the bond. If a bond is symmetrical or has zero dipole moment, the applied field does not interact with the bond as strongly, and this very weak vibration is said to be *IR inactive*.

Measuring IR Spectra

IR spectra are measured using liquid, solid or gaseous samples placed in a beam of infrared light. Typically, if the sample is a liquid, the compound can be thinly spread *neat* (without solvent) between two thick plates of sodium chloride, which are transparent to infrared light for most of the important wavelength regions. Solid samples are usually prepared by grinding a sample into a paste with an organic oil known as nujol (a type of paraffin oil) forming a mull, which is also sandwiched between two thick NaCl plates. A more modern approach is to place a solid on an ATR diamond or ZnSe window cell and a spectrum taken directly (**Figure 32.7**). ATR stands for attenuated total reflectance. Gases typically require specialized cells.



▲ **Figure 32.7 Attenuated total reflectance (ATR) IR spectroscopy.** Modern IR spectrometers use a direct approach by measuring the transmittance of electromagnetic radiation through a sample placed on a diamond or ZnSe surface.

TABLE 32.1 Bond-stretching frequencies and their relationship to functional groups

Functional group	Stretching vibration frequency (cm^{-1})	Strength of IR band	Bond energy ($kJ\ mol^{-1}$)*
O—H	3200–3500	Strong, broad	465
N—H	3100–3500	Medium	390
C—H	2700–3100	Strong to medium	415
C≡N	2200–2400	Strong to medium	890
C≡C	2000–2200	Weak	840
C=O	1630–1800	Strong	800
C=N	1630–1680	Strong	615
C=C	1600–1680	Weak	615

* Bond energies rounded to the nearest 5 kJ mol.

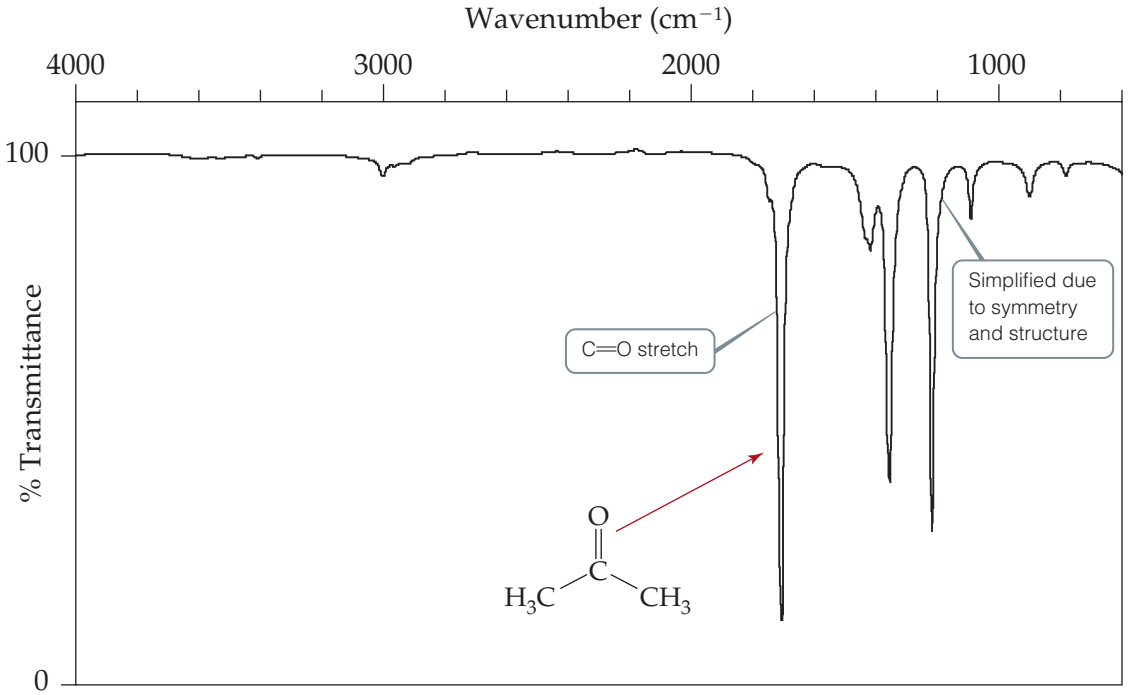
Table 32.1 illustrates the predicted regions where the most common functional groups absorb IR radiation. As mentioned earlier, strong bonds generally absorb at higher frequencies because of their greater "stiffness." Thus C—C single bonds absorb around 1200 cm^{-1}, C=C double bonds around 1600–1680 cm^{-1} and C≡C triple bonds around 2200 cm^{-1}. The absorption of C=C double bond vibrations in an IR spectrum are diagnostic and useful for structure determination. The position of C—C single bond absorptions in an IR spectrum are not very diagnostic because they occur in most organic compounds as part of the molecules' framework. Most double bonds produce observable absorptions in the region 1600–1680 cm^{-1}. Conjugation of the double bond has the effect of reducing the stretching frequencies from 1620–1640 cm^{-1} (in the case of an aliphatic C=C) to approximately 1600 cm^{-1} for an aromatic C=C. The lowering in frequency can be attributed to the loss of electron density in the double bonds due to the conjugation. As a result, conjugated double bonds are a little less stiff and vibrate a little more slowly than isolated double bonds, giving them lower frequencies of absorption.

Alkanes, alkenes, and alkynes have characteristic C—H stretching bands around 3000 cm^{-1}. Because of the prevalence of C—H bonds in organic molecules, the presence of a band at 3000 cm^{-1} makes it easy to identify the presence of an organic compound by IR spectroscopy. However, some organic molecules have very weak absorbances in this area. For example, the C—H stretching band in an IR spectrum of propanone (**Figure 32.8**) is very weak.

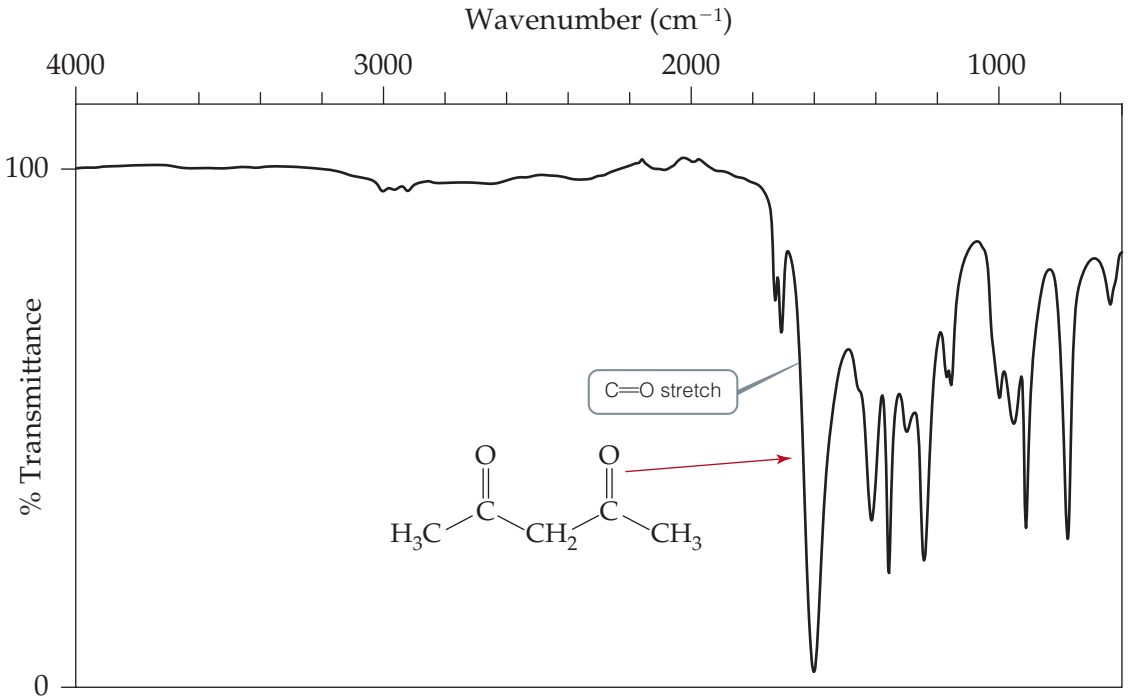
The large dipole moment change associated with the C=O double bond produces a strong IR stretching band around 1700 cm^{-1} as shown in Figure 32.8. The exact position of this band within the IR spectrum depends on the specific functional group present (ketone, aldehyde, amide, carboxylic acid or ester) and the environment created by the rest of the molecule. For these reasons, IR spectroscopy is often the best method for detecting and identifying the type of carbonyl group in an unknown compound.

The C=O double bond stretching vibrations of simple ketones, aldehydes and carboxylic acids occur around 1710 cm^{-1} (**Figure 32.9**). These are slightly higher than those of a C=C double bond because of the relative bond strengths (C=C < C=O, see Table 32.1). Some carbonyl absorptions do occur above 1710 cm^{-1}. For example, simple carboxylic esters absorb around 1735 cm^{-1} and ring-strained carbonyl groups, such as those found in cyclobutanone, occur around 1785 cm^{-1}. In addition to the C=C stretching band, an aldehyde shows the characteristics of two C—H stretching bands around 2700 cm^{-1} and 2800 cm^{-1} corresponding to the aldehyde C—H stretch, whereas a ketone or an acid does not produce these absorptions. Carboxylic acids produce a characteristic O—H absorption around 3000 cm^{-1} in addition to the intense carbonyl stretching absorption. The position of this O—H stretch within the IR spectrum is usually complicated as a result of the carboxyl group participating in hydrogen bonding, which also results in the broadening of the strong carbonyl absorption.

The carbonyl groups of amides absorb at particularly low IR frequencies (1640–1680 cm^{-1}). This very low frequency might be mistaken for an alkene C=C stretch if it weren't for two important features of its IR spectrum. The amide carbonyl absorption is much stronger than that of an alkene bond due to the difference in dipole moment



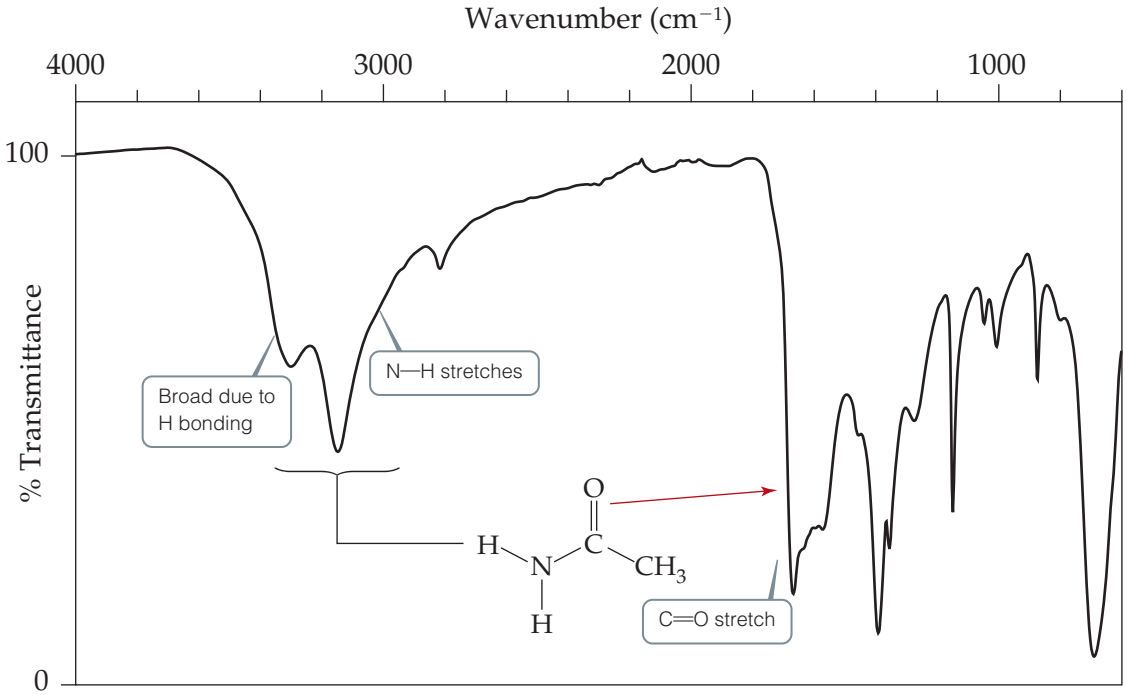
▲ **Figure 32.8 IR spectrum of propanone (acetone).** Note the simplicity of the spectrum and the presence of the dominant C═O stretch at 1710 cm^{-1}.



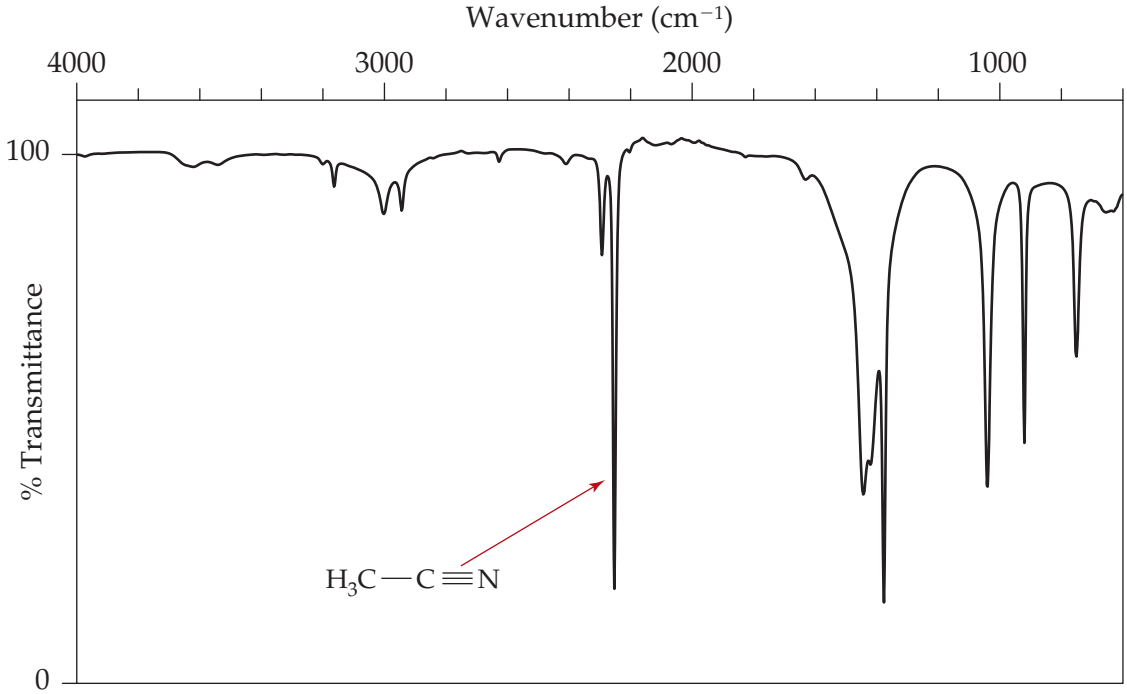
▲ **Figure 32.9 IR spectrum of 2,4-pentanedione.** Note the intense carbonyl stretching band at 1700 cm^{-1}.

between the two unsaturated bond types. Primary and secondary amides are also identified by the addition of a N—H stretching absorption around 3200 cm^{-1} (**Figure 32.10**).

The only other multiple bond stretch that we need to consider is that of the nitrile bond (C≡N). Because of the polarity of this C≡N triple bond, nitriles usually exhibit very strong absorbances around 2200 cm^{-1} (**Figure 32.11**) within their IR spectra. This value is similar to that for an alkyne (C≡C) stretch, although nitriles tend to absorb above 2200 cm^{-1} whereas alkynes absorb below 2200 cm^{-1}.



▲ **Figure 32.10 IR spectrum of acetamide.** This spectrum was taken of a sample as a crystalline solid, hence there is more information contained within the spectrum than is usually needed for functional group identification.



▲ **Figure 32.11 IR spectrum of acetonitrile.** This simple nitrile shows the characteristic and distinctive IR absorption band for C≡N at 2280 cm^{-1}.

The vibrational frequencies of O—H bonds (alcohols) and N—H bonds (amines) occur at higher wavennumbers than for C—H bonds. Alcohol O—H bands are typically broad, absorbing over a wide range of frequencies centered around 3300 cm^{-1}. Their broadness is attributed to hydrogen-bonding arrangements between functional groups within the same molecule—that is, they are *intramolecular*—or to interactions with other molecules, including solvent or absorbed water, interactions that are described as *intermolecular*. Therefore, the purity of a sample with respect to absorbed water needs to be taken

Sample Exercise 32.1

Distinguishing between constitutional isomers

How would you be able to use IR spectroscopy to distinguish between the following compounds:
(a) butan-1-ol and diethyl ether,
(b) ethyl acetate and butanoic acid?

SOLUTION

Analyze We are asked to differentiate between functional groups in compounds using IR.

Plan We need to identify the difference in functional groups between the two isomers in each set.

Solve Butan-1-ol shows a strong absorption in the O—H stretching frequency region, 3100–3300 cm^{-1}. Diethyl ether is devoid of any characteristic functional group absorptions $> 1500\ cm^{-1}$, apart from C—H stretching vibrations. In this case, the absence of the O—H absorption is diagnostic.

Both ethyl acetate and butanoic acid show a strong C=O stretching frequency absorption around 1710–1730 cm^{-1}. Although variations in this stretching frequency are possible and somewhat diagnostic, the best answer to this question is the addition of a strong absorption in the O—H stretching frequency region, approximately 3100 cm^{-1} for butanoic acid.

Practice Exercise

How would you be able to use IR spectroscopy to distinguish between these compounds:
(a) cyclohexane and cyclohexene,
(b) acetamide and ethylamine?

into account. Any water that is present will also absorb at these frequencies, complicating the results by giving a false positive for an O—H group. This is usually overcome by extended drying of the sample before analysis by IR spectroscopy.

The amine N—H bond also has a stretching frequency around 3300 cm^{-1} and, like alcohols, these amines participate in *intra-* and *inter*-molecular hydrogen bonding. The difference between O—H and N—H stretches lies in the shape of the band. Although O—H stretches are broad, N—H stretches are sharper. Primary amines typically have two absorptions in their N—H absorption band, whereas secondary amines have only a single absorption band. The presence of water in an amine sample typically leads to one or two sharp spikes superimposed on the broad area of the water O—H stretching absorption. Again, drying the sample distinguishes a wet sample from one containing both an O—H and N—H functional group.

Being able to interpret an IR spectrum is a useful skill. Typically, IR spectra need to be interpreted in conjunction with other techniques. Sections 32.3 and 32.4 deal with two other powerful spectroscopic techniques.

Self-Assessment Exercise

32.2 A molecule of formula C_4H_8O has a weak absorption around 1600 cm^{-1}, no absorption in the region 1630–1800 cm^{-1} and no absorption in region 3200–3500 cm^{-1}. Which of the following compounds would fit this data?

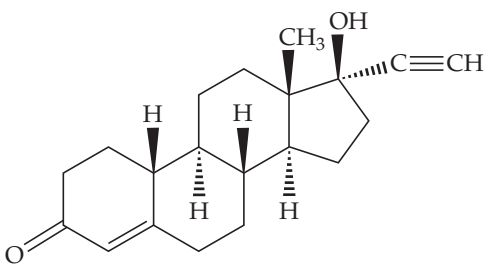
(a) but-3-en-1-ol
(b) butanal
(c) butanone
(d) ethoxyethene

Exercises

32.3 Identify a possible functional group that might be responsible for the following IR absorptions:

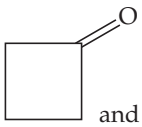
(a) 3500 cm^{-1}
(b) 1705 cm^{-1}
(c) 1650 cm^{-1}
(d) 1710 and 3400 cm^{-1}
(e) 1680 and 3200 cm^{-1}

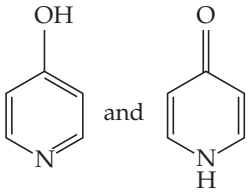
32.4 Norethidrone is a steroid used primarily as an oral contraceptive. Its synthesis was first achieved in 1951. Indicate which parts of the structure of norethidrone have characteristic absorptions identifiable by IR spectroscopy. Indicate their approximate positions in wavenumbers (cm^{-1}).



32.5 How might you use IR spectroscopy to help distinguish between the following pairs of compounds?

(a) $CH_3CH_2OCH_2CH_3$ and $CH_3CH_2CH_2CH_2OH$

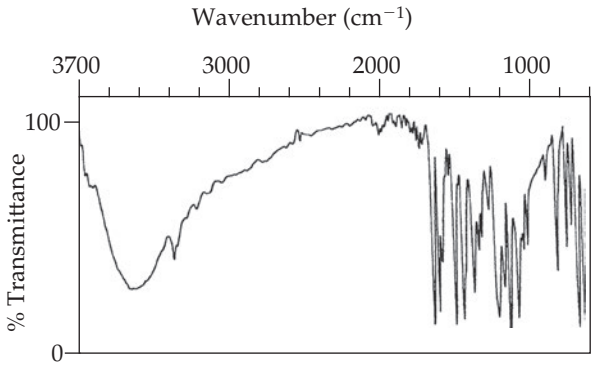
(b)  and $CH_2{=}CHCH_2OH$

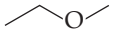
(c) 

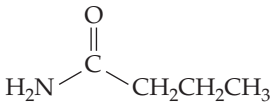
(d)  and $CH_3CH{=}CHCH_2CH_3$

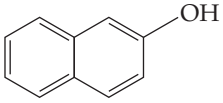
(e) $(CH_3)_3N$ and $CH_3CH_2NHCH_3$

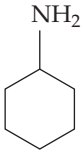
32.6 Which of the following structures is consistent with the IR spectrum shown here?



(a) 

(b) 

(c) 

(d) 

Answers to Self-Assessment Exercises

32.2 (d)

32.3 Nuclear Magnetic Resonance (NMR) Spectroscopy



The twin discoveries that led to superconducting magnets were made by Dutch man Heike Kamerlingh Onnes. In 1908, he was the first to liquify helium, and, three years later, he was the first to observe superconductivity in metals cooled to extreme temperatures.

Helium boils at −269 °C, just four degrees above absolute zero, and it was at this temperature that Onnes observed that the resistance of a mercury wire dropped to zero. He adopted the term *superconductivity* to describe this new state and recognized the potential to construct extremely strong magnets. However, it was not for another forty years that a material (niobium) was found that could handle the large current densities present in an ultra-strong magnet. Now, a niobium-titanium or a niobium-tin alloy is used in superconducting magnets. This metal core is cooled by liquid helium, which is surrounded by a jacket of liquid nitrogen. The magnet field produced is typically ten times stronger than can be achieved with traditional iron-core magnets as well as being a more stable, homogenous field.

The discovery of superconducting magnets opened many doors. In this section and the next, we examine two techniques, both of which utilize superconducting magnets in order to achieve very high-resolution analysis. Superconducting magnets are also pivotal to the magnetic resonance imaging of soft body tissue, research into nuclear fusion reactors, and the construction of magnetically levitated trains being developed in Japan.

By the end of this section, you should be able to:

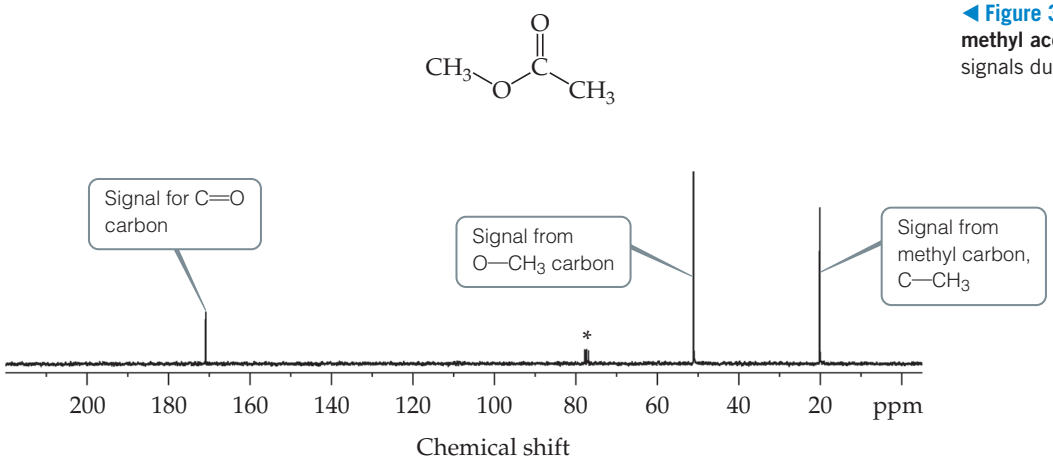
- Identify nuclei that can resonate in a magnetic field (i.e., are NMR active)
- Predict the NMR spectra of simple organic molecules
- Interpret an NMR spectrum to give structural information on a molecule

As a technique, **nuclear magnetic resonance (NMR) spectroscopy** is probably the most powerful tool in the organic chemist's research arsenal. It is a non-destructive technique that requires little sample (typically 2–10 mg for ^{1}H NMR and 20–40 mg for ^{13}C NMR spectroscopy). It has become a routine technique, due mainly to the advent of Fourier Transform NMR (FT-NMR), which provides for very rapid data acquisitions (typically 10 minutes), although more demanding experiments take longer (overnight). NMR gives us information about structure, so it is extremely useful for identifying unknown substances or confirming known structures. In the latter case, NMR spectroscopy is also useful for indicating the purity of a sample (to approximately 97%) and for observing the stability of a substance in solution. Even if you are do not intend to study chemistry in future years, the logical nature of the problem-solving skills developed by using this and the other techniques discussed in this chapter will be beneficial for your chosen science.

NMR spectroscopy is a technique that yields important structural information about a molecule by observing the interplay of the different nuclei, such as ^{1}H, ^{13}C, ^{15}N, ^{31}P, contained within it. The sensitivity of NMR spectroscopy allows us to also identify subtle differences in the same nuclei within a molecule based on their neighboring functional groups, whose influence over a strong magnetic field is measurable. This section concentrates on two forms of NMR spectroscopy: ^{1}H and ^{13}C NMR spectroscopy. Information about the number and different types of hydrogen environment within a compound, their connectivity and their relationships will be explored using ^{1}H NMR spectroscopy. Information on the different types of carbon environment present in a compound will be gained using ^{13}C NMR spectroscopy.

Let us begin our discussions on NMR spectroscopy by looking at a simple example. The ^{13}C NMR spectrum shown in **Figure 32.12** has three signals (or peaks), indicating that there are three different types of carbon environments within this compound, methyl acetate. The positions of these signals along the axis yields information about neighboring functional groups that allows us to assign each carbon environment to a signal with confidence. However, to understand the reasons why we can interpret the spectrum shown in Figure 32.12 the way we do, we need to gain an understanding of the background theory to NMR spectroscopy.

From Chapter 6, you should already be familiar with the concept that an electron has an associated magnetic field. Any atomic nucleus that has an odd number of protons or an odd number of neutrons will have a non-zero nuclear *spin* and resulting nuclear magnetic moment (μ). Like electron spin, nuclear spin is quantized. The allowed nuclear magnetic spin states are determined by the nuclear spin quantum number (I) of the nucleus.

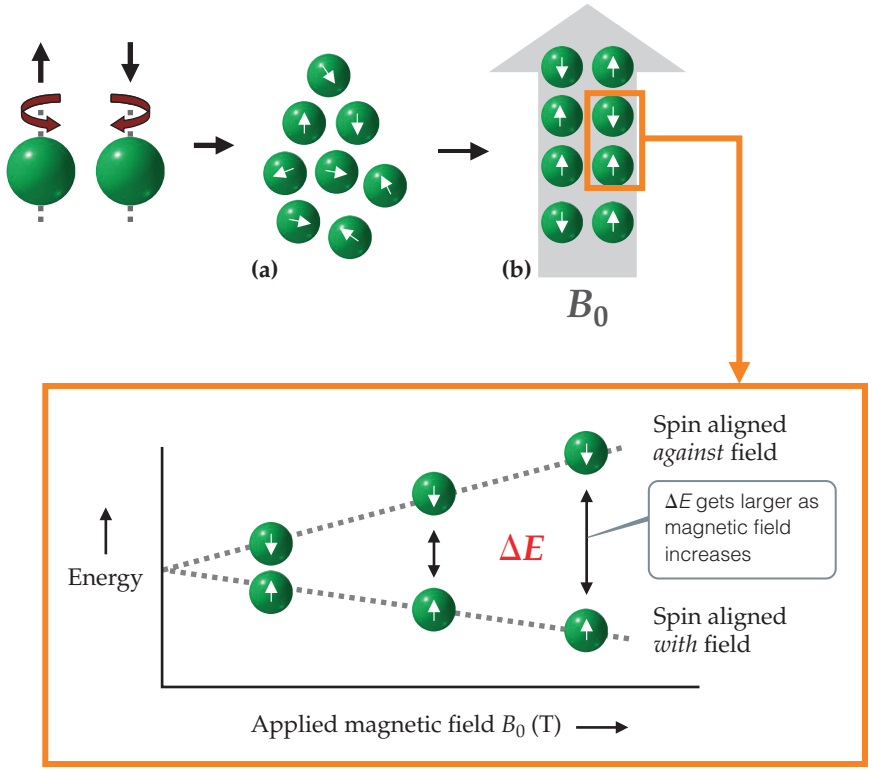


◀ **Figure 32.12 ^{13}C NMR spectrum of methyl acetate.** The asterisk indicates signals due to $CDCl_3$ solvent.

A nucleus with a spin quantum number of I ($I = 0, \frac{1}{2}, 1, \frac{3}{2}, 2$, etc.) has $(2I + 1)$ spin states. If $I = \frac{1}{2}$, as for ^{1}H and ^{13}C, there are two allowed spin states with values of $+\frac{1}{2}$ and $-\frac{1}{2}$. This spinning charge creates an associated magnetic field that behaves as if it is a tiny bar magnet with a magnetic moment (μ).

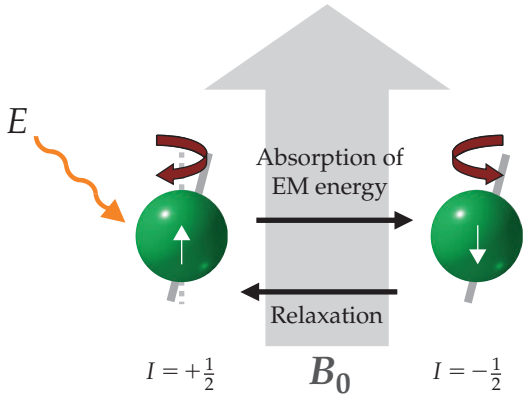
In the absence of external effects, such as an applied magnetic field, the two spin states have the same energy, as shown in **Figure 32.13(a)**, and completely random orientations. However, when the nuclei are placed in a strong external magnetic field, their spins can align parallel (with) or anti-parallel (against) to the field, giving rise to two energy

Go Figure Why would an increase in applied magnetic field strength increase the population differences between two spin states?



▲ **Figure 32.13 Nuclear spin.** Like electron spin, nuclear spin generates a small magnetic field and has two allowed values for ^{1}H and ^{13}C. In the absence of an external magnetic field (a), the two spin states have the same energy and a random orientation. If an external magnetic field is applied (b), the parallel alignment of the nuclear spin to the magnetic field is lower in energy than the anti-parallel alignment. The energy difference, ΔE, corresponds to the radiofrequency portion of the electromagnetic spectrum. The weaker the applied magnetic field, the smaller this difference is.

states. The parallel alignment is lower in energy than the anti-parallel one by an amount of energy ΔE, the size of which depends on the strength of the applied magnetic field (B_0) and the type of nucleus absorbing the radiation (Figure 32.13). For an applied field strength of 7.05 T (T = Tesla), which is readily available with modern-day superconducting electromagnets, the difference in energy between the two aligned spin states (with and against) is about 0.1 J/mol. This is a very small quantity on the chemical energy scale. NMR spectroscopy is considered a ground-state phenomenon.



▲ **Figure 32.14 Nuclear spin flip.** When Rf radiation of a frequency that corresponds to ΔE is applied, the parallelspin nuclei absorb this energy and their spins flip to an anti-parallel orientation. Although nuclei are described as aligning in a parallel or anti-parallel fashion, the axis of rotation is tilted, causing the nucleus to precess about its own axis of spin in a similar manner to a spinning top.

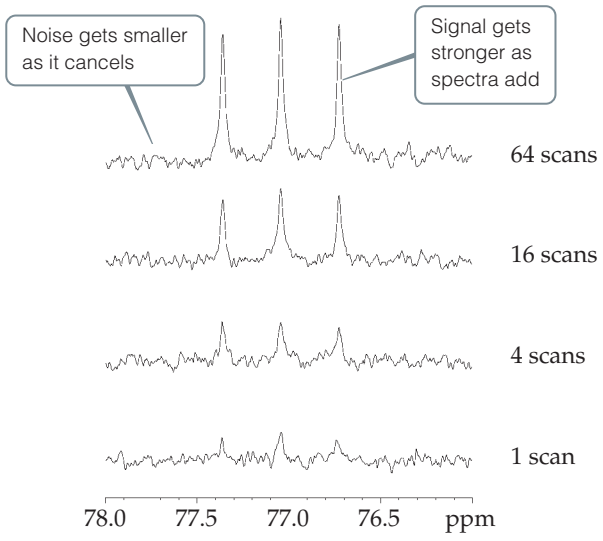
Nuclear Magnetic Resonance Frequencies

Based on your knowledge of thermodynamics, you would expect that the lower-energy state would have a higher population of nuclear spins aligned with the field compared with those aligned anti-parallel to the field (despite the small value of ΔE) because these aligned spins are lower in energy. If the nuclei being monitored by NMR spectroscopy are irradiated with electromagnetic radiation equal to the difference in energy between the two spin states in the applied magnetic field (ΔE), energy is absorbed and the spin of the nuclei can be "flipped"—that is, excited from a parallel to an anti-parallel alignment, as shown in **Figure 32.14**. The radiation used in ^{1}H NMR spectroscopic experiments is in the radiofrequency (Rf) range, typically 200–900 MHz. This radiofrequency is known as the spectrometer's **operating frequency**. The frequency at which the nuclei absorb energy is called the **Larmor frequency**. The absorption of this electromagnetic radiation, and the flip of its nuclear spin from a lower state to a higher state (and *vice versa*), is called **resonance**. Detection of the flipping of nuclei between the two spin states leads, after detection and mathematical manipulation (called Fourier Transform), to the NMR spectrum.

For NMR spectroscopy to be useful, the difference in population between the two aligned spin states needs to be significant. The greater the applied magnetic field, the greater the population difference between the two states (Figure 32.13). The more significant this difference is, the more *sensitive* the technique becomes. A greater sensitivity improves the spectrum acquisition time and lowers the amount of sample needed by providing a better *signal-to-noise ratio*. Acquiring and adding together multiple spectra of the same sample also increases the *signal-to-noise ratio* as shown in **Figure 32.15**. An increase in resolution allows us to gain more information on the connectivity of nuclei within a molecule. This is why chemists desire to have spectrometers with more powerful superconducting magnets (**Figure 32.16**).

From our discussions on NMR theory so far, you might expect that all ^{1}H or ^{13}C nuclei in a molecule would absorb energy at the same frequency. If this were the case, this technique would be of little use for structural determination. Luckily, the absorption frequency is not

▶ **Figure 32.15 75 MHz ^{13}C NMR spectrum of $CDCl_3$** showing improvement of the signal-to-noise ratio from one scan (bottom spectrum) to 64 scans (top spectrum).





(a) (b)

◀ **Figure 32.16 A modern NMR spectrometer**. This 400 MHz NMR spectrometer shows (a) the superconducting magnet in the foreground with the return lines required to pump the liquid helium into the system to cool the magnet. In the background is the computer mainframe required for Fourier transformations. (b) The desktop computer, showing an initial free induction decay (FID) curve, is interfaced with the spectrometer for data manipulation.

the same for all ^{1}H or all ^{13}C nuclei because, in organic molecules, these nuclei are not isolated from each other or other atoms. Each nucleus is surrounded by electrons from other atoms, or groups of atoms, that can create local magnetic fields (B_{local}) that influence the applied field. This statement can be written in the following way:

$$B_{effective} = B_{applied} - B_{local} \qquad [32.4]$$

The result of the influence of these local magnetic fields is a **shielding** of the nuclei in question from the applied field by reducing its effect. In some instances, the local magnetic field of neighboring electrons can add to the applied field, **deshielding** the nuclei in question. The difference in resonance frequencies for various ^{1}H or ^{13}C nuclei within a molecule due to shielding or deshielding is generally very small but measurable. Such a difference leads the two nuclei in question to be *magnetically inequivalent*.

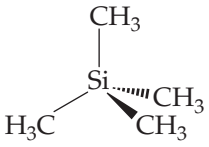
In fact, for a particular magnetic field B_0, the resonance frequencies of ^{1}H and ^{13}C are quite different. This is naturally advantageous when investigating either type of nuclei in isolation.

The Chemical Shift

Let us now consider the simplest case of a single ^{1}H nucleus within an applied magnetic field. Absorption of energy at the resonance frequency, which leads to the nuclear spin flip as shown in Figure 32.14, results in a detectable signal. However, because the resonance frequency depends on several factors, including the magnetic field strength (B_0) and the operating frequency of the spectrometer, chemists have developed a dimensionless quantity called the **chemical shift (δ)**, expressed in parts per million (ppm), to quantify the result. The chemical shift scale takes into account the shift in frequency of a particular nucleus from a standard (accepted universally to be tetramethylsilane, TMS), as well as the operating frequency of the spectrometer:

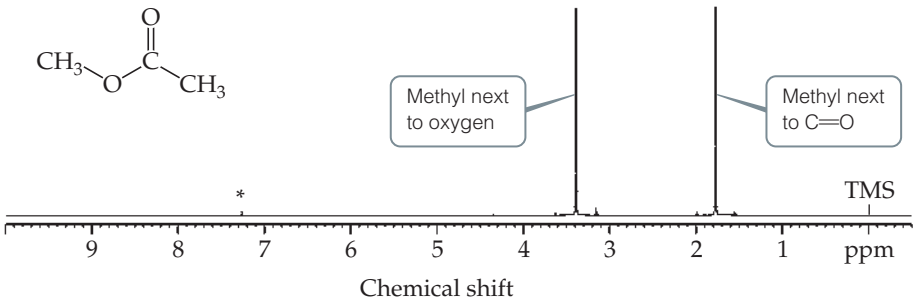
$$\delta = \frac{\text{Shift in resonance frequency from TMS (Hz)}}{\text{Operating frequency of the spectrometer (MHz)}} \qquad [32.5]$$

The chemical shift of an NMR absorption signal is constant, regardless of the operating frequency of the instrument. This is because the chemical shift scale is relative. Using δ allows a comparison between NMR spectra obtained on different spectrometers in different laboratories across the world.



tetramethylsilane

The chemical shift of a ^{1}H nucleus that is strongly influenced by the electrons of an adjacent atom has a different chemical shift from a nucleus that is weakly influenced by neighboring electrons. This change in chemical shift is important and is diagnostic. Any competent organic chemist can use the information of functional group effects on



▶ **Figure 32.17 300 MHz ^{1}H NMR spectrum of methyl acetate** (inset) acquired in $CDCl_3$ solvent. The residual solvent is marked with an asterisk (*). Compare with the ^{13}C NMR spectrum of the same compound in Figure 32.12.

chemical shift to identify potential "leads". For example, the ^{1}H NMR spectrum of methyl acetate is shown in **Figure 32.17**. This compound has two "different" types of methyl groups: one adjacent to the carbonyl group and the other directly bonded to oxygen. The difference lies in the fact that the two methyl groups are *not* related by symmetry, that is, they are non-identical. Their effective magnetic fields, and hence δ, differ because the effects of the electrons associated with the neighboring carbonyl group and oxygen atom on the applied field are different—this is called *magnetic inequivalence*.

If a hydrogen is partially shielded from the applied field by local magnetic fields, the signal occurs *upfield* towards tetramethylsilane (TMS) (**Figure 32.18**). This is a shift to lower frequency. If the magnetic environment reinforces the applied field, the hydrogen is deshielded and the signal moves *downfield*, away from TMS. This is a shift to higher frequency. So, in the example of methyl acetate, the signal at δ3.39 is *downfield* of the signal at δ1.78.

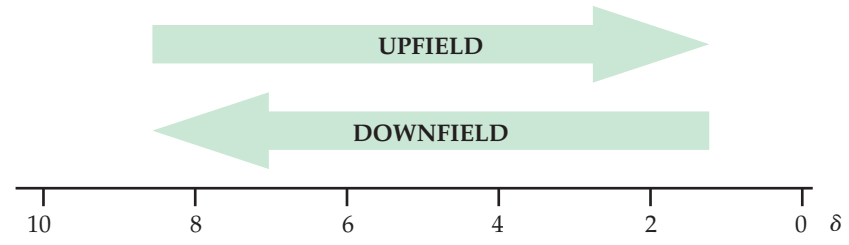
Notice that the hydrogen atoms on each methyl group are equivalent to each other but different from the other methyl hydrogen atom set. Hence only two signals are seen, at 1.78 ppm and 3.39 ppm, in the ^{1}H NMR spectrum. The reason why the hydrogens of a methyl group form part of the same signal lies in the speed of rotation about the C—CH_3 or O—CH_3 bonds in methyl acetate. We mentioned in Chapter 24 that aliphatic alkanes are dynamic molecules, with free rotation about any single bond. This rotation is faster than the timescale of the NMR spectrometer at 300 K (which is the standard operating temperature of a spectrometer), so each hydrogen on the methyl group appears to be equivalent.

A spectrometer with an operating frequency of 400 MHz has a timescale of 400 000 000 times per second. Although several molecular dynamic events, such as rotation about a C—C bond, are faster than this, quite a few are slower—for example, hydrogen exchange rates and some conformational processes. These differences in timescale mean that NMR spectroscopy is a useful technique with which to study kinetic events.

Sample Preparation

Two other signals in the ^{1}H NMR spectrum of methyl acetate need to be accounted for. The first signal is arbitrarily assigned to 0.00 ppm and is a result of the 12 equivalent hydrogens of the reference compound, TMS, which is added to the NMR solvent. Historically, all other

Go Figure Is a methyl group resonance at 3.4 ppm shielded or deshielded compared with one at 1.8 ppm?



▲ **Figure 32.18 Chemical shift.** The term *downfield* refers to a higher chemical shift. Nuclei at high chemical shift are relatively *deshielded* by neighboring electron motions. A hydrogen resonance that is *upfield* resonates at a lower chemical shift value. These hydrogens are relatively *shielded* and are the furthest from the resonance of a bare hydrogen atom.

TABLE 32.2 Common solvents used for sample preparation in ^{1}H and ^{13}C NMR spectroscopy and the chemical shift of the residual solvent signal

Solvent	Residual solvent	δ_H (ppm)	δ_C (ppm)
$CDCl_3$	$CHCl_3$	7.26	77.16
CD_3OD	CHD_2OH	3.31	49.00
CD_3COCD_3	CHD_2COCD_3	2.05	29.84 206.26[a]
D_2O	HOD	4.79	—
CD_3CN	CHD_2CN	1.94	1.32 118.26[b]
$(CD_3)_2SO$	CHD_2SOCD_3	2.50	39.52

Data: H.E. Gottlieb, V. Kotlyar, A. Nudelman, *Journal of Organic Chemistry*, 1997, *62*, 7512.
[a] Value corresponds to carbonyl carbon.
[b] Value corresponds to nitrite carbon.

^{1}H signals are reported by their shift from TMS. Modern NMR spectroscopy, however, typically uses the *residual solvent signal* as the spectrum reference (see **Table 32.2**). There are two reasons for this. The addition of TMS (1% *v*/*v*) to a sample compromises the purity of the sample, even though it is usually removed easily by evaporation. Second, the sample needs to be in solution for this technique to be effective and, as there is usually some source of ^{1}H present in the solvent, a marker independent of the sample exists. This leads us to the last signal to be discussed from Figure 32.17, that of solvent.

Recall from our initial discussion on the theory of NMR spectroscopy that any nuclei with a magnetic moment other than zero would produce an NMR spectrum. This means that ^{13}C produces an NMR signal while ^{12}C does not. Another way of saying this is that ^{12}C is *transparent* to the technique of NMR spectroscopy at the frequencies employed.

Typically, organic chemists use solvents to prepare an NMR sample, as a means of making the sample *homogeneous*. The type of solvent used is important because we need to distinguish between signals attributable to the sample and those from the solvent, especially when the solvent is in concentrations greater than 500 times that of the compound of interest in the preparation. This means that any solvent that contains hydrogens will also give rise to a ^{1}H NMR signal, which will be at least 500 times stronger than that of the sample. The effect is to "lose" the important sample signals.

To counter this problem, organic chemists use a range of ^{1}H NMR transparent (known as *deuterated*) solvents. Solvents such as deuterated chloroform ($CDCl_3$) or d_4-methanol (CD_3OD) become useful and common solvents in ^{1}H NMR spectroscopy because ^{2}H absorbs at a completely different frequency from ^{1}H, so does not interfere. However, although $CHCl_3$ or CH_3OH become unattractive in ^{1}H NMR spectroscopy for reasons described earlier, they are acceptable solvents in ^{13}C NMR spectroscopy. It is almost impossible (and certainly very expensive) to produce large quantities (liters) of 100% (v/v) pure deuterated solvents. Typically, an NMR spectroscopy laboratory would stock, for example, 99.8% $CDCl_3$ solvent. The extra 0.2% would contain protium rather than deuterium. This amount of $CHCl_3$ is still enough to produce a significant signal (known as the *residual solvent signal*) in the ^{1}H NMR spectrum of any sample (see Figure 32.17).

Interpreting NMR Spectra

Three components of an NMR spectrum provide useful structural information about a molecule. They are:

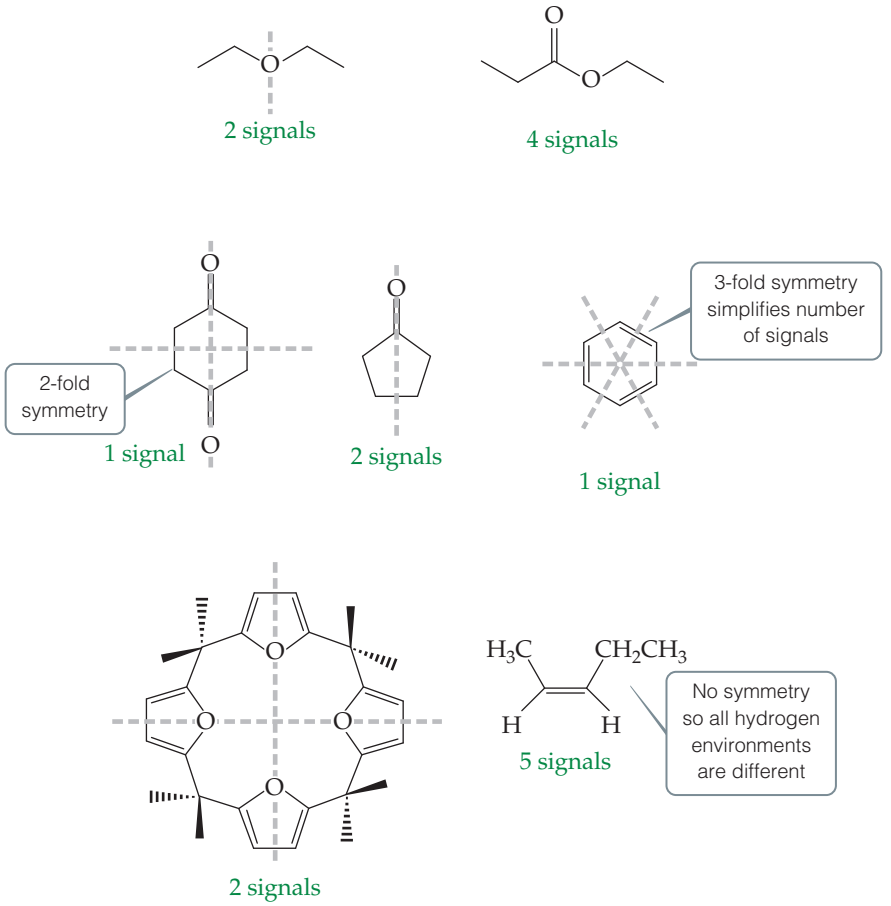
- *chemical shift* (δ)—gives evidence on neighboring functional groups;
- *integration* of the NMR signal—relative areas of signals in a ^{1}H NMR spectrum are proportional to the number of hydrogens giving rise to each signal;
- *coupling constant* (*J*)—measured in hertz (Hz), the coupling constant is extremely useful for determining the connectivity of nuclei within a molecule.

As you might expect, the result of an NMR spectroscopic experiment could become very complicated even with simple molecular structures. Luckily, molecular symmetry elements help to simplify matters. These symmetry elements occur in two ways. If the molecule has a plane of symmetry, then the two halves are identical and we need only concern ourselves with one-half of the molecule in order to work out its NMR spectrum. A few examples of the effects of symmetry on ^1H are shown in **Figure 32.19**.

The second factor that simplifies a NMR spectrum was introduced in our earlier discussion on rotation about C—CH_3 bonds. In fact, this dynamic behaviour of rotation about C—C bonds usually leads to the two hydrogens on a methylene (CH_2) group being chemically and magnetically equivalent (Figure 32.19). This simplification using symmetry is a powerful way to differentiate between two constitutional isomers.

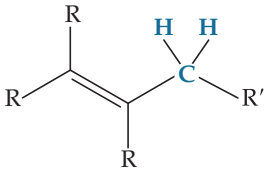
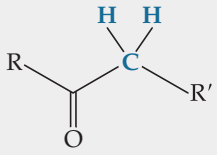
The typical ^1H and ^{13}C NMR chemical shifts for hydrogens and carbons with neighboring common functional groups are shown in **Table 32.3**. The ^1H signal associated with simple alkanes tends to resonate between 0.8 and 1.8 ppm, depending on their classification as primary, secondary or tertiary hydrogen atoms. The general trend for all other organic molecules is that δ depends on the electronegativity of nearby atoms and the hybridization of adjacent atoms. Thus the greater the electronegativity of a neighboring group (F > Cl > Br > I), the more deshielded the ^1H nucleus will be and the further downfield (higher δ) the ^1H NMR signal will lie. More than one electronegative group influences the signal even more, causing the ^1H signal to move further downfield (**Figure 32.20**).

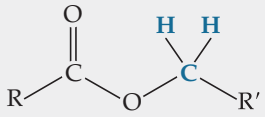
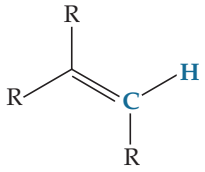
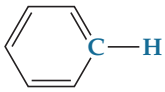
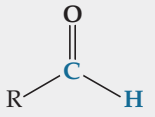
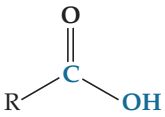
Go Figure How many signals would you expect in the ^{13}C NMR spectrum of the molecules shown in this figure?



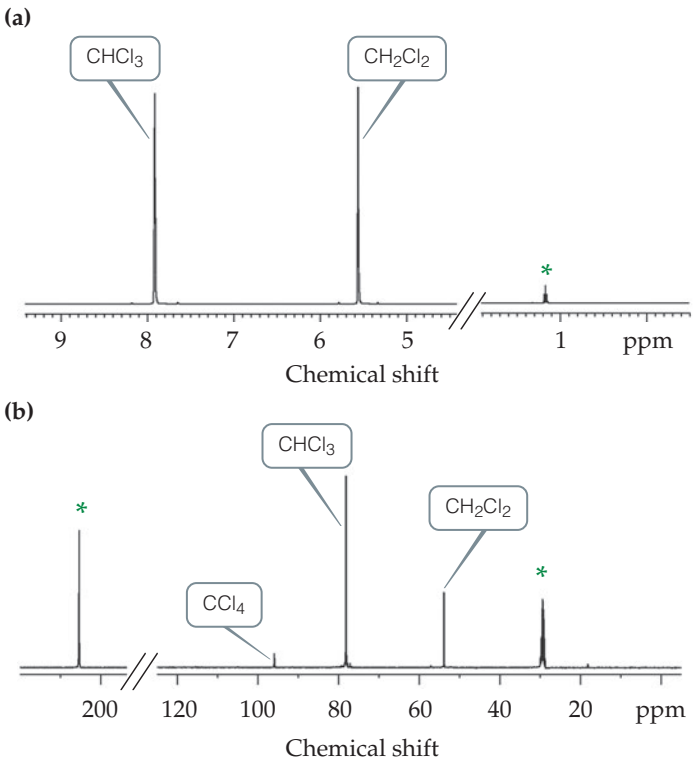
▲ **Figure 32.19 Symmetry.** The number of NMR signals present in a spectrum depends on the symmetry of the compound in question. The higher the symmetry, the smaller the number of signals in the spectrum. Molecules with a single set of equivalent hydrogens will give rise to one ^1H NMR signal. Two or more sets of equivalent hydrogens will give different ^1H NMR signals for each set. Here, the number of signals seen in the ^1H NMR spectrum of each compound is indicated.

TABLE 32.3 Approximate chemical shift regions for ^1H and ^{13}C nuclei (colored) neighboring the most common functional groups

Type of neighboring group[a]	δ_H[b,c]	δ_C[c]
R**C**H_3, R**C**H_2R′, R_3**C**H	0.8–1.6	10–55
	1.5–2.5	40–80
	2.0–2.8	40–80
Ar**C**H_3, Ar**C**H_2R	2.0–3.0	20–40
R—C≡C—**H**	2.0–3.0	65–85
R**C**H_2X (X=Cl, Br, I)	3.0–4.0	40–80
R**C**H_2OR′	3.0–4.0	40–80
R**C**N	n/a	110–130

Type of neighboring group[a]	δ_H[c]	δ_C[c]
	3.5–4.5	40–80
	4.5–6.0	100–150
RO**H**, RNH_2[d]	0.5–6.0	n/a
	6.5–8.5	110–160
	9.5–10.5	180–210
	10–13	175–185

[a] R and R′ refer to simple aliphatic groups; Ar refers to an aromatic ring.
[b] Note that, when the symbol δ is used, there is no need to add ppm. Remember, chemical shift is dimensionless and ppm is not a dimension.
[c] Chemical shifts referenced to TMS.
[d] Both OH and NH NMR absorptions are typically broad as a result of the hydrogen exchange they exhibit with solvent and traces of water within the solvent.



◀ **Figure 32.20 Effect of electronegative atoms neighboring ^1H and ^{13}C nuclei on their chemical shift.** (a) 300 MHz ^1H NMR spectrum of $CHCl_3$ and CH_2Cl_2 in $(CD_3)_2CO$. (b) 75.5 MHz ^{13}C NMR spectrum of CCl_4, $CHCl_3$ and CH_2Cl_2 in $(CD_3)_2CO$. Asterisks indicate solvent or residual solvent signals.

Sample Exercise 32.2

Determining the number of NMR signals in a spectrum

How many absorptions would you expect in the ^{1}H NMR spectra of:
(a) 1,1-dimethylcyclohexane,
(b) ethyl methyl ether?

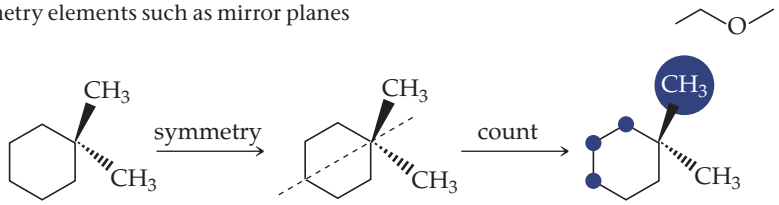
SOLUTION

Analyze We are asked to determine the number of "different" hydrogen environments in two molecules.

Plan We need to draw out the structure of each compound and look for symmetry. If no symmetry elements such as mirror planes exist, we then count up the number of *different* hydrogen atoms, remembering that hydrogens on the same carbon are equivalent in an alkane.

Solve

(a) The answer is four absorptions.
(b) The answer is three absorptions. In this case, there is no symmetry across the molecule.

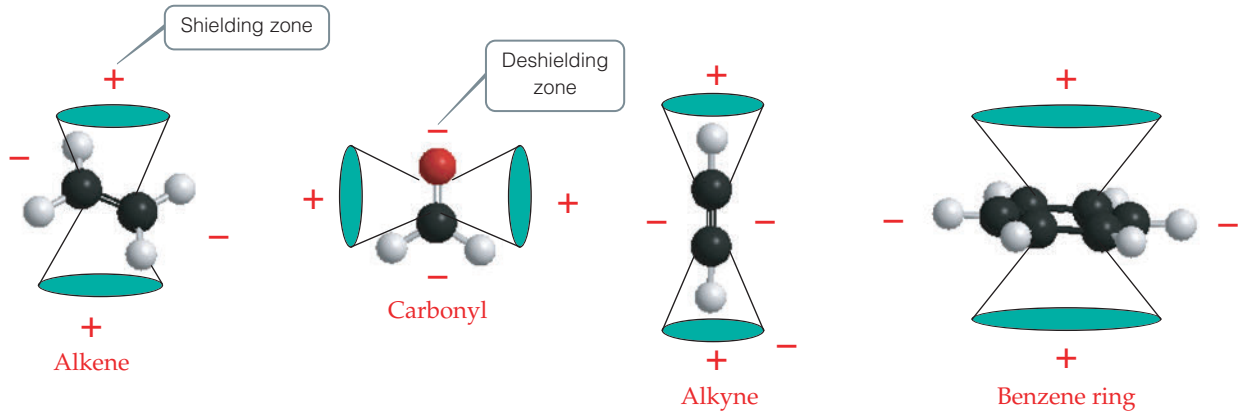


Practice Exercise
How many absorptions would you expect in the ^{13}C NMR spectra of:
(a) cyclohexanone
(b) 2-methyl-2-butene?

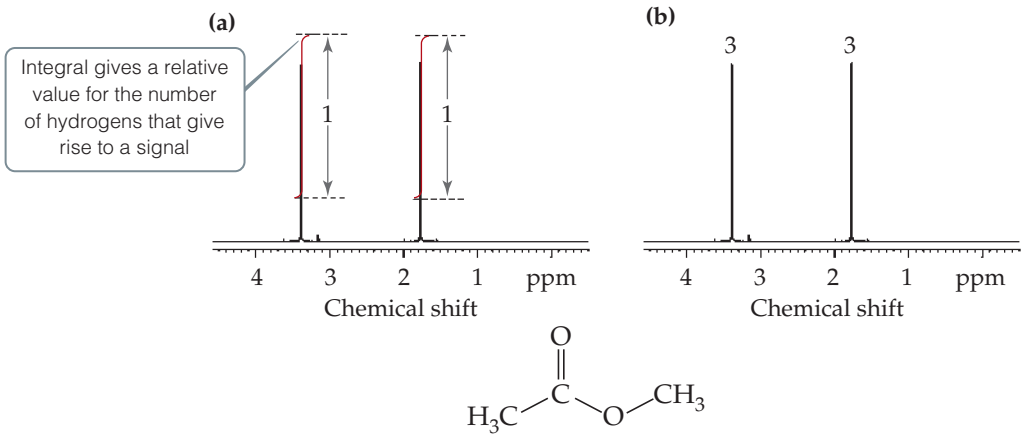
The chemical shift is also influenced by the hybridization of neighboring atoms (Figure 32.21). Generally, the more *p* character in a neighboring atom ($sp > sp^2 > sp^3$), the higher the chemical shift will be for the observed nucleus. This change in δ is due to the deshielding effect from the applied magnetic field produced by these bonds, as indicated in Figure 32.21. Note that orientation is an important factor in this generalization. The hydrogens on benzene are in a deshielding (−) zone, whereas those of ethyne, the carbons of which have more *p* character, are in a shielding (+) zone. In any case, the chemical shift of the signals attributable to either set of hydrogens is higher than that of a simple alkane.

Integration

Recall that in mathematical terms, **integration** refers to the area under a curve. The term *integration* in NMR is used to describe the area under each signal and is proportional to the number of equivalent nuclei that give rise to that signal. Integration is diagnostic in ^{1}H NMR experiments but used rarely in ^{13}C NMR experiments.



▲ **Figure 32.21** Deshielding effects in alkenes, carbonyls, alkynes and benzene. The magnetic fields associated with the π-electrons of the *sp* and sp^2 hybridized atoms cause regions of shielding (+) and deshielding (−) that influence the chemical shift of adjacent nuclei.



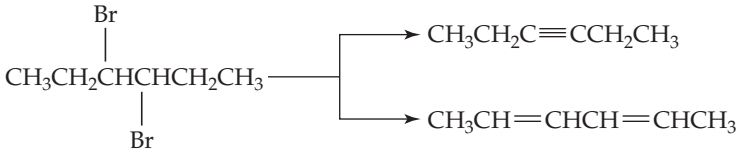
◀ **Figure 32.22 Integration.** (a) Integral lines indicate the area under the signal. This technique doesn't necessarily indicate how many hydrogens each signal accounts for, only their relative areas. (b) This method indicates the number of hydrogens associated with each signal. Both (a) and (b) yield the same information.

Two conventions describing the integration of a signal are used, as shown in **Figure 32.22**. The first method uses the height of the integral to give an area relative to other signals. For example, a ratio of areas that is 1 : 1 may in fact refer to a hydrogen ratio within the compound of 3 : 3, as for methyl acetate. An alternative method (and the one we use more often) does all the hard work for you. The numbers above the signals in Figure 32.22(b) equate to the numbers of protons that give rise to those signals. This result is based on the integration shown in Figure 32.22(a) and its application to the compound in question—methyl acetate in this example. Integration can help in structural analysis, particularly when determining symmetry.

Sample Exercise 32.3

Differentiating between products of a reaction

3,4-Dibromohexane can undergo base-induced double dehydrobromination to yield either 3-hexyne or 2,4-hexadiene. How could you use NMR spectroscopy to identify the product formed?

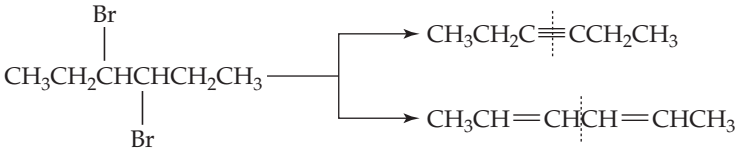


SOLUTION

Analyze We are asked to distinguish between the two possible products using NMR spectroscopy.

Plan As with all NMR questions of this kind, start with symmetry. Once identified, or not, count up the number of different carbon or hydrogen environments. Look for differences.

Solve Each potential product has a mirror plane, as shown here. Bearing this in mind, both products will exhibit three absorptions in their ^{13}C NMR spectrum.

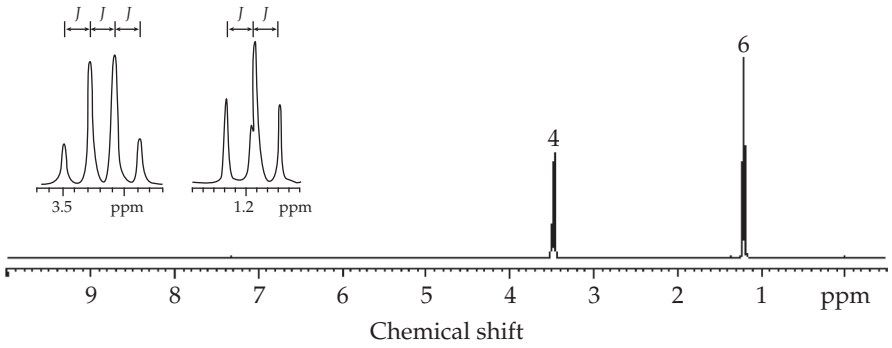


However, the numbers of absorptions in the two ^{1}H NMR spectra are different. The alkyne will exhibit two absorptions while the diene exhibits three. Purely on this basis, the two potential products are distinguishable.

▶ Practice Exercise

Propene reacts with HBr potentially to produce two alkylbromides. Only one is formed, the outcome following Markovnikov's rule. How could you use NMR to determine which alkylbromide is the Markovnikov product?

Go Figure What does the very small signal at 7.3 ppm represent?



▲ **Figure 32.23 300 MHz ^{1}H NMR spectrum of diethyl ether in $CDCl_3$.** Inset: Expansions of the two signals showing the multiplicity of each signal.

singlet	1					
doublet	1	1				
triplet	1	2	1			
quartet	1	3	3	1		
quintet	1	4	6	4	1	
sextet	1	5	10	10	5	1

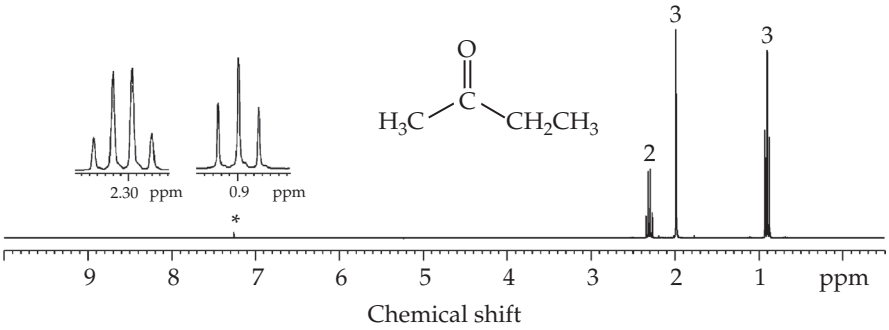
▲ **Figure 32.24 Multiplicity.** J is a quantitative measure of the magnetic interaction of coupled nuclei. The splitting pattern for nuclei with $I = \frac{1}{2}$ follows a binomial distribution. For example, if a signal is split into two peaks of equal intensity, that signal is called a doublet.

Spin–Spin Coupling

The last piece of NMR evidence we consider is probably the most powerful in determining structure. The concept is called **spin–spin coupling** or *J coupling*. So far we have looked at ^{1}H and ^{13}C nuclei in isolation. When two or more nuclei are close enough for their spins to interact or *couple*, the resulting signals split. This typically occurs if there are hydrogen atoms neigboring the nucleus that you are observing. The **splitting pattern** formed is characteristic of the coupling and yields more information about the nucleus's neighbor than it does about itself. For example, diethyl ether ($CH_3CH_2OCH_2CH_3$) has two sets of different hydrogens (as a result of symmetry), leading to two signals in the ^{1}H NMR spectrum (Figure 32.23). The chemical shift of these signals is influenced by the ether oxygen, with the hydrogens of the CH_2 being more deshielded. Closer inspection of the signals shows them to be complicated by very uniform patterns. This complicated pattern is a result of the *through-bond* communication between ^{1}H nuclei across the CH_2 and CH_3 groups. For any set of coupled hydrogens, the distance between peaks in each splitting pattern, termed the **coupling constant** (J), is identical. The magnitude of the coupling depends on the nature and number of intervening bonds between the two (or more) nuclei. The further away the coupling nuclei are from each other, the smaller the value for J. Therefore, a ^4J coupling (in which there are four intervening bonds) is smaller than a ^3J coupling (in which there are three intervening bonds). The pattern, or **multiplicity**, of the signals is derived from the number of identical nuclei that couple, and follows a binomial distribution, shown in Figure 32.24.

Hydrogen coupling does not usually proceed past a functional group within the carbon framework that doesn't contain ^{1}H. Figure 32.25 shows the ^{1}H NMR spectrum of 2-butanone to illustrate this point. The spectrum is dominated by three signals at 0.9, 2.0 and 2.3 ppm. An enlarged view of the resonance attributable to the methyl attached to the carbonyl group shows this signal to be a single sharp peak (or *singlet*), demonstrating

▶ **Figure 32.25 300 MHz ^{1}H NMR spectrum of butan-2-one in $CDCl_3$.** Despite the four intervening bonds linking ^{1}H nuclei, no ^4J coupling is observed at this operating frequency due to the carbonyl group. Residual solvent is marked with an asterisk (*).



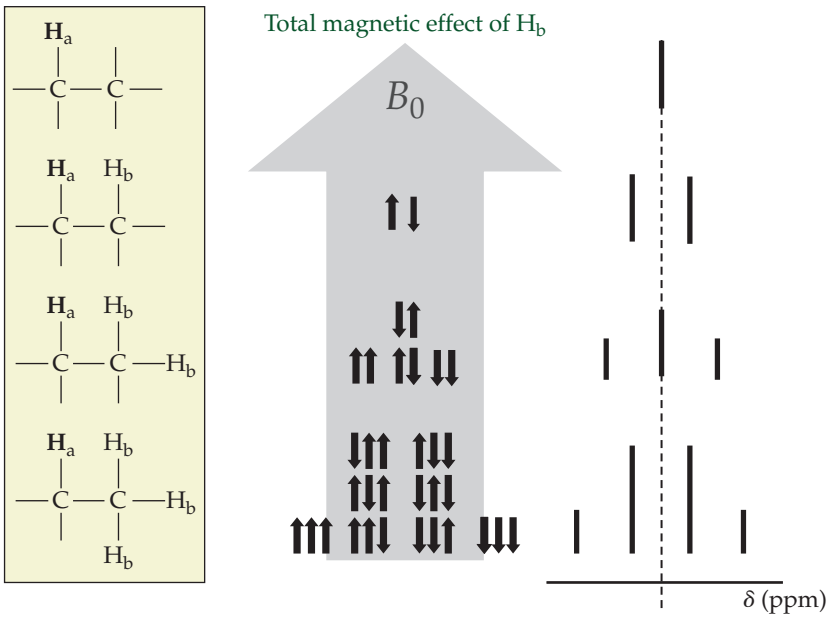
that no coupling across the C═O group from the CH_2 group is seen. As with the ^1H NMR spectrum of diethyl ether (Figure 32.23), a characteristic splitting pattern is shown for the hydrogens of an ethyl group. Let's now take a more detailed look at this splitting pattern and why it occurs.

A nucleus coupled to n other equivalent nuclei (each with $I = \frac{1}{2}$) appears as a *multiplet* (Figure 32.24). The multiplicity attained for the signal of the coupled nuclei can be described as containing $(n + 1)$ peaks. The origin of this phenomenon, known as the **(n + 1) rule**, can be ideally described by considering two non-equivalent hydrogens, H_a and H_b, found on adjacent carbons. **Figure 32.26** illustrate the principle as well as the underlying reasoning. The chemical shift of H_a is influenced by H_b. In fact, this influence (and hence the multiplicity) is a result of the two possible spin orientations of H_b. The parallel orientation of nuclear spins adds to the applied field, causing the signal attributable to H_a to appear at a lower applied field (higher δ), whereas the anti-parallel orientation causes H_a to appear at a higher field (lower δ). These two signals (combined they are termed a *doublet*) occur on either side of the position H_a would occupy in the absence of the influence of H_b.

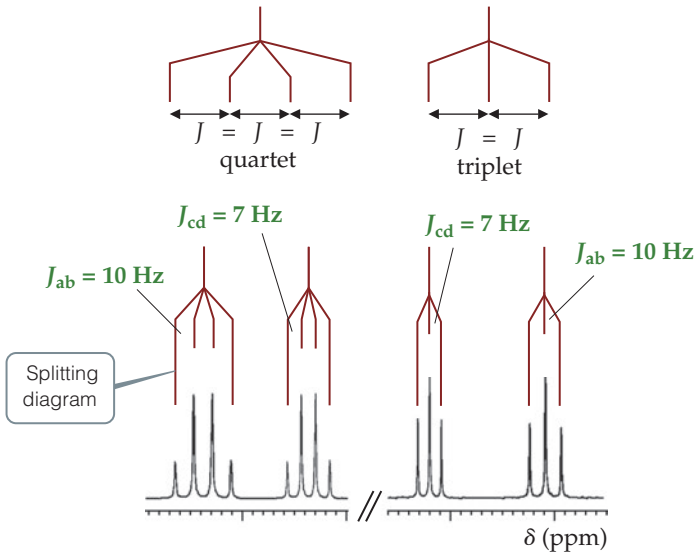
If we turn our attention back to the expanded region of the ^1H NMR spectrum of diethyl ether (Figure 32.23), we see that the CH_2 group is *coupled* to the three equivalent hydrogens of the methyl group. This coupling causes the signal attributable to the CH_2 hydrogens to split into four $(3 + 1)$ peaks with intensities in the ratio 1 : 3 : 3 : 1. This specific pattern is called a *quartet* (see Figure 32.24). Conversely, the methyl group couples

Go Figure

Determine the possible connectivity between hydrogen nuclei that show as a doublet and septet multiplicity with integration in the ratio 6 : 1, respectively, within the 1H NMR spectrum.



▲ **Figure 32.26 Origins of complex signal splitting.** The influence of the spin states of n neighboring H_b on the applied field causes the signal for H_a to split into 'n + 1' peaks. The splitting pattern and the relative peak heights are attributable to the additive and cancelling effect of H_b spins.



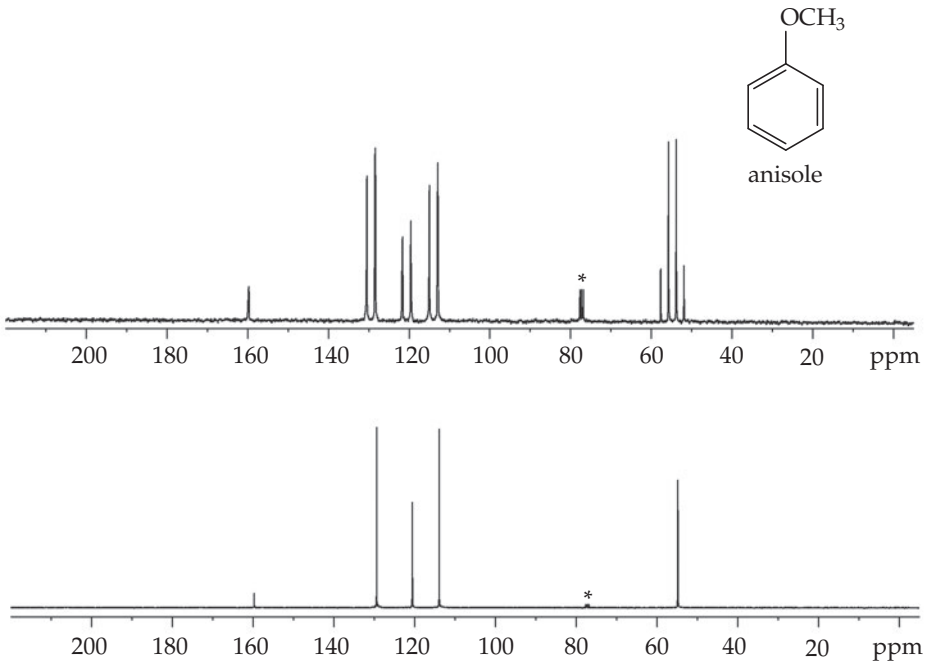
▶ **Figure 32.27 Coupling constants.** The spacing between each peak in a multiplet is called the coupling constant, *J*, expressed in hertz (Hz). Note that the *J* value between two mutually coupled nuclei is the same and different from that attained for other coupled pairs of nuclei. The coupling constant yields information on connectivity.

to the CH_2 group, splitting into three (2 + 1) signals in the ratio 1 : 2 : 1, with the distance between each signal in the *triplet* (known as the *J* value) being equivalent to those in the quartet. The permutations of nuclear spin "up" and "down" leading to the triplet and quartet are shown in Figure 32.26.

As organic chemists, we can use the information derived through individual *J* values to determine the connectivity of a carbon framework. **Figure 32.27** illustrates how the connectivity of two nuclei can be expressed by the magnitude of *J*. This spectrum contains two sets of triplets and two sets of quartets for an unknown compound. The triplet/quartet pattern is diagnostic of an ethyl group. So, intuitively, we might expect two sets of ethyl groups within the structure of the unknown. The difficulty lies in distinguishing between the two sets. Determination of the coupling constants, however, soon identifies which triplet is *coupled* to which quartet. We can use this information, together with the chemical shifts of the quartets, to determine the likely connectivity of the ethyl groups to other functional groups. Looking for sets of signals with the same *J* allows information to be extracted from very complex overlapping spectra. Because *J* values do not depend on the spectrometer, a spectrometer with a higher operating frequency will show the splitting of the signal compressed to a shorter distance on a δ scale, one more reason why higher operating frequencies are preferred for studying complex molecules.

^{13}C NMR Spectra

^{13}C NMR spectra are often used by chemists to indicate the number of different carbon atoms, as well as to provide some evidence on the nature of the functional groups contained within a molecule. In order to do this, ^{13}C NMR spectra often remove the multiplicity displayed by C–H coupling—a process called **decoupling**. As shown in **Figure 32.28** coupling of carbon to hydrogen complicates the spectrum to an unnecessary degree. By decoupling the ^{1}H and ^{13}C nuclei, all multiplicity is lost and the signals are simplified to singlets. This type of experiment is called a *heteronuclear decoupling* experiment because it decouples the effect of ^{1}H nuclei on ^{13}C nuclei. Note that the reverse is not necessary, that is, the need to decouple the effects of ^{13}C coupling on the ^{1}H NMR experiment. The reason is that ^{1}H is approximately 99% naturally abundant and ^{13}C is only 1% naturally abundant. Having such a low natural abundance means that, for the most part, the effect of ^{13}C nuclei contained within the sample is below the level of sensitivity for ^{1}H NMR spectroscopy. In ^{13}C NMR spectra, there are a number of factors that influence the intensity of the signal, not just the number of carbon atoms of a particular environment in the molecule. Consequently, integration is not usually performed on these signals.

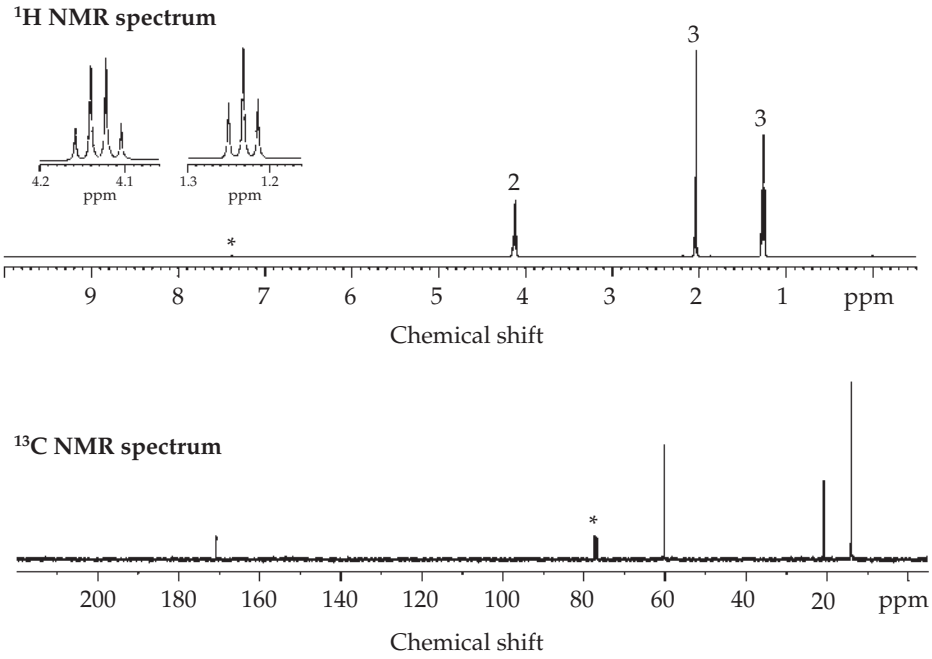


◀ Figure 32.28 ^{13}C NMR spectra—when too much information complicates interpretation. Routinely, organic chemists undertake ^{13}C NMR experiments that involve decoupling the effect of ^{1}H to which it is attached. *Top spectrum*: Coupled ^{13}C NMR spectrum of anisole. *Bottom spectrum*: Decoupled ^{13}C NMR spectrum of anisole. Asterisks (*) denote $CDCl_3$ solvent.

Sample Exercise 32.4

Using NMR to Solve a Chemical Unknown

Compound A, with molecular formula $C_4H_8O_2$, has the following ^{1}H and ^{13}C NMR spectra. Deduce its structure using this information.



Note Numbers on top of signals represent integration values. Asterisk indicates signals due to solvent.

SOLUTION

Analyze We have been asked to use NMR spectra to deduce the molecular structure of a compound containing C, H and O.

Plan Based on chemical shift (δ) and splitting patterns in the ^{1}H NMR spectrum, we can deduce the structure of compound A. We will use the ^{13}C NMR spectrum to confirm the choice of structure.

Solve The ^{1}H NMR spectrum contains three signals at about 1.2, 2.0 and 4.1 ppm, with integration in the ratio 3 : 3 : 2. This

Continued

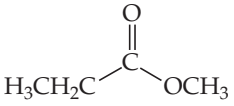
integration totals the number of hydrogens in the molecular formula and so represents the molecule as a whole (no further symmetry).

Two of these hydrogen signals are split, forming a triplet and a quartet. This combined pattern is indicative of an ethyl group (CH_3CH_2) following the $n + 1$ rule, a deduction helped by the integration ratio.

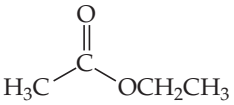
The third signal is a three-hydrogen singlet, which means that the hydrogens on this methyl group (because it integrates for three hydrogens) do not couple. The chemical shift of this resonance implies that this methyl group is bonded to a carbonyl group, consistent with the lack of coupling within the signal (that is, a singlet).

At this stage we have accounted for all atoms in the molecule except for an oxygen atom. This must be linked between the ethyl and carbonyl groups in order to give rise to the chemical shift seen by the CH_2 group at 4.10 ppm.

Placing all this information together, suggests our unknown must be ethyl acetate.



Note the other ester



would have a chemical shift of 2.2 ppm for the CH_2 group, and a three-hydrogen singlet at 4.10 ppm.

Check Our deduction is confirmed by the four signals within the ^{13}C NMR spectrum. The signal at 171 ppm indicates the presence of a carbonyl group. The signal at 60 ppm is indicative of a carbon attached to oxygen (in this case, as part of the ester group), with the two other signals at 13 ppm and 21 ppm consistent with the two methyl carbon atoms. Contrast this result with the spectrum of butan-2-one (Figure 32.25).

▶ Practice Exercise

A liquid sample has a band in the infrared spectrum at 1710 cm^{-1}. The NMR spectrum shows two ^1H resonances in the ratio of 3 : 2. The molecular formula of the unknown is $C_5H_{10}O$. Deduce its structure.

Self-Assessment Exercises

32.7 Which of the following nuclei will give an NMR spectrum: ^{16}O, ^{19}F, ^{31}P, and ^{32}S?

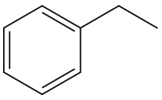
(a) ^{16}O and ^{19}F only

(b) ^{19}F and ^{31}P only

(c) ^{16}O and ^{32}S only

(d) ^{19}F and ^{31}P only

32.8 Consider ethylbenzene. How many signals do you predict would be in the ^1H NMR spectrum and what would be the relative sizes of the signals?

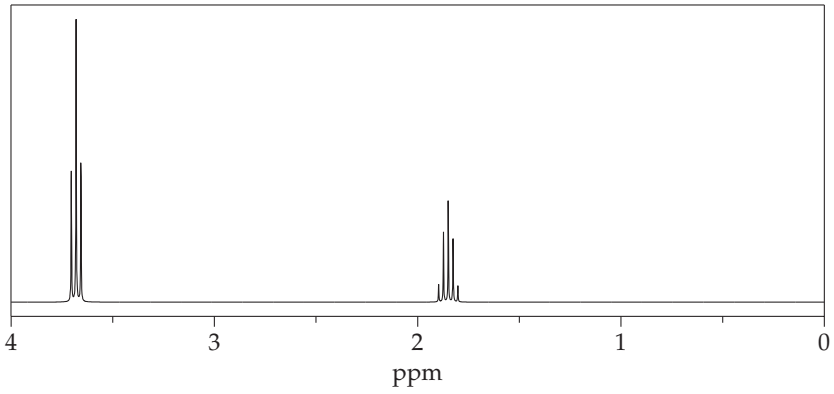


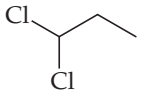
(a) Three signals in the ratio 2:2:1

(b) Five signals in the ratio 3:2:2:2:1

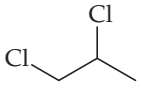
(c) Seven signals in the ratio 3:2:1:1:1:1:1

32.9 There are four constitutional isomers of dichloropropane, $C_3H_6C_{l2}$, shown here. Which one would have the ^1H NMR spectrum shown?

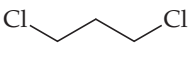




(a)



(b)



(c)



(d)

Exercises

32.10 Which of the following solvents could be used in ^{1}H NMR spectroscopy? Acetone (CH_3COCH_3), methanol-d_4 (CD_3OD), tetrachloromethane (CCl_4), water (H_2O), diethyl ether ($CH_3CH_2OCH_2CH_3$). Explain your choice.

32.11 Indicate the number of different absorptions and the relative intensities expected in the ^{1}H NMR spectra of:

(a) 2,2-dimethylbutane **(b)** ethanol

(c) acetone **(d)** 2-chloropropane

(e) cyclohexane **(f)** cyclohexanone

(g) ethyl methyl ether

32.12 Indicate the number of different absorptions expected in the ^{13}C NMR spectra of:

(a) 2,2-dimethylbutane **(b)** ethanol

(c) acetone **(d)** 2-chloropropane

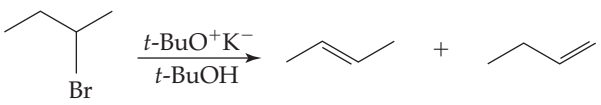
(e) cyclohexane **(f)** cyclohexanone

(g) ethyl methyl ether

32.13 Predict the splitting pattern observed in the ^{1}H NMR spectrum for each of these compounds:

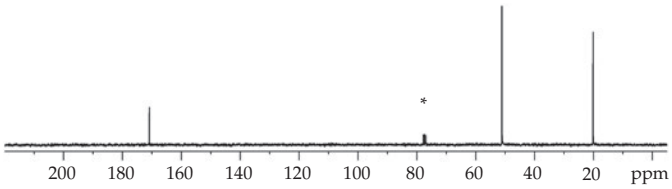
(a) CH_3CHBr_2 **(b)** $(CH_3)_2CHCl$ **(c)** $(CH_3)_3CBr$

32.14 2-Bromobutane undergoes a β-elimination reaction in the presence of potassium *tert*-butoxide to produce one of two isomeric alkenes.



How could you use NMR spectroscopy to determine which alkene is formed as the major product?

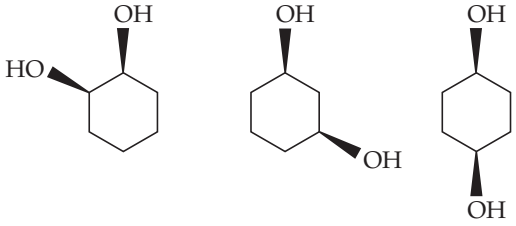
32.15 The reaction of an unknown with ethanol in the presence of a small amount of H_2SO_4 leads to a compound that smells distinctly like rum. The hydrogen-decoupled ^{13}C NMR spectrum of the product is shown here (* = solvent).



(a) What is the structure of the unknown?

(b) What other structure(s) would be consistent with this ^{13}C NMR spectrum?

32.16 Two bottles labelled *cis*-cyclohexandiol were found in a laboratory. Because of their differing melting points, the bottles clearly contained two different *cis*-cyclohexandiol isomers. To determine which isomer was in which bottle, the chemist decided to run ^{13}C NMR spectra on a sample of each. The three possible isomers were:

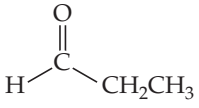


The two ^{13}C NMR hydrogen-decoupled spectra contained the following data:

- spectrum of sample in bottle A: 20.20, 62.55
- spectrum of sample in bottle B: 16.09, 29.52, 36.15, 63.08

Identify which isomer was present in each bottle.

32.17 The 200 MHz ^{1}H NMR spectrum of propanal (shown) has three distinctive resonances: δ9.5 (1H, singlet), 2.2 (2H, quartet), 1.0 (3H, triplet). Assign each resonance to the structure.



Answers to Self-Assessment Exercises

32.7 (d) **32.8** (b) **32.9** (c)

32.4 Mass Spectrometry



All international airports and many of the larger domestic airports require passengers to go through a security screening process. This generally involves two stages, the first being that all passengers pass through a metal detector while their hand luggage passes through an X-ray machine, both of which can detect metallic weapons. The second is a random check of a person's clothes and hand luggage using an explosive trace detector (ETD). Explosives are typically of rather few classes of compound, many of them containing nitro groups. These can be detected in minute quantities, well below that of visible particles. Mass spectrometry provides a fast and accurate means of identifying very small quantities of material. Now that compact 'bench-top' instruments are available, a mass spectrometer tuned to detect certain classes of compounds is a powerful ETD.

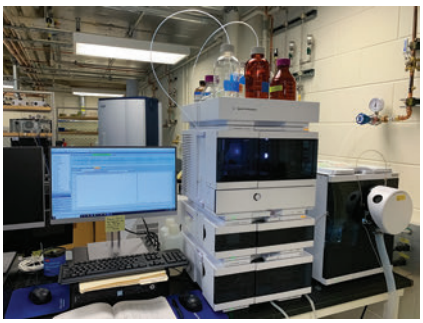
In this section, we examine how this technique can help identify unknown compounds. By the end of it, you should be able to:

- Understand the principle behind mass spectrometry
- Interpret simple spectra to provide some structural knowledge of a molecule

Mass spectrometry is distinctly different from the other characterization techniques introduced in this chapter. This technique does not depend on the absorption of electromagnetic radiation, but instead examines what happens when a molecule is bombarded with high-energy electrons. These electrons are used for two purposes. The molecule is *ionized* by the electrons and the electrons are used to break the molecule apart or **fragment** it, in a similar way to hitting a cricket ball through a pane of glass. The masses of the fragments are measured and brought together (in analysis) in order to reconstruct the molecule. Apart from determining the masses of the fragments, mass spectrometry can also indicate the mass of the *parent structure*, which in most instances, coincides with the signal of highest mass. This signal is called the **molecular ion**, or parent ion peak. Mass spectrometry is a technique used routinely to determine the molecular weight of a compound. The fragmentation pattern can give information on the functional groups present in molecules.

Mass spectrometry employs many different ionization techniques, including electron impact ionization (EI), chemical ionization (CI), fast atom bombardment (FAB) and more advanced techniques such as matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) methods. Each of these different techniques has certain advantages, and the modern organic chemist uses more than one mass spectrometry technique to solve the structure of an unknown.

Mass spectrometry is also routinely employed in analytical laboratories as part of the identification of compounds in complex reaction mixtures, in the separation and identification of minute quantities of biologically active compounds, or in the identification of drugs in hair samples or trace explosives on luggage. **Figure 32.29** shows an ESI mass spectrometer (right) linked to a high-performance liquid chromatography (LC) unit (left), which is an instrument routinely used for separating complex mixtures. The combination, known as LCMS, is a powerful analytical technique.



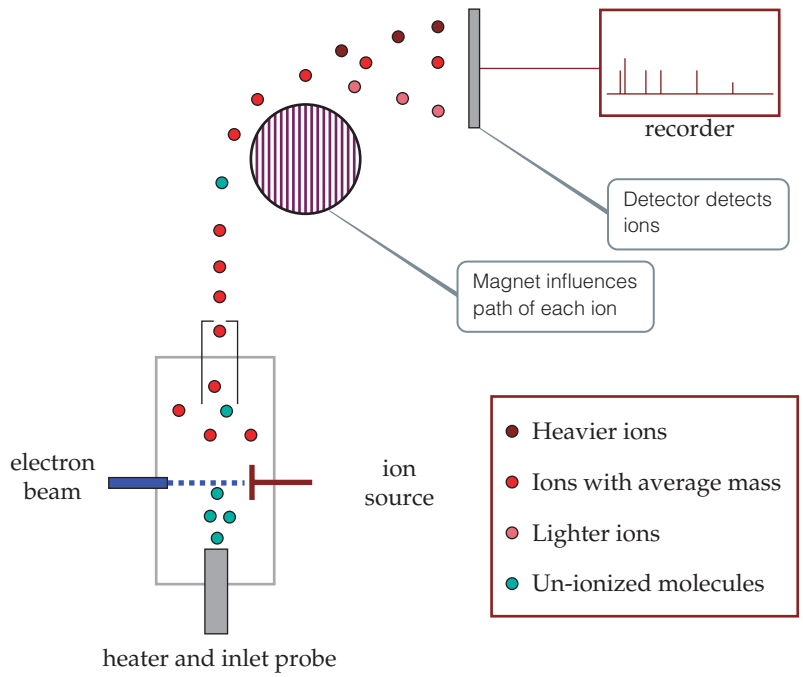
▲ **Figure 32.29 A modern LCMS.** Mass spectrometry is often used in combination with other techniques, typically separation techniques such as liquid chromatography (LC) or gas-phase chromatography (GC). This LCMS is made up of three components: auto-sampler (left), liquid chromatography instrument (center) and electrospray mass spectrometer (right). As different compounds are separated from a mixture by LC, they are analyzed for their molecular mass.

Electron Impact Ionization Mass Spectrometry

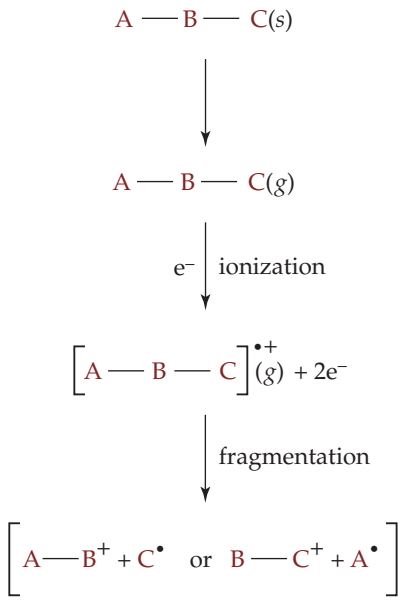
In this section, we concentrate on **electron impact ionization (EI) mass spectrometry (EIMS)** because it most clearly shows the principles of mass spectrometry, even though more complex methods are used more often today. Mass spectrometers using the EI technique operate by determining the *mass-to-charge ratio* (m/z) for ions in the gas phase. **Figure 32.30** illustrates how a result is obtained using an EI mass spectrometer. There are three principal components to EIMS: an ion source, which ionizes molecules in a high vacuum and accelerates them to form a beam; a strong magnet to deflect or separate the ions according to their masses; and a detector that records the masses of the ions generated. The intensity of each signal is then plotted as a function of the mass-to-charge ratio (m/z).

The sample to be analyzed by EIMS is vaporized by heating to the gas phase within the inlet probe. Ionization of the sample occurs when a beam of high-energy electrons (10–70 eV, 1 eV = 96 kJ/mol) collides with the sample. Energy is transferred as a result of that collision, removing an electron from the molecule and yielding a positive ion. In this case, we say that the organic molecule has been *ionized* by electron impact and the signal that results is called the molecular ion signal (M^+). This molecular ion has the same mass

Go Figure Why are neutral species not detected by this method?



▲ **Figure 32.30 The principle behind electron impact ionization mass spectrometry.** The technique relies on generating charged species (ions) by bombarding a gas-phase sample with high-energy electrons.



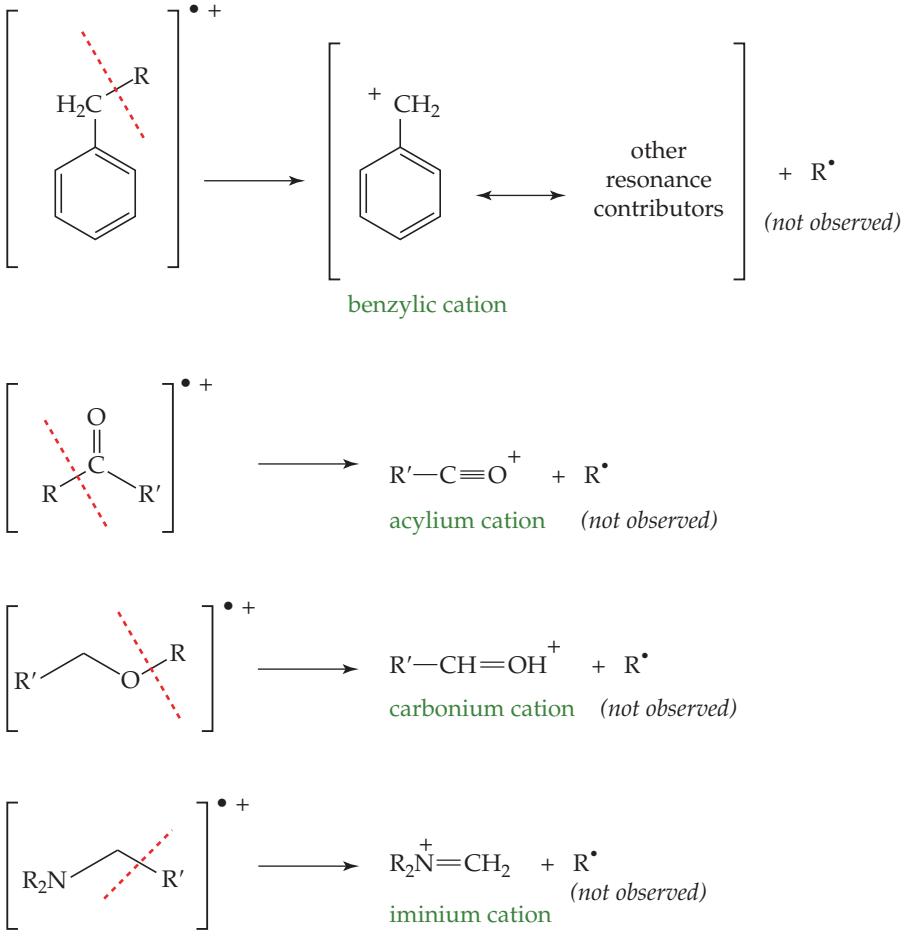
▲ **Figure 32.31** **Ionization and fragmentation.**

as the neutral molecule less the mass of a single electron, which is of course negligible compared with the mass of the molecule.

If the electron collides with the molecule at higher energy (that is, around 70 eV), it not only brings about the ionization of the molecule but also causes dissociation or *fragmentation* of the molecule, as shown in **Figure 32.31**. This fragmentation process gives a characteristic mixture of charged ions and uncharged radicals. The ions are detected easily, whereas the uncharged radicals are neither accelerated nor detected, but can be inferred by the difference in the mass between the molecular ion and the observed fragment. The type of cation (and radical) formed depends on the nature of the functional groups present, so fragmentation becomes diagnostic for functional group types. Those fragments able to stabilize the positive charge, such as allylic cations (derived from alkenes), benzylic cations ($C_6H_5CH_2^+$), acylium cations (derived from aldehydes and ketones), iminium cations (derived from amines) or oxonium cations (derived from alcohols and ethers), are always favored (**Figure 32.32**).

Once the ionization and fragmentation processes have occurred, the ions formed are separated and detected. Initially, the positively charged ions are attracted to a negatively charged accelerator plate that forms a narrow slit, allowing only a stream of ions to pass through. Once past the slit, the positive ion enters an evacuated tube where its flight path is perturbed by the poles of a large magnet. As the positive ion passes through the magnetic field, its path is bent. The degree of bending depends on the mass of the fragments but also on their charge. The detector then converts the signal it receives into a mass spectrum.

Go Figure Using resonance contributors, describe how a benzylic cation is able to be stabilized.



▲ **Figure 32.32** **Fragmentation of molecular ions.**

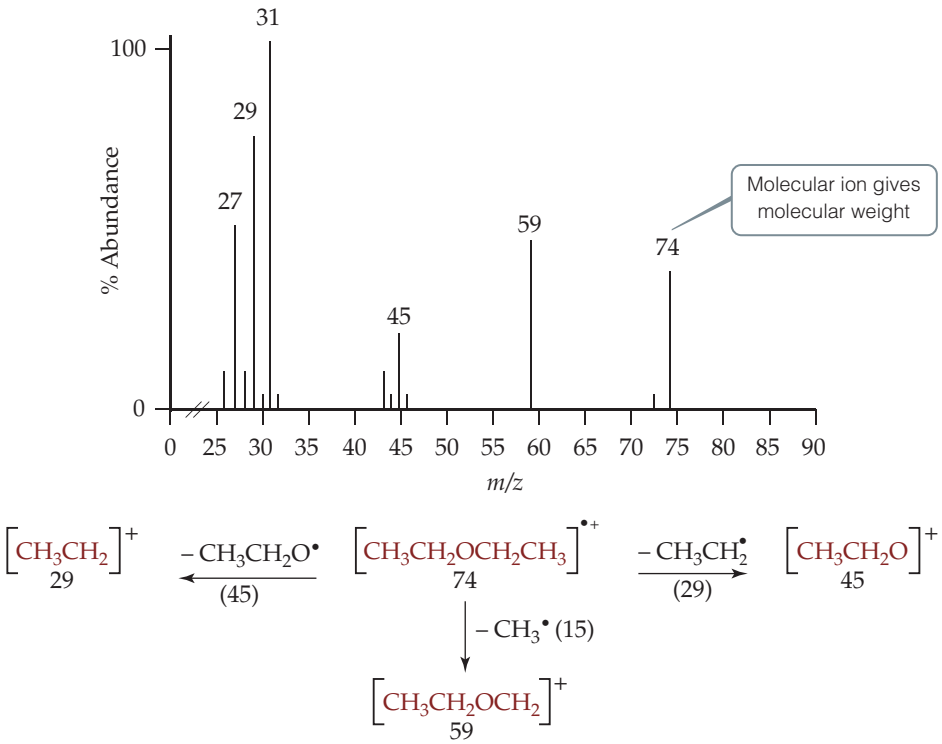
Interpreting Mass Spectra

Two aspects of a mass spectrum lead the chemical detective to the identity of a compound. The first, called the **mass-to-charge ratio,** is symbolized by m/z (see Figure 32.33), where m equals the mass of the ion (in u) and z is its charge. Typically, organic chemists use the term m/z as a dimensionless quantity. As the charges on ionized or fragmented molecules almost always equate to +1, the mass-to-charge ratio for a particular signal in the mass spectrum is equal to the mass of that ion. These signals are assigned as a percentage abundance with respect to the most intense signal in the spectrum, called the **base peak**. The base signal does not necessarily correspond to the mass of the molecular ion—it is simply the most intense signal in the spectrum. For example, the base peak in Figure 32.33 occurs at $m/z = 31$ and is the result of fragmentation leading to the cation CH_2OH^+. The molecular ion is found at $m/z = 74$. Figure 32.33 also illustrates the possible fragmentations leading to each of the signals within the mass spectrum. Note that only the positively charged fragments lead to the signals in the spectrum. All the neutral fragments are unaffected by the magnet and do not impact on the detector.

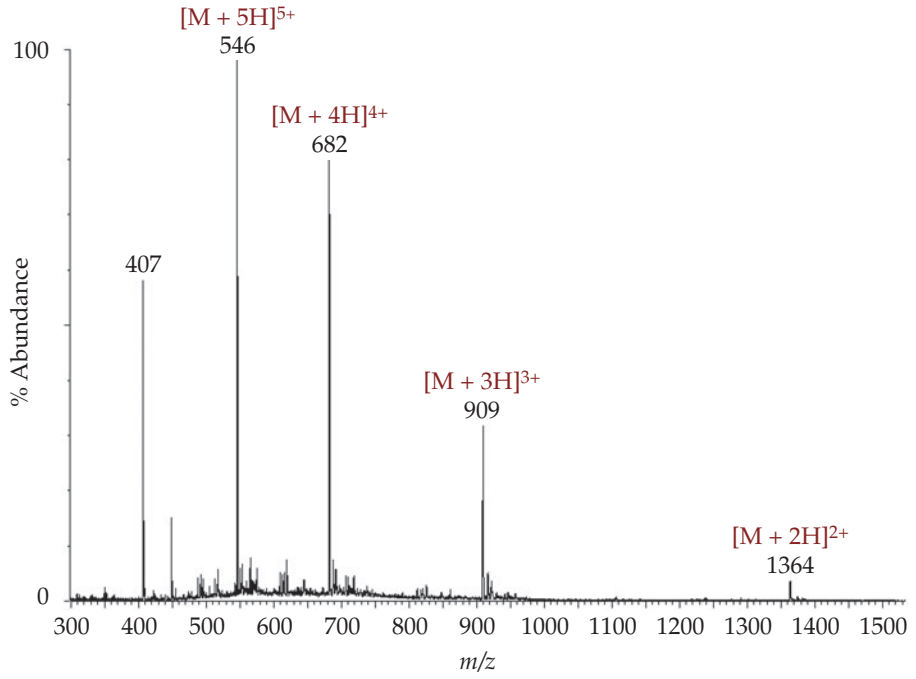
Figure 32.34 illustrates the principle of the mass-to-charge ratio by looking at species containing z values greater than 1. The signals at $m/z = 546, 682, 909$ and 1364 all equate to the same molecular weight, 2726 u. The non-unity charge is due to this molecule's ability to react with H^+ at multiple sites, leading to multiple-charged species. This effect is common in subtle techniques such as ESI rather than in the chemically harsher techniques of EI and CI.

Routine mass spectrometry such as the type we have been describing is a low-resolution technique, meaning that the particle masses are rounded typically to a whole number. This means that carbon is taken as 12 u (^{12}C), oxygen as 16 u (^{16}O) and nitrogen as 14 u (^{14}N). However, most elements exist in more than one isotopic form. The heavier isotopes also give rise to small signals in the mass spectrum, higher than that of the molecular ion signal. These signals are sometimes called the $[M + 1]^+$ or $[M + 2]^+$ signals and can be very diagnostic in some instances. Table 32.4 gives the isotopic composition of some common elements, showing how they contribute to $[M + 1]^+$ or $[M + 2]^+$ signals. The isotopes for chlorine and bromine are highlighted as they show the most diagnostic abundance distributions.

For the most part, the $[M + 1]^+$ and $[M + 2]^+$ signals are significantly smaller (less than 1%) than the parent ion or molecular ion signal. However, chlorine exists as two



◀ **Figure 32.33 EI mass spectrum of diethyl ether**. The fragmentation pattern seen within the EI spectrum is also deduced, showing the loss of different radicals from the initially ionized diethyl ether. Remember, uncharged fragments such as $CH_3^•$ and $CH_3CH_2^•$ are not observed.



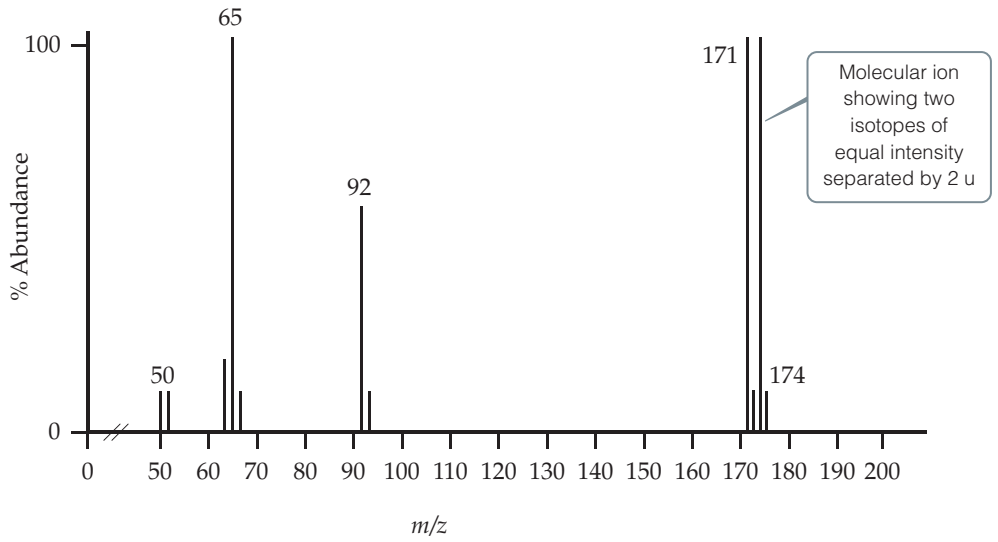
▶ **Figure 32.34 Mass-to-charge ratio.** Multiple charged fragments yield signals within the mass spectrum corresponding to greater masses. For example, a molecule with molecular mass *M* will yield a signal at *M*/2 when doubly charged. This electrospray spectrum is of a new type of therapeutic agent designed to interfere with the translation of the mRNA code to protein. Notice that this type of ionization leads to very little fragmentation, but does allow the sample molecules to accumulate protons, leading to multiple charged ions.

TABLE 32.4 Isotopic distributions for some common elements

Element	M	% Abundance	M + 1	% Abundance	M + 2	% Abundance
Hydrogen	^{1}H	100				
Carbon	^{12}C	98.9	^{13}C	1.1		
Nitrogen	^{14}N	99.6	^{15}N	0.4		
Oxygen	^{16}O	99.8			^{18}O	0.2
Sulfur	^{32}S	95.0	^{33}S	0.8	^{34}S	4.2
Chlorine	^{35}Cl	75.5			^{37}Cl	24.5
Bromine	^{79}Br	50.5			^{81}Br	49.5
Iodine	^{127}I	100				

isotopes, ^{35}Cl and ^{37}Cl, with respective isotope abundances of 75.5% and 24.5%. Bromine is the most easily recognized of the halogens. It has two signals, one for ^{79}Br and one for ^{81}Br, of near equal intensity (50.5% and 49.5%, respectively). What this means is that, if bromine is present in a molecule, the $[M + 2]^+$ ion has an intensity nearly equal to the molecular ion. This is illustrated in the EIMS spectrum of 4-bromoaniline, shown in **Figure 32.35**. Iodine is typically recognized by the presence of iodine cation (I^+) at *m/z* 127. This clue is also combined with a characteristic 127 separation in the mass spectrum between the molecular ion signal and the first fragmentation. If chlorine is present, the $[M + 2]^+$ signal is about one-third as large as the M^+ signal.

There is one last aspect of mass spectrometry that we should discuss. To do this, we consider the molecules propane, acetaldehyde and CO_2. Each one produces a molecular ion with a mass of 44 u. Under the low-resolution methods we have been applying to date, we would not be able to tell these molecules apart. If, however, we use a high-resolution approach by not considering the mass of atomic hydrogen (^{1}H) as 1 u but as 1.0078 u and ^{16}O as 15.9949, then the three molecules in question (with different molecular formulas) will correspond to different exact masses—C_3H_8, C_2H_4O and CO_2 have exact masses of 44.0626, 44.0262 and 43.9898 u. For this high-resolution technique to be useful, accurate masses are always quoted to four decimal places. Analysis requires a highly accurate measurement (± 1 part in 10^6). The result can then be compared with exact masses calculated for various element combinations. Note that, by definition, ^{12}C has an atomic weight of 12.0000 u.

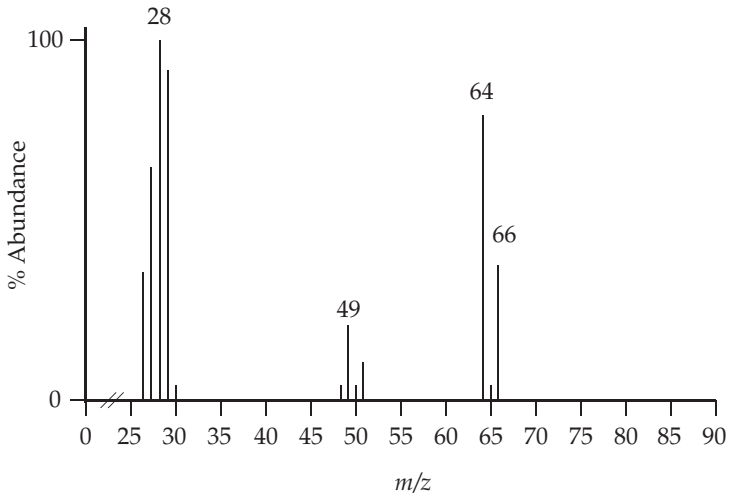


◀ Figure 32.35 EI mass spectrum of 4-bromoaniline. Note the diagnostic M^+ and $[M + 2]^+$ signals of equal intensity and the spacing of 79 u between the molecular ion and first fragmentation. These clues all indicate that the molecule contains bromine.

Sample Exercise 32.5

Interpreting Mass Spectra

An EI mass spectrum of compound B, a simple haloalkane, is shown here. Deduce its structure.



SOLUTION

Analyze We are asked to deduce the structure and hence molecular formula based on the mass spectrum observed.

Plan Use the M^+ and $[M + 2]^+$ signals to deduce the halide present, as well as the molecular formula. Use the fragmentation patterns to confirm your deduction.

Solve The relative abundance of the M^+ and $[M + 2]^+$ signals suggests that chlorine is the likely halide, although the observed ratio of these two signals is slightly different from the expected 3 : 1 ratio. The presence of Cl within the structure is confirmed by the difference between the M^+ and the second fragmentation of 29 u (difference = 35). The position of this second fragmentation also coincides with the cation $CH_3CH_2^+$. Hence, the structure of our unknown must correspond to *chloroethane*.

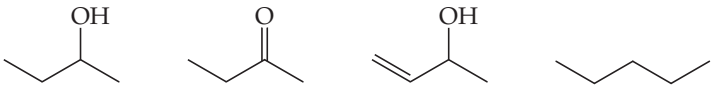
Check The fragmentation signal at 49 u corresponds to the loss of a methyl radical (15 u) from M^+.

▶ Practice Exercise

The mass spectrum of compound C contains major peaks at m/z = 88, 73, 45, 43 and 29. Confirm that this fragmentation pattern is consistent with compound C being ethyl acetate.

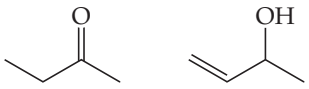
Self-Assessment Exercises

32.18 Which molecule will have a molecular ion at $m/z = 74$ in its mass spectrum?



(a) **(b)** **(c)** **(d)**

32.19 A mass spectrum has signals at m/z = 72, 57, 43, 29, and15. Which molecule will give rise to this pattern?



$m/z = 72$ $m/z = 72$

(a) **(b)**

Exercises

32.20 Carbon tetrabromide shows nine signals in the region $m/z = 328–337$ of the EI mass spectrum. Account for each of these signals.

32.21 An aliphatic compound gives the following result from microanalysis: C, 66.6%; H, 11.2%. The mass spectrum reveals a molecular ion signal at $m/z = 72$. Determine the compound's molecular formula.

32.22 **(a)** What are the labels on the axes of a mass spectrum?

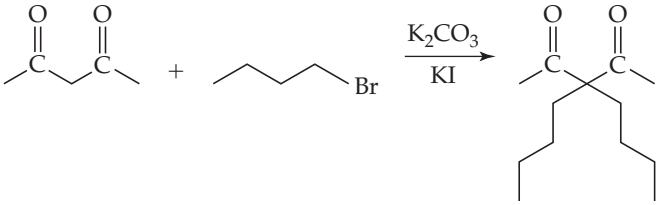
(b) In order to measure a mass spectrum of an atom or molecule, the atom or molecule must first lose (or gain) one or more electrons. Why is this so?

32.23 Illustrate the stability of the following cations by drawing any contributing resonance structures.

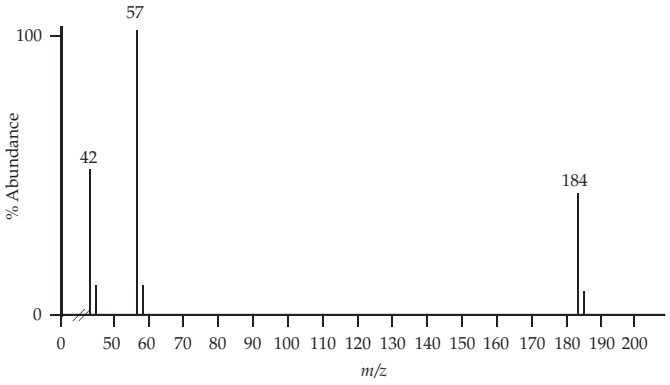
(a) acylium cation **(b)** carbonium cation

(c) iminium cation

32.24 Following a literature procedure, a student added butyl bromide (three equivalents) to 2,4-pentanedione in the presence of excess potassium carbonate and potassium iodide, as shown in the following reaction scheme:



As well as isolating the product, the student also isolated a clear oil which she promptly submitted for EIMS. The results are shown here. What is the structure of the by-product? [*Hint:* Look at the difference in mass between the molecular ion and the base peak.]



32.25 With the aid of a diagram, describe what the EI mass spectrum of 2-chloropropane might look like.

Answers to Self-Assessment Exercises

32.18 (a) **32.19** (a)

32.5 Compound Identification Using Spectra



Whether you are a police scientist in a forensic laboratory, a medical scientist in a pathology laboratory, or a research scientist in a synthesis laboratory, you will come across substances that need identifying. More often than not, a combination of techniques including chemical observations as well as instrumental analysis will be needed. Being able to pick the salient information from each bit of data and put it together to generate a structure based on evidence is a skill that takes practice to acquire. Often, an iterative process is useful. First, you "skim" the information to give a "first guess" at the substance. You then use this structure to see if it matches the information from the tests and analysis, refining the structure when the data is inconsistent with your first guess. Eventually, you refine the structure to a point when all the evidence you have is consistent with that structure.

In this section, we introduce this process and show how a combination of chemical tests and instrumental techniques may be used to solve a structure. By the end of this section, you should be able to:

- Identify simple substances based on chemical analysis and instrument data.

Deducing the Molecular Formula of an Organic Compound

To work out the empirical formula of an organic compound, an organic chemist subjects a small amount of sample to *microanalysis*. This destructive technique combusts the sample and analyses the amount and type of gas released. From these data, a percentage C, H, N is obtained based on weight. The remaining percentage is inferred as the content of O in the sample. Manipulation of these percentages, by taking into account the atomic masses of C, H, N and O leads to an empirical formula, from which a molecular formula can be determined, normally in conjunction with the value for the molecular ion signal in the mass spectrum.

In Chapters 24 and 26, we identified the general molecular formula of an alkane as C_nH_{2n+2}, a cycloalkane is C_nH_{2n} and the corresponding alkene also has the same general molecular formula, C_nH_{2n}. This difference in molecular formula between, for example, alkanes and alkenes actually yields important structural information. While the example

Sample Exercise 32.6

Microanalysis to Molecular Formula

The IR spectrum of a liquid aromatic compound has a broad band in the range 3000–3500 cm^{-1}. EIMS indicates a molecular ion signal at $m/z = 108$ and a sample of the unknown does not dissolve in 1 M NaOH. Microanalytical results for this unknown are: C, 78%; H, 7.4%. Deduce the molecular formula of this unknown.

SOLUTION

Analyze We are asked to use a set of analytical and chemical data for an unknown and asked to calculate its molecular formula.

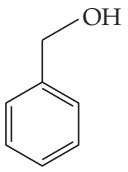
Plan Work out the empirical formula and use the molecular ion result from EIMS to yield the molecular formula.

Solve The elements present are C = 78%, H = 7.4% and O = 14.6%. Taking into account their atomic weights:

$$\begin{aligned} C : H : O &= \frac{78}{12} : \frac{7.4}{1} : \frac{14.6}{16} \\ &= 6.5 : 7.4 : 0.91 \text{ (divide by smallest number)} \\ &= 7 : 8 : 1 \end{aligned}$$

Therefore the empirical formula is C_7H_8O. The empirical mass is equivalent to the molecular ion signal, so the molecular formula is also C_7H_8O.

Although this answers the question, let's use the extra information given to us to deduce a structure. We know that the molecule is aromatic (therefore it contains C_6) and contains an O—H stretching band in the IR spectrum (therefore it contains OH). Eliminating these fragments from the molecular formula leaves CH_7. Not being soluble in 1 M NaOH rules out that the unknown is a phenol. Using the remaining carbon atom to bridge the aromatic and OH groups yields benzyl alcohol as a likely suspect.



Practice Exercise

(a) An unknown liquid has an IR spectrum with a band at 3330 cm^{-1}. EIMS indicates a molecular ion signal at $m/z = 60$. Microanalytical results are: C, 60%; H, 13.4%. Deduce the molecular formula of the unknown.
(b) An unknown compound has a band at 1710 cm^{-1} in the IR spectrum. EIMS indicates a molecular ion signal at $m/z = 88$ and a base signal at $m/z = 43$. Microanalysis gives: C, 54.5%; H, 9.15%. Deduce the molecular formula of the unknown.

is trivial, knowing something about the **index of hydrogen deficiency (IHD)**, which is essentially the summation of all π-bonds and rings within a molecule, is useful when determining possible structures of compounds, especially alkenes, ketones and aldehydes, amines, alkyl halides and so on. The IHD quantity is determined by comparing the number of hydrogens in the molecular formula of an unknown with that of an *alkane* reference containing the same number of carbon atoms as the unknown. This last statement can be summarized in the following way:

$$\begin{aligned} \text{IHD} &= \text{Number double bond or ring equivalents} \\ &= \frac{\text{maximum number H possible per C} - \text{actual number H per C}}{2} \end{aligned} \qquad [32.6]$$

Let's investigate the molecular formula, $C_4H_8O_2$, used in Practice Exercise 32.6(b). The index of hydrogen deficiency is

$$\text{IHD} = \frac{\overbrace{(2n+2)}^{\text{maximum number of H atoms possible}} - \overbrace{8}^{\text{actual number}}}{2}$$

where $n = 4$

$$\begin{aligned} \text{IHD} &= \frac{(2 \times 4 + 2) - 8}{2} \\ &= 1 \end{aligned}$$

which means that one double bond (or a ring system) must exist within the molecule. This unknown is ethyl acetate. The presence of a C=O double bond in ethyl acetate supports our IHD calculations. While this calculation works for compounds containing C, H and O, other elements can complicate matters.

To help us, several guidelines have been devised to determine IHD.

1. Work out the molecular formula of the *reference alkane* based on the number of carbon atoms in the unknown's molecular formula.
2. For each halogen in the unknown's molecular formula, *subtract* one hydrogen off the reference's molecular formula.
3. For each nitrogen in the unknown's molecular formula, *add* one hydrogen to the reference's molecular formula.
4. Make no modifications for oxygen or sulfur in the formula.

Chemical Wet Testing: Tests for Functional Groups

As long as enough of an unknown compound is present, chemical wet tests are useful for providing clues to the types of functional groups present. These tests may be as simple as solubility in aqueous solution or as complex as two- or three-step processes in a micro-test tube. **Figure 32.36** illustrates the process of using functional group tests to offer clues to an unknown's structure. This flow diagram has a significant amount of chemistry, so we will briefly point out the requirements for a positive test for each functional group. Much of this chemistry has been dealt with in the preceding chapters.

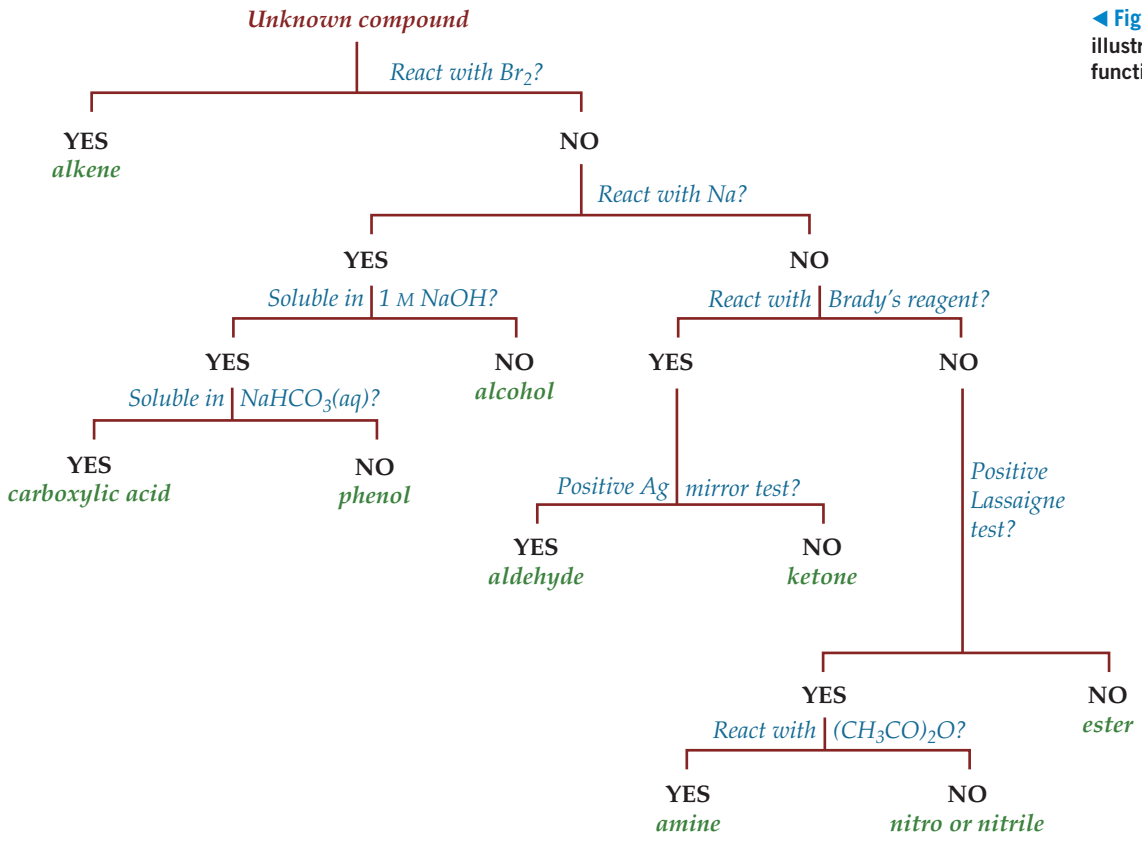
Alkenes: The decolorization of a bromine solution when applied to an organic molecule usually indicates the presence of an alkene.

Alcohols: Alcohols of low molar mass, such as CH_3OH and CH_3CH_2OH, mix completely with water, but those with larger non-polar alkyl groups have low solubility. The addition of sodium metal to alcohols will evolve hydrogen gas (bubbles) generating the alkoxide.

$$2\ ROH + 2\ Na \longrightarrow 2\ RO^- + 2\ Na^+ + H_2(g) \qquad [32.7]$$

Alcohols do not react with aqueous hydroxide.

Phenols: Phenols behave as weak acids with pK_a about 10. As a result, they are soluble in 1 M NaOH but not soluble in saturated aqueous sodium bicarbonate solution.



◀ **Figure 32.36** **Flowchart illustrating some simple functional group tests.**

Carboxylic acids: Carboxylic acids react with saturated aqueous sodium bicarbonate solution, with the release of CO_2 from solution.

$$RCOOH + HCO_3^- (aq) \longrightarrow RCOO^- (aq) + H_2O + CO_2 (g) \quad [32.8]$$

Aldehydes and ketones: Both aldehydes and ketones react with 2,4-dinitrophenylhydrazine (DNP), also known as Brady's reagent, to form highly colored precipitates. A generalized equation for this reaction is:

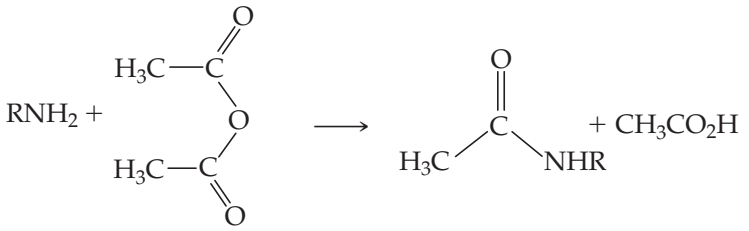
$$R_2C{=}O + H_2NR' \longrightarrow R_2C{=}NR' + H_2O \quad [32.9]$$

To distinguish aldehydes from ketones, a silver mirror test is usually employed.

$$RCHO + 2\ Ag^+ (aq) + 3\ OH^- (aq) \longrightarrow RCOO^- (aq) + 2\ Ag(s) + 2H_2O \quad [32.10]$$

Nitrogen: The Lassaigne sodium fusion test is a dramatic test that requires the use of molten sodium metal and ferrous sulfate. The bright blue color of the product, $NaFe[Fe(CN)_6]$ (also known as Prussian blue), indicates a positive test. The nitrogen can be present in amines, nitro compounds, nitriles and amides.

Amines: Amines are soluble in 1 M HCl and give alkaline solutions when mixed with water. Primary aromatic amines yield bright red/orange-colored azo-dyes when mixed with nitrous acid and 2-naphthol. Amines form amides by reaction with acetic anhydride.



[32.11]

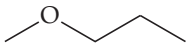
Using Analysis from Instrumental Techniques

We are now ready to tackle an advanced problem as a chemical detective. To help you to become familiar with the process, here are some guidelines.

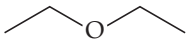
1. *Determine the molecular formula and index of hydrogen deficiency.* Calculate the empirical formula, determine the mass of the molecular ion (from the mass spectrum) and hence calculate the molecular formula and IHD.
2. *Check the IR spectrum.* Look for stretching bands indicative of functional groups O—H, N—H, C=O and so on.
3. *^{1}H NMR spectrum: number of signals and their positioning.* Determine the number of non-equivalent hydrogens by counting the number of signals present. Determine their chemical shift and relate this to potential neighboring functional groups—for example, CH_2—O at about 4 ppm, $CH_2C{=}O$ at about 2.5 ppm. Remember, this is only a guide.
4. *^{1}H NMR spectrum: integration.* Determine the relative number of equivalent hydrogens in each signal by measuring the area under each signal. Of course, this may already be done for you (Figure 32.22). The integral value could be exact in terms of the number of hydrogens or, based on extra symmetry within the molecule, may be a fraction of it.
5. *^{1}H NMR spectrum: splitting pattern.* Use your knowledge of splitting patterns and the $(n + 1)$ rule to determine the connectivity between groups of atoms. Learn to recognize ethyl groups by their characteristic splitting pattern.
6. *Deduce the structure.* Using all this information (including chemical tests), try to deduce the structure. Remember, it might not be the first one you draw.
7. *Check.* Use the ^{13}C NMR spectrum and any distinguishable fragmentation patterns in the mass spectrum to confirm your choice of structure. Use this information to distinguish isomers.

Self-Assessment Exercise

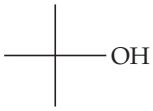
32.26 After a stocktake in a chemical store, two partially labelled bottles containing liquids with different odours remained. The label on both bottles was C_4H_xO where the value of x was unreadable. The bottles were marked A and B. The store's card index showed that there were five possibilities for A and B, numbered 1–5.



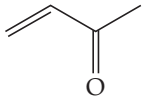
1



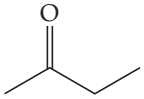
2



3



4



5

The ^{1}H NMR and IR spectra of A and B were recorded and are described here. For each bottle and its contents, suggest a possible conclusion for the information presented—for example, IR band at 2950 cm^{-1} indicates C—H present—and deduce the structures of A and B.

- *Bottle A:* Strong IR band near 1700 cm^{-1}, ^{1}H NMR spectrum: three signals in the ratio 3 : 3 : 2.
- *Bottle B:* Strong IR band near 3500 cm^{-1}, ^{1}H NMR spectrum: two signals in the ratio 9 : 1.

(a) Bottle A contains compound 4 and bottle B contains compound 2.

(b) Bottle A contains compound 1 and bottle B contains compound 3.

(c) Bottle A contains compound 3 and bottle B contains compound 5.

(d) Bottle A contains compound 5 and bottle B contains compound 3.

Exercises

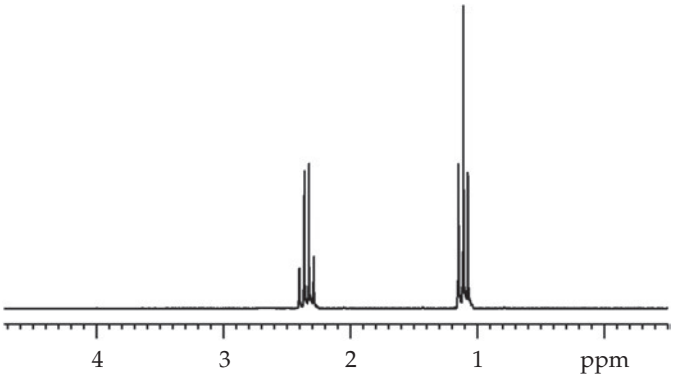
32.27 Calculate the IHD for the following compounds:

(a) cholesterol, $C_{27}H_{46}O$ **(b)** acetic acid, $C_2H_4O_2$

(c) aspirin, $C_9H_8O_4$ **(d)** naphthalene, $C_{10}H_8$

(e) ascorbic acid, $C_6H_8O_6$ **(f)** cocaine, $C_{17}H_{21}NO_4$

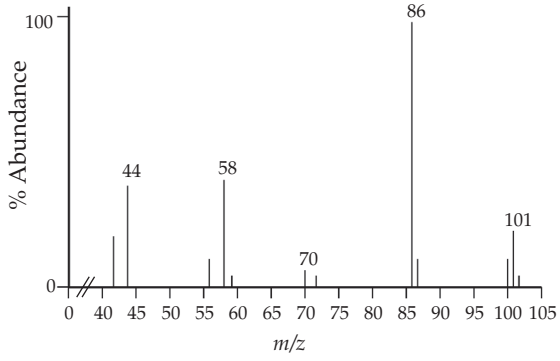
32.28 The product formed upon oxidation of an unknown organic compound with chromic acid has the molecular formula $C_5H_{10}O$. The ^{1}H NMR spectrum of the product is shown here and its IR spectrum has a strong band at 1700 cm^{-1}. Using this information, deduce the structure of the product and hence the structure of the unknown compound.



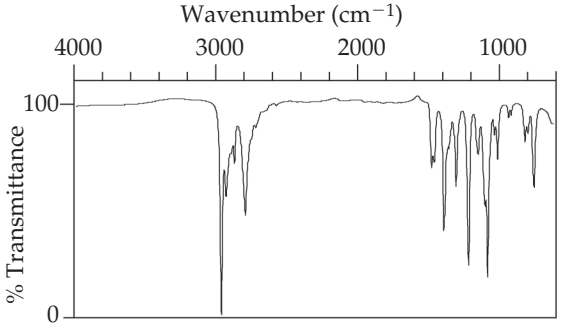
32.29 An acidic liquid has a broad band at 3300 cm^{-1} and a sharp band at 1710 cm^{-1} in the infrared spectrum. One mole of this unknown reacts with one mole of NaOH. The ^{1}H NMR spectrum shows three signals in the ratio 2: 2 : 1. Microanalysis gave C, 33.2%; H, 4.6%; Cl, 32.7%. Deduce the structure of the unknown.

32.30 This basic compound gives a positive result to the Lassaigne test. Microanalysis gave the following result: C, 71.22; H, 14.94; N, 13.84. Use this information and the accompanying spectra to deduce the structure of the unknown.

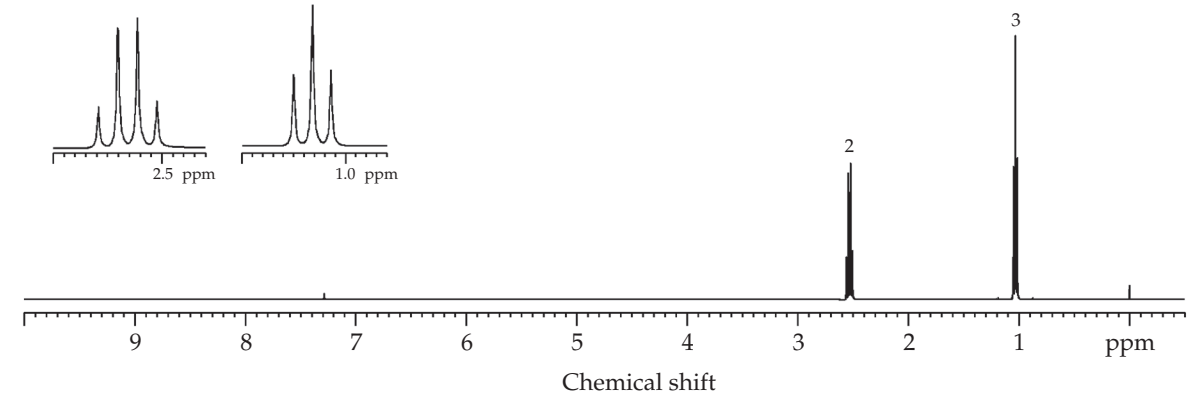
Mass spectrum



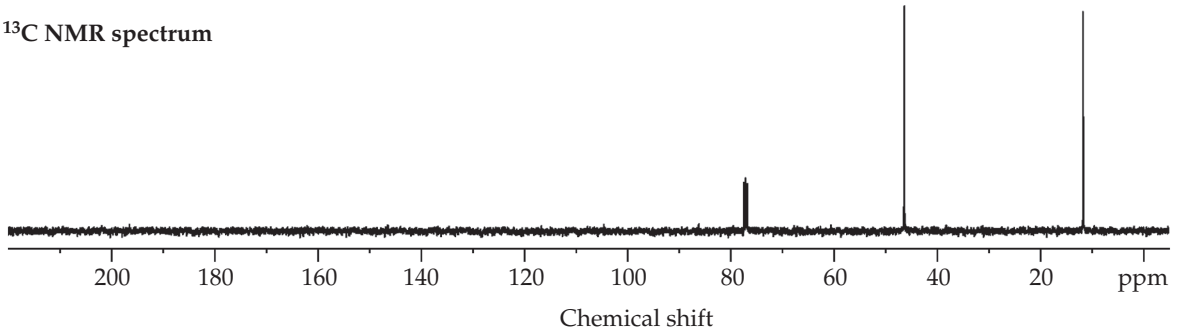
IR spectrum



^{1}H NMR spectrum

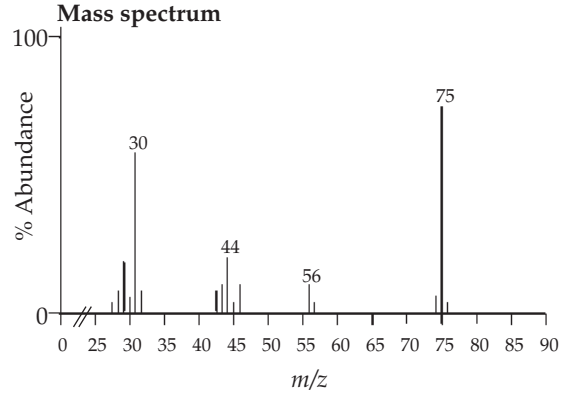


^{13}C NMR spectrum

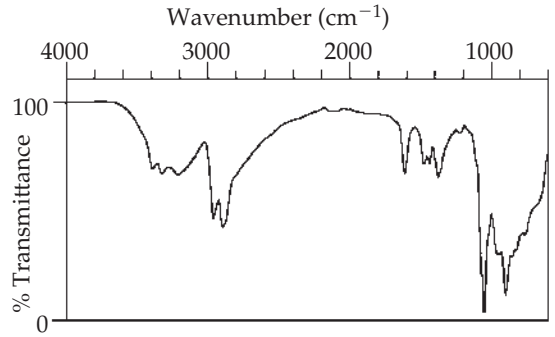


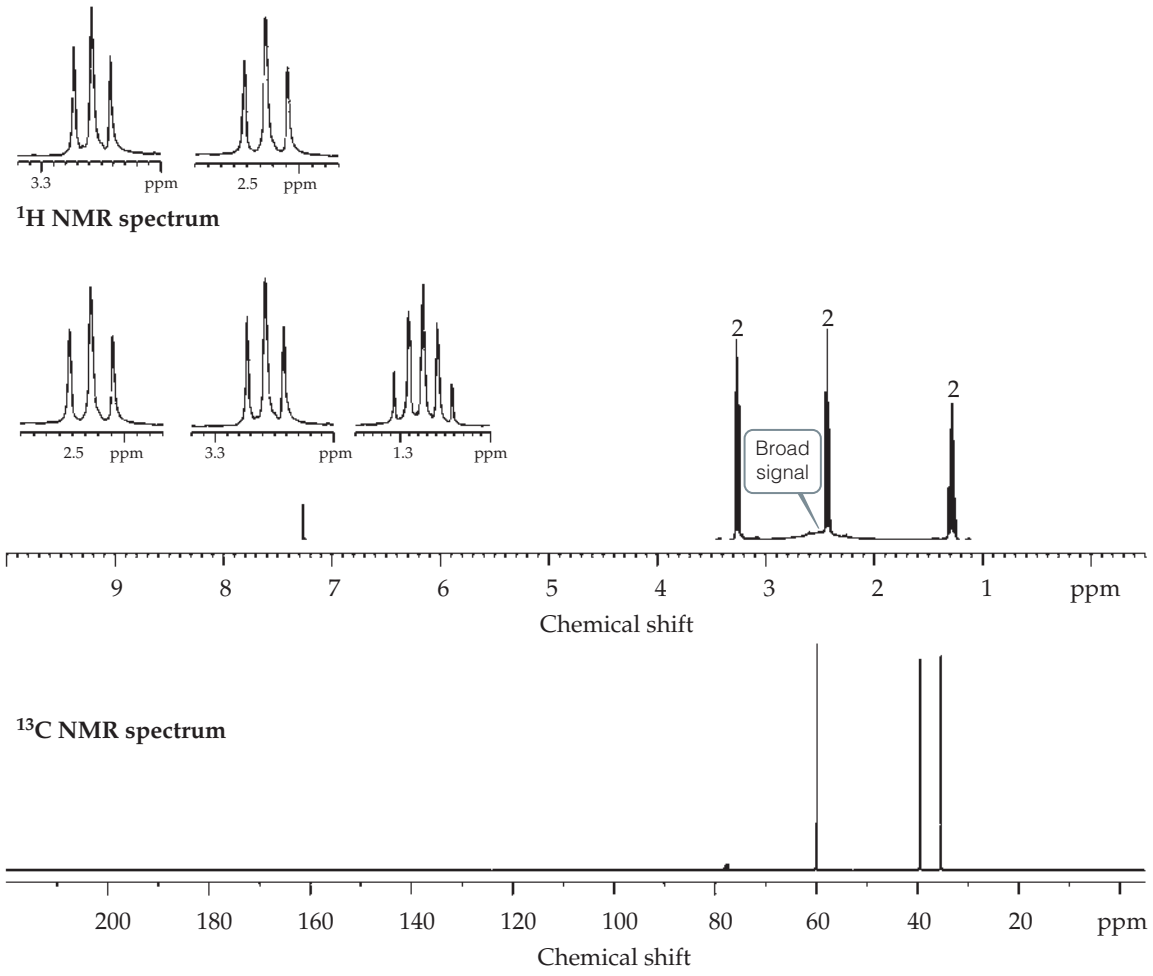
32.31 This unknown liquid is miscible with water, giving a mildly basic solution. Microanalysis gave the following result: C, 47.97; H, 12.08; N, 18.65. The broad, three-hydrogen signal within the ^{1}H NMR spectrum (indicated) disappears on the addition of D_2O. Use all the information available to deduce the structure of the unknown.

Mass spectrum

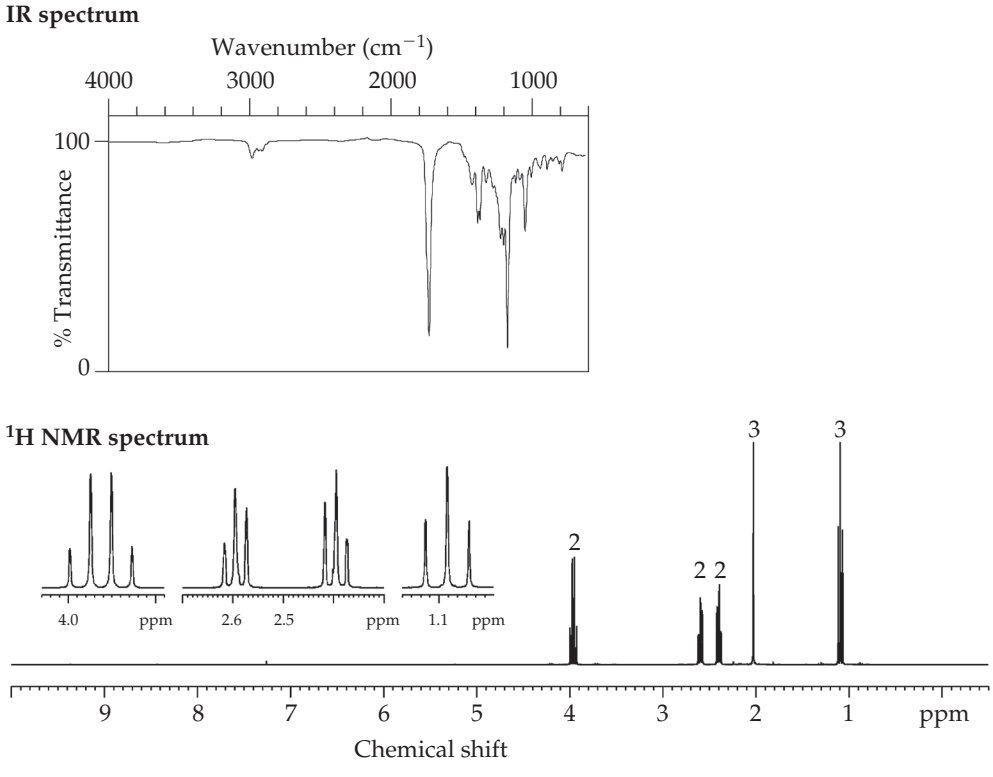


IR spectrum

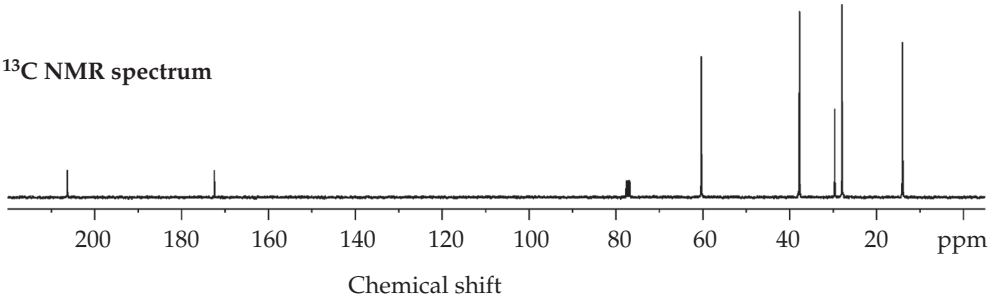




32.32 This unknown liquid reacts with Brady's reagent to form a highly colored precipitate. The electrospray mass spectrum (not shown) has a signal at $m/z = 145$ corresponding to $[M + H]^+$. Microanalysis gave the following result: C, 58.32; H, 8.39. Use all the information available to deduce the structure of the unknown.



^{13}C NMR spectrum



Answers to Self-Assessment Exercise

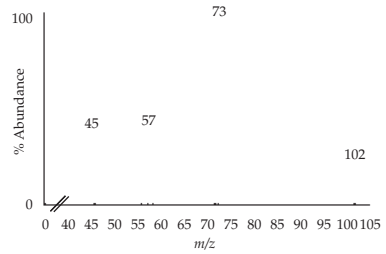
32.26 Bottle A contains butanone (compound 5); Bottle B contains 2-methylpropan-2-ol (compound 3).

Sample Integrative Exercise

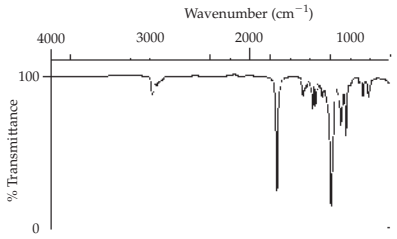
Putting Concepts Together

Unknown D is a sweet-smelling liquid. Microanalytical results for this unknown give C, 58.80%; H, 9.87%, and the characterization spectra acquired for this unknown are shown here. Use the information to deduce the structure of unknown D.

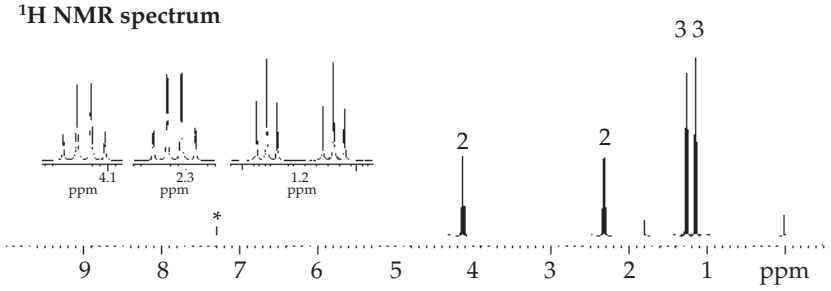
EI mass spectrum



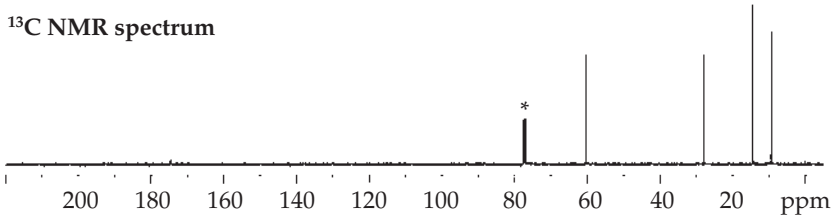
IR spectrum



^{1}H NMR spectrum



^{13}C NMR spectrum



Asterisks denote solvent signals.

Analyze We are asked to use a set of analytical and chemical data for an unknown and asked to determine its structural formula.

Plan Use all the information given in the form of spectra and microanalytical data to deduce the structure of the unknown.

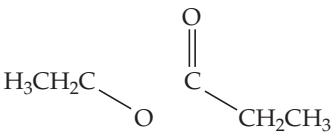
Solve The microanalytical data give an empirical formula of $C_5H_{10}O_2$, which has a mass equal to the molecular ion signal. Hence the molecular formula is also $C_5H_{10}O_2$. The IHD is 1, suggesting the presence of either a ring or double bond within the structure, but not both.

The IR spectrum shows a strong band at about 1750 cm^{-1}, attributable to a C=O stretching frequency. There is no O—H stretch, which means the extra oxygen atom in the molecular formula must be of ester or ether origin.

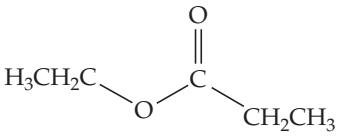
There are four signals in the ^1H NMR spectrum with integration in the ratio 2 : 2 : 3 : 3, which accounts for all the hydrogens in the molecular formula.

The chemical shifts of the two sets of quartets indicates that one set (approximately 4 ppm) neighbors oxygen and the other neighbors a carbonyl C=O group. Using the $(n + 1)$ rule, the hydrogens responsible for the quartet splitting patterns must be coupled to methyl groups. Hence, two different ethyl groups exist in this structure.

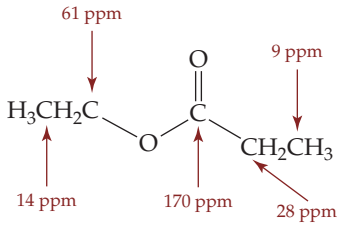
Putting together the clues to date, we have the following fragments:



These fragments make up the molecular formula of the unknown. Knowing that the unknown shows a positive test for esters (and is sweet-smelling) would confirm the choice in structure. Hence, our unknown is *ethyl propanoate*.



Check Use the ^{13}C NMR data to confirm the structure. The structure of ethyl propanoate has five different carbon atoms, the same number of signals as found in the ^{13}C NMR spectrum. In terms of chemical shift, the signals would be distributed as follows:



Practice Exercise
A number of these problems can be found in the end-of-chapter Exercises.

Chapter Summary and Key Terms

SECTION 32.1 All molecules absorb electromagnetic radiation to some degree and hence give rise to absorption spectra. The amount and type of absorption depends on the energy of radiation and the nature of the molecule, its bond types and its electronic structure. **Beer–Lambert's law** can be used to relate the amount of energy being absorbed to the concentration of the substance absorbing the energy in **UV-visible spectroscopy**.

SECTION 32.2 **Infrared spectroscopy** observes the vibrations of covalent bonds. The difference in vibration energy is a result of the stiffness of the covalent bond. This principle follows **Hooke's law** and provides useful evidence for the presence of functional groups in molecules. Compounds are measured either as solids, liquids or gases. An **infrared spectrum** is usually plotted as percentage **transmittance** (%T) versus **wavenumber** (cm^{-1}). The region below 1400 cm^{-1} is known as the **fingerprint region**.

SECTION 32.3 **Nuclear magnetic resonance (NMR) spectroscopy** is a method for observing nuclear spin transitions, giving information on the connectivity of nuclei (atoms). The technique relies on the difference in energy levels between nuclear spins of $I > 0$ ($I = \frac{1}{2}$ for ^1H and ^{13}C), within a strong magnetic field. The absorption of radiation at the **Larmor frequency**, which leads to an NMR spectrum, is termed **resonance**. The frequency of an NMR spectrometer is called its **operating frequency**.

The electrons within these functional groups also have a spin that creates local magnetic fields that **shield** or **deshield** the neighboring nuclei from the applied magnetic field. Three aspects of an NMR spectrum are important: the **chemical shift** (δ) of a signal, the area under the signal (available by **integration**) and the **splitting pattern** of the signal all yield diagnostic information about the molecular structure. Equivalent hydrogens or carbons within a molecule by symmetry give rise to identical chemical shifts in ^1H or ^{13}C NMR spectra, respectively.

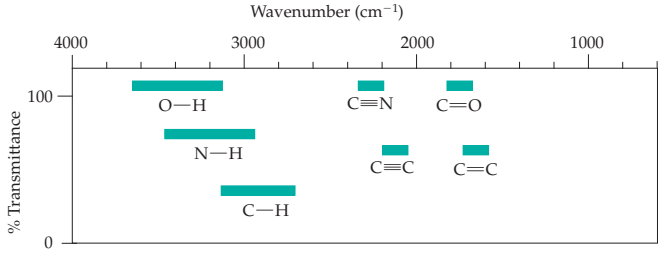
An NMR signal is split by the influence of adjacent atoms on the local magnetic field of the nucleus in question. This splitting is called **spin–spin coupling**. The splitting pattern that results follows the **$(n + 1)$ rule**. Splitting patterns are commonly described in terms of their **multiplicity**—for example, singlets, doublets, triplets, quartets, multiplets. Two (or more) coupled nuclei share the same **coupling constant** (J), which allows for easy tracing of the molecule's connectivity. ^{13}C NMR spectra are commonly devoid of coupling because they are recorded in a hydrogen-decoupled mode. **Decoupling** is used either to simplify a spectrum or to indicate coupled nuclei.

SECTION 32.4 **Electron impact ionization mass spectrometry (EIMS)** uses high-energy electrons to bombard a sample compound, causing it to *ionize* or **fragment**. The **molecularion** (M^+) formed upon ionization has a **mass-to-charge ratio** (m/z) equal in quantity to the molecular weight of the sample being tested. Signals with a mass spectrum are assigned a percentage abundance with respect to the **base peak**. Mass spectrometry often provides clues to the structure and functional groups contained within a molecule through either fragmentation or isotopic patterns.

SECTION 32.5 Using the **index of hydrogen deficiency (IHD)**, the chemist can determine the number of double bond or ring equivalents within a molecular formula.

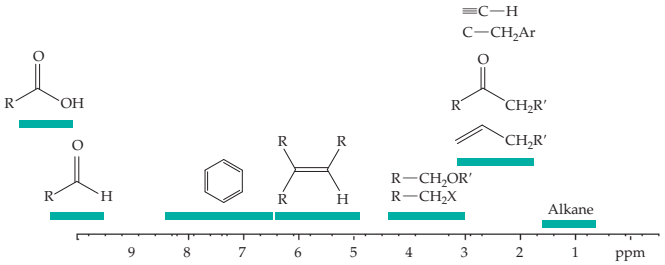
Key Skills

- Understand how to use Beer–Lambert's law. (Section 32.1)
- Be able to identify O—H, C—H, C≡C, C═C, C═O stretches in IR spectra. (Section 32.2)

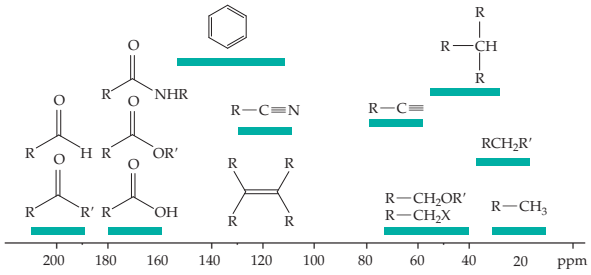


- Apply NMR chemical shifts to determine possible functional group types based on: (Section 32.3)

(a) ^{1}H NMR spectroscopy



(b) ^{13}C NMR spectroscopy



- Apply multiplicity and J in ^{1}H NMR to determine connectivity within organic molecules. (Section 32.3)
- Be able to identify the molecular ion signal and apply fragmentation patterns to determine functional groups and molecular weight. (Section 32.4)
- Be able to determine molecular formula from percentage composition and mass spectra. (Section 32.5)
- Calculate IHD based on a molecular formula. (Section 32.5)

Key Equations

- Beer–Lambert's law

$$A = \varepsilon c l \qquad [32.1]$$

- Transmittance

$$\text{Absorbance} = -\log_{10}(\text{transmittance})$$
$$\text{or}$$
$$A = -\log_{10} T \qquad [32.2]$$

- IHD

IHD = Number double bond or ring equivalents

$$= \frac{\text{maximum number H possible per C} - \text{actual number H per C}}{2} \qquad [32.6]$$

- Effective magnetic field

$$B_{\text{effective}} = B_{\text{applied}} - B_{\text{local}} \qquad [32.4]$$

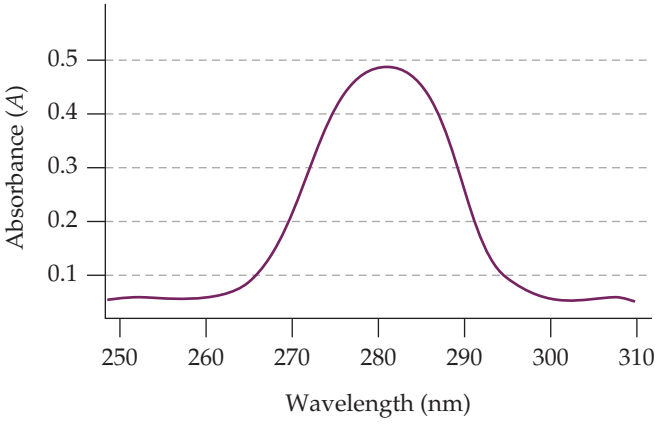
- Chemical shift

$$\delta = \frac{\text{Shift in resonance frequency from TMS (Hz)}}{\text{Operating frequency of the spectrometer (MHz)}} \qquad [32.5]$$

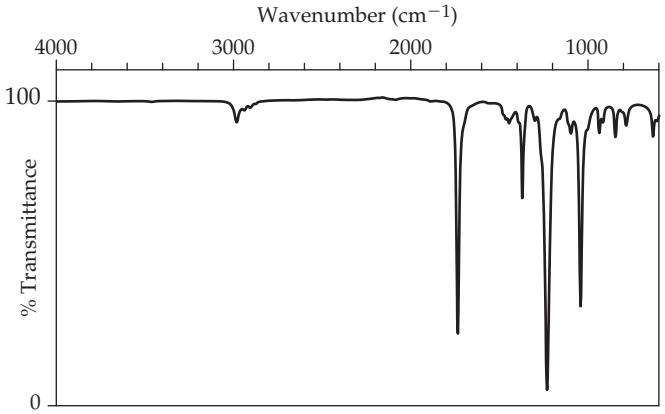
Exercises

Visualizing Concepts

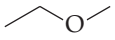
32.33 **(a)** An aqueous solution of 4-aminobenzoic acid gives a maximum absorbance of 0.21. What is the percentage transmittance? **(b)** The absorption spectrum of a solution of naphthalene ($\varepsilon = 300\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$) in hexane obtained through a path length of 1.0 cm is given here. What is the concentration of the sample? [*Hint:* You will need to estimate the absorbance value by reading off the graph.] [Section 32.1]



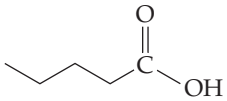
32.34 Determine which of the following compounds would be likely to give this IR spectrum. [Section 32.2]



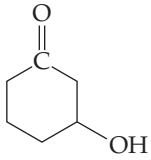
(a)



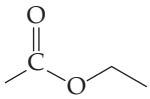
(b)



(c)



(d)



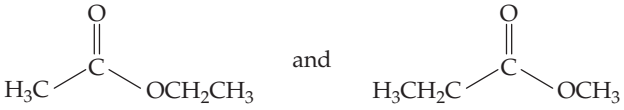
32.35 Magnetic Resonance Imaging is a medical equivalent to NMR spectroscopy. **(a)** Instruments for obtaining MRI data are typically labelled with a frequency, such as 600 MHz. Why do you suppose this label is relevant to the experiment? **(b)** In general, the stronger the magnetic field, the greater the information obtained from an NMR or MRI experiment. Why do you suppose this is the case? **(c)** What safety precautions do you think are relevant around superconducting magnets? [Section 32.3]



32.36 How could you use both ^{1}H and ^{13}C NMR to distinguish between these isomers? [*Hint:* Look for symmetry elements.] [Section 32.3]

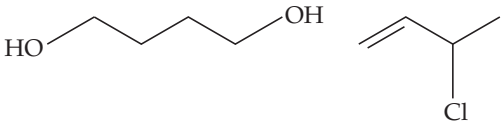
(a) $CH_3CH_2OCH_2CH_3$ and $CH_3CH_2CH_2CH_2OH$

(b)

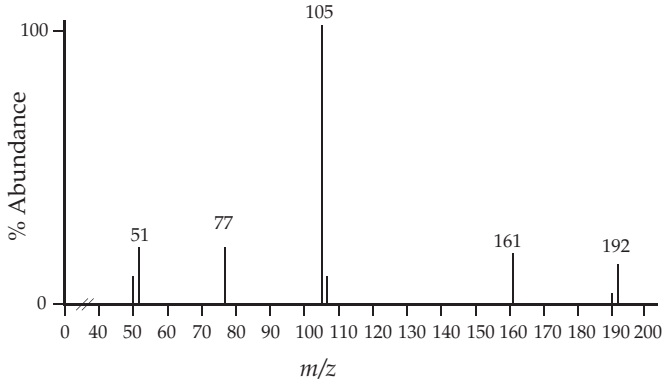


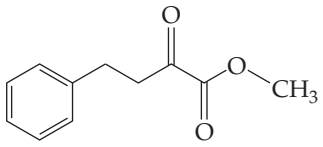
(c) $CH_3CH_2CH_2Br$ and $CH_3CHBrCH_3$

32.37 The two compounds shown here have a molecular ion signal at $m/z = 90$. Describe two ways, using mass spectrometry, of distinguishing between them. [Section 32.4]



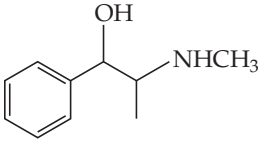
32.38 Confirm that the fragmentation pattern seen in the following EI mass spectrum is consistent with the structure shown here. What chemical wet test(s) could you perform to support the structure shown? [Sections 32.4 and 32.5]



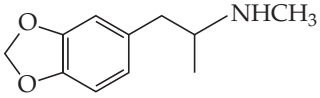


Infrared Spectroscopy (Section 32.2)

32.39 Ephedrine is produced by a number of the *Ephedra* species of plants. Its medicinal properties have been related to respiratory conditions since 200 AD. Its structure was elucidated in 1923 and ephedrine began clinical trials in 1926 as a bronchodilator for asthma. In the late 1990s, a new recreational drug, ecstacy, became popular with people in their 20s. Its structure is similar to ephedrine, which also acts as a heart stimulant.



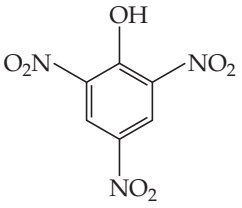
ephedrine



ecstacy

Could police and customs officials use IR spectroscopy to distinguish between the two compounds? Explain.

32.40 Picric acid is an aromatic compound used extensively before 1960 as an agent for co-crystallising liquid organic samples so that a melting point determination could be made. Picric acid is not a carboxylic acid but instead a phenol bearing nitro substituents at the 2,4, and 6 positions. How could you use IR spectroscopy to determine that picric acid was indeed a phenol and not a carboxylic acid?



32.41 **(a)** Of the functional groups O—H, C=O, C≡N, which would be most diagnostic for bioimaging? Why? **(b)** Can you name another functional group that could be used for diagnostic purposes using the IR technique? What problems might arise?

NMR Spectroscopy (Section 32.3)

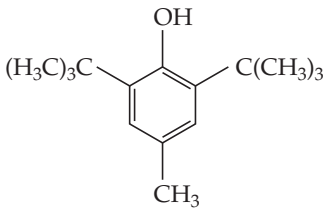
32.42 The ^{1}H NMR spectrum of acetone recorded on a spectrometer with an operating frequency of 200 MHz has a single resonance signal at 2.1 ppm.

(a) What is the difference in Hz between this signal and that of tetramethylsilane (TMS)?

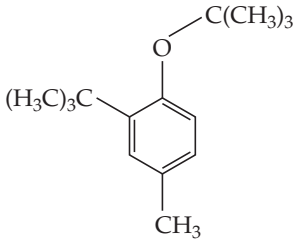
(b) At what δ value does this signal lie if recorded using a 400 MHz spectrometer?

(c) How many Hz away from TMS does the absorption in the 400 MHz spectrum correspond to?

32.43 When the antioxidant BHT was first prepared, chemists were not sure of its structure. The chemical formula was determined by elemental analysis, but NMR, which would have instantaneously revealed the structure, had not yet been discovered. The problem arose because BHT failed the usual tests for phenols; for example, it was not soluble in dilute basic solution. Because of this, chemists thought the second 2-methylpropyl (*t*-butyl) group was linked to oxygen to form an ether. Of course, the reason BHT does not behave like other phenols is because the OH group is hindered by the two neighboring 2- methylpropyl groups, a protective quality that also allows this molecule to be used as a commercial antioxidant.



BHT



Supposed BHT

In terms of the number of equivalent hydrogens present, how could ^{1}H NMR spectroscopy be used to verify the correct structure for BHT?

32.44 Two bottles labelled propanol were found in a laboratory. Because of their differing boiling points, the bottles clearly contained the two propanol constitutional isomers. To determine which propanol was in which bottle, a ^{1}H NMR spectrum was obtained on each sample. Draw the two possible isomers and describe how NMR might be used to distinguish between them.

32.45 Predict the splitting pattern observed in the hydrogen-coupled ^{13}C NMR spectrum for each of these compounds:

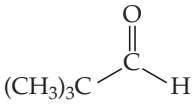
(a) CH_3CHBr_2 **(b)** $(CH_3)_2CHCl$ **(c)** $(CH_3)_3CBr$

32.46 The spin of an electron generates a magnetic field, with "spin-up" and "spin-down" electrons having opposite fields. In the absence of a magnetic field, a "spin-up" and a "spin-down" electron have the same energy. **(a)** Why do you think that the use of a magnet was important in the discovery of electron spin? **(b)** A phenomenon called electron spin resonance (ESR) is closely related to nuclear magnetic resonance. In ESR, a compound with an unpaired electron is placed in a magnetic field, causing the unpaired electron to have two different energy states similar to our discussion of nuclear spin (see Figure 32.13). ESR uses microwave radiation instead of radiofrequency radiation to excite the unpaired electron from one state to the other. Does an ESR experiment require photons of greater or lesser energy than an NMR experiment?

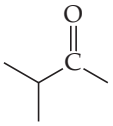
32.47 2-methylbut-2-ene contains signals at δ20.3, 22.5, 22.9, 110.3 and 111.5 in the ^{13}C NMR hydrogen-decoupled spectrum, whereas 2-methylbutane contains only four signals. Explain why this is so.

32.48 Predict the number of ^{1}H NMR signals and also the splitting pattern of each of these compounds in the ^{1}H NMR spectrum.

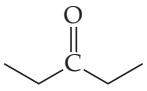
(a)



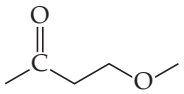
(b)



(c)

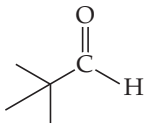


(d)

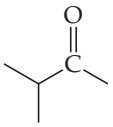


32.49 Predict the number of ^{13}C NMR signals in the hydrogen-decoupled spectrum of the following:

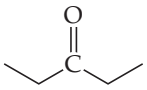
(a)



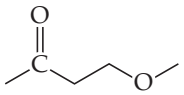
(b)



(c)

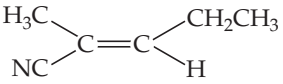


(d)



32.50 ^{31}P is NMR active ($I = \frac{1}{2}$) and is also the only naturally occurring phosphorus isotope. Describe the splitting you would see in both the ^{1}H NMR and ^{31}P NMR spectra of PH_2Cl.

32.51 The 200 MHz ^{1}H NMR spectrum of 2-cyanopent-2-ene has four distinctive resonances: δ5.3 (1H, singlet), 2.1 (2H, quartet), 1.9 (3H, singlet), 1.0 (3H, triplet). Assign each resonance to the structure.

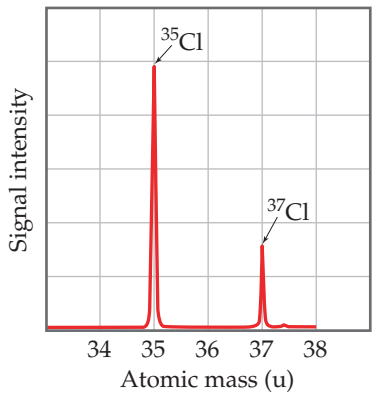


Mass Spectrometry (Section 32.4)

32.52 Triethylborane has two signals at *m/z* 97 and 98 in its EI mass spectrum. Account for the two signals.

32.53 An aliphatic compound contains C, 39.76%, and H, 7.34%, but doesn't contain oxygen. The EI mass spectrum shows a molecular ion at $m/z = 150$ and a second signal of equal intensity at $m/z = 152$. Determine this compound's molecular formula.

32.54 **(a)** The mass spectrometer in Figure 32.31 has a magnet as one of its components. What is the purpose of the magnet? **(b)** The atomic weight of Cl is 35.5 u. However, the mass spectrum of Cl, shown here, does not have a signal at this mass. Explain.



32.55 What is meant by these terms?

(a) M^+ **(b)** $[M+2]^+$ **(c)** base peak

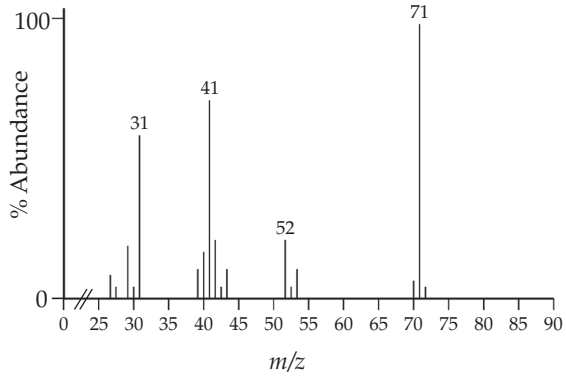
(d) *m/z* **(e)** EIMS

Integrative Exercises

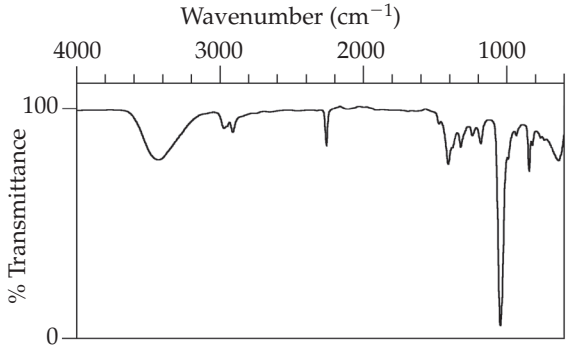
32.56 The guidelines for determining the IHD of a compound are listed on page 1488. Using examples as appropriate, discuss why, for each nitrogen in the unknown's molecular formula, one hydrogen needs to be added to the reference molecular formula, but for oxygen nothing is added.

32.57 This unknown evolves gas when a small amount of sodium metal is added. Microanalysis gave the following result: C, 50.69; H, 7.09; N, 19.71. Use all the information available to deduce the structure of the unknown.

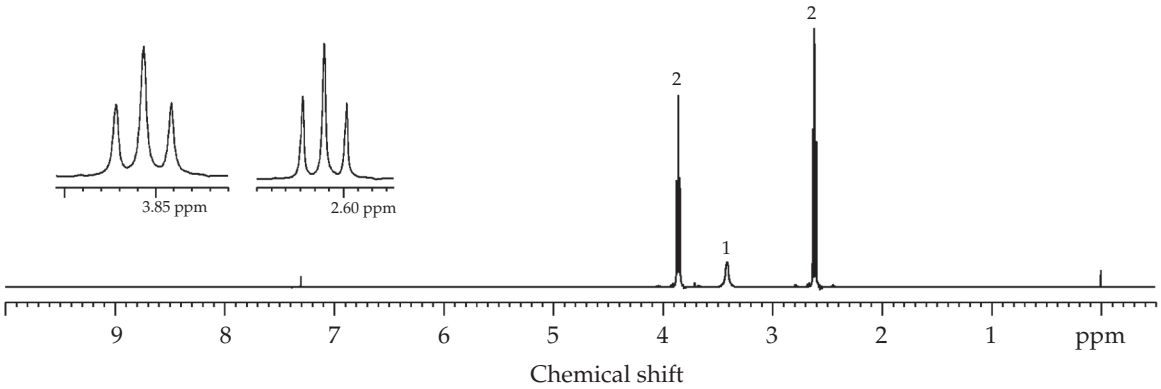
Mass spectrum



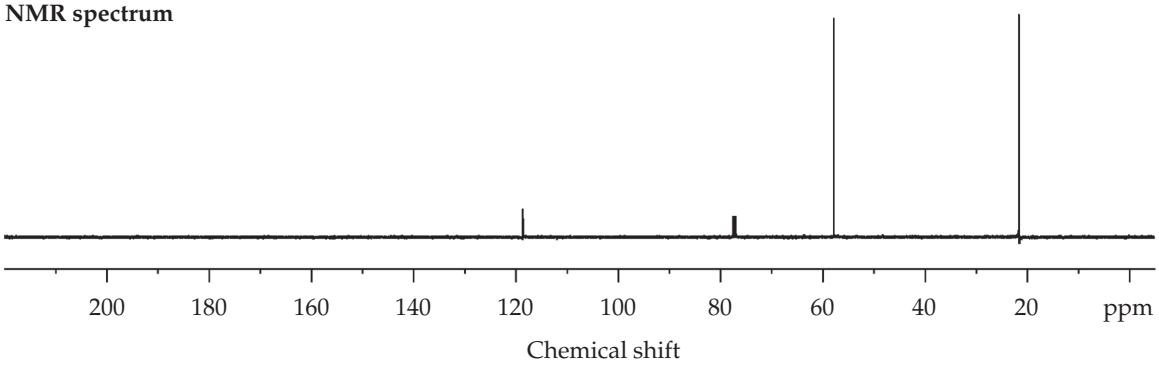
IR spectrum



^{1}H NMR spectrum

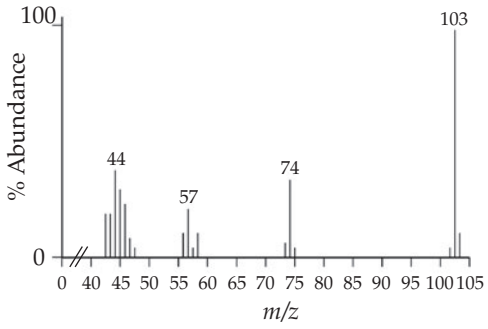


^{13}C NMR spectrum

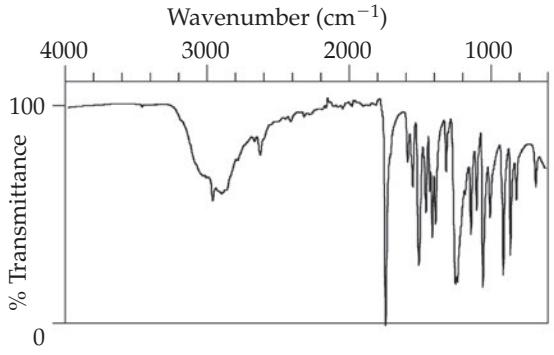


32.58 This unknown is a derivative of an amino acid. Microanalysis gave the following result: C, 46.59; H, 8.80; N, 13.58. Solvent signals within the ^{1}H NMR spectrum are labelled with an asterisk. Use all the information available to deduce the structure of the unknown.

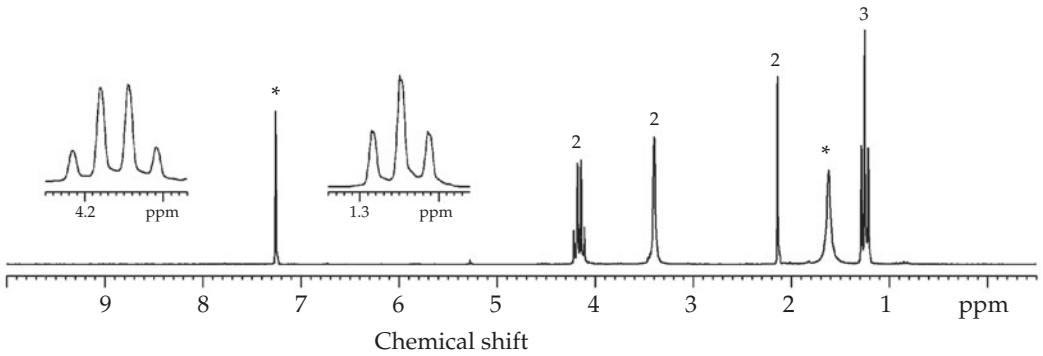
Mass spectrum



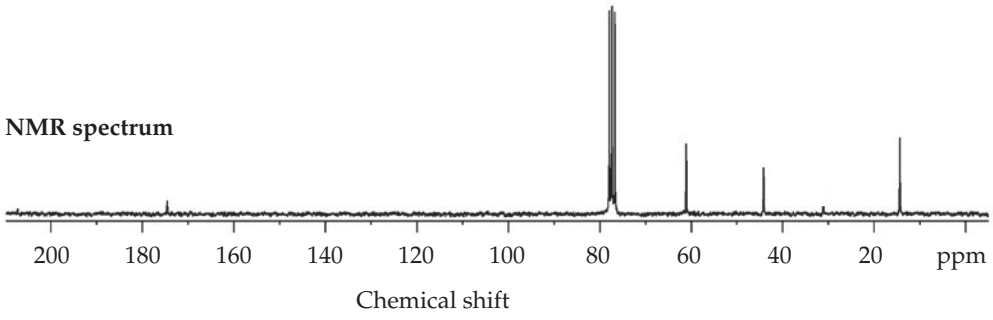
IR spectrum



^{1}H NMR spectrum

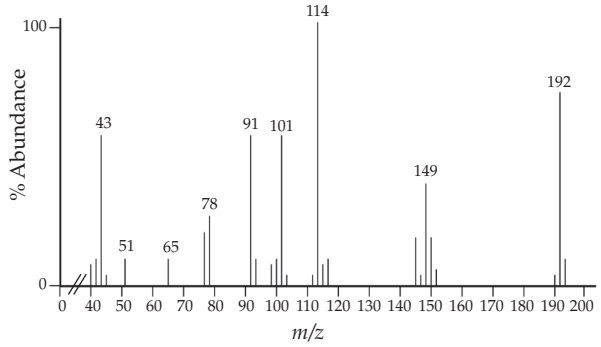


^{13}C NMR spectrum

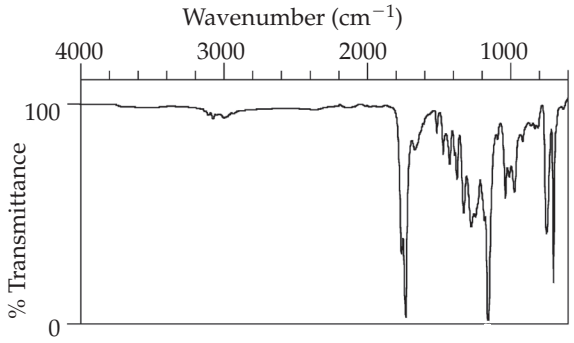


32.59 When this unknown is saponified, it leads to the isolation of benzyl alcohol as one of the products. Microanalysis gave the following result: C, 68.74; H, 6.29. Use all the information available to deduce the structure of the unknown.

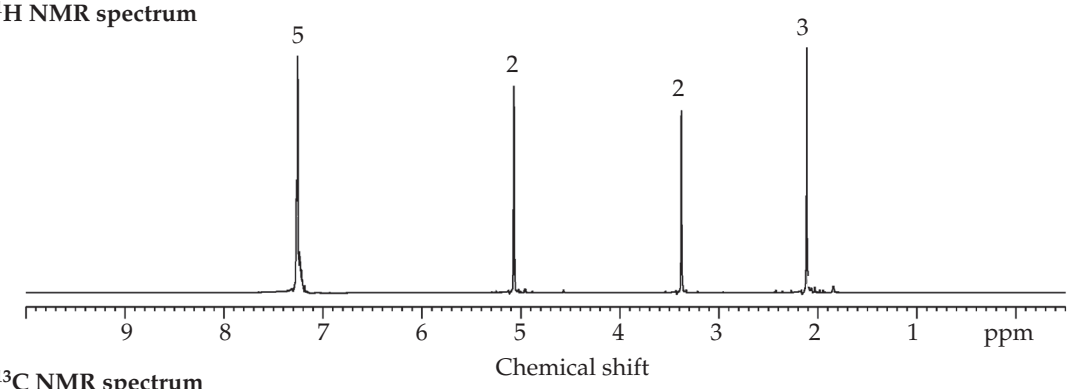
Mass spectrum



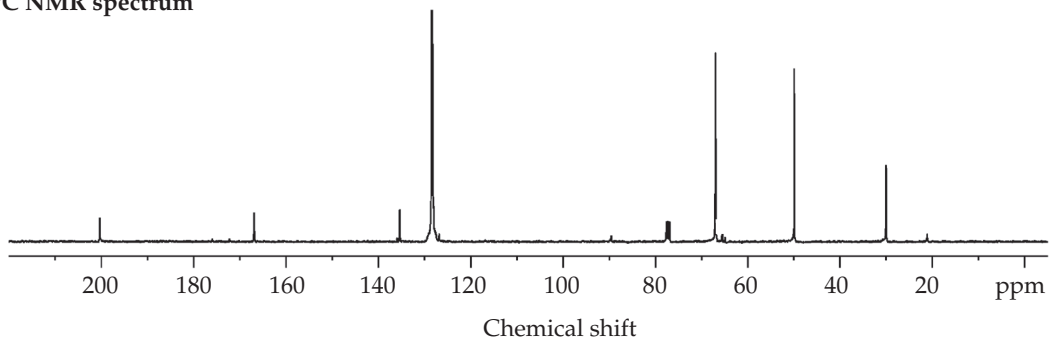
IR spectrum



^{1}H NMR spectrum

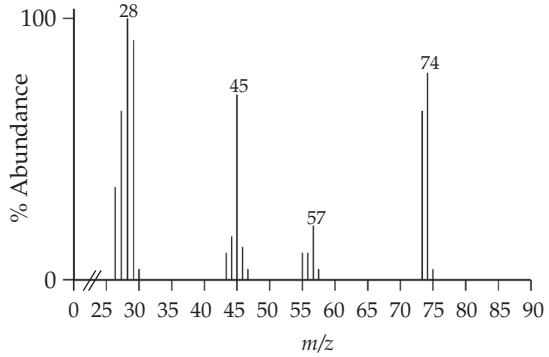


^{13}C NMR spectrum

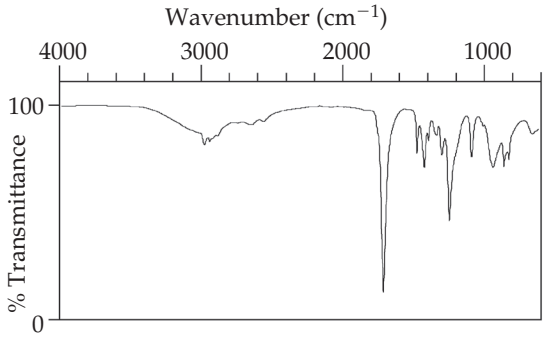


32.60 This unknown liquid evolves a gas when dissolved in aqueous sodium bicarbonate. Microanalysis gave the following result: C, 48.64; H, 8.16. Use all the information available to deduce the structure of the unknown.

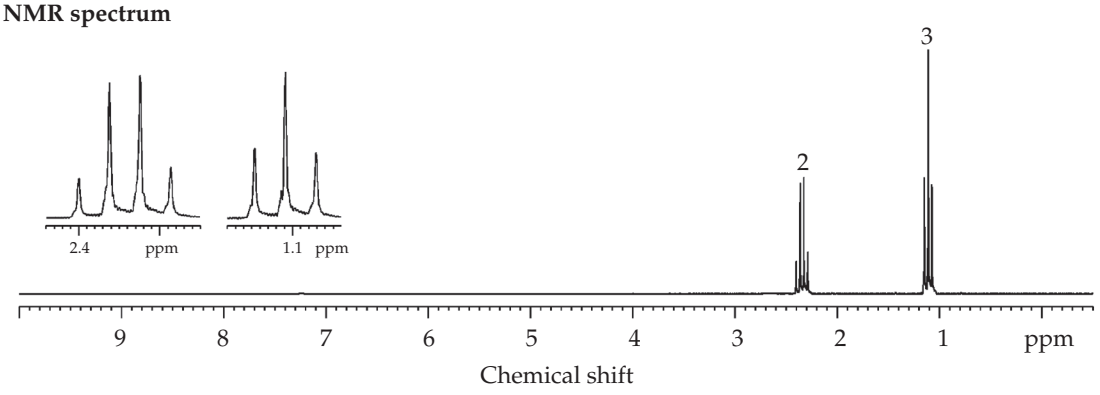
Mass spectrum



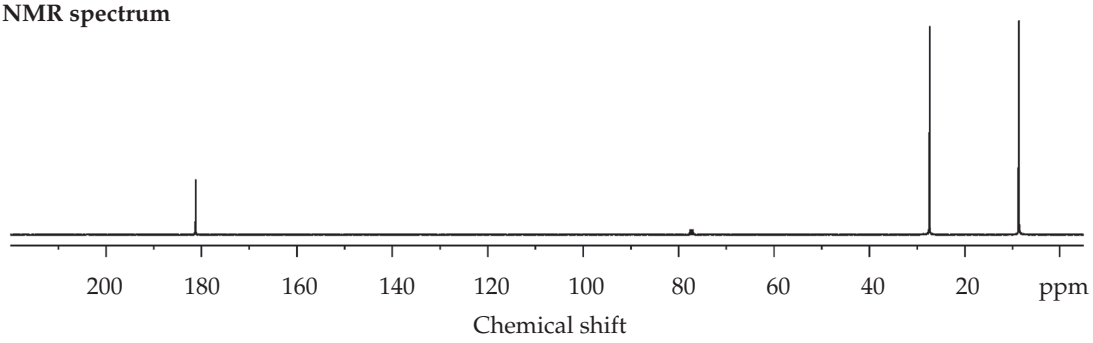
IR spectrum



^{1}H NMR spectrum

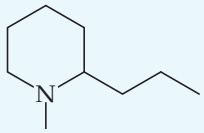


^{13}C NMR spectrum



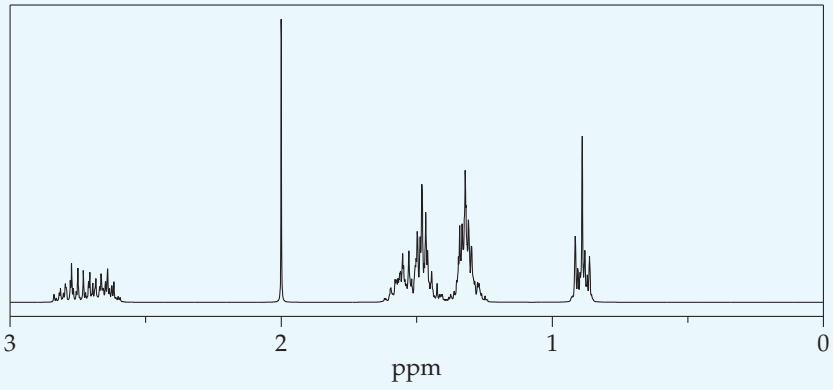
Design an Experiment

The poison hemlock plant (*Conium maculatum*) is toxic to mammals and can be fatal. All parts of the plant are poisonous, and as few as about ten leaves can kill a human. You are asked to help investigate the sudden death of some cattle that are thought to have eaten hemlock, and the vet has provided you with a small sample of a substance taken from the dead animals for you to identify. You suspect the substance to be coniine, one of the active components of hemlock.



Coniine

What precautions would you take when handling this substance? What chemical tests would you perform, and what would you expect them to show? If an elemental analysis were carried out, what percent of C, H, and N would you expect for coniine? What instrumental method would you use to determine the molecular mass of the substance and what would you calculate it to be for coniine? You run an IR spectrum of the substance – which regions of the IR would give you information about what functional groups were, or were not, present in the sample? The ^{13}C NMR contains eight signals between 10 and 60 ppm. Is this consistent with the structure of coniine? The ^{1}H NMR spectrum contains many overlapping signals and is reproduced here. Does it help with your identification? If you are asked how confident you were with your identification, what would you say?



APPENDIX

A

MATHEMATICAL OPERATIONS

A.1 | Exponential Notation

The numbers used in chemistry are often either extremely large or extremely small. Such numbers are conveniently expressed in the form

$$N \times 10^n$$

where N is a number between 1 and 10, and n is the exponent. Some examples of this *exponential notation*, which is also called *scientific notation*, follow.

1,200,000 is 1.2×10^6	(read "one point two multi ten to the sixth power")
0.000604 is 6.04×10^{-4}	(read "six point zero four times ten to the negative fourth power")

A positive exponent, as in the first example, tells us how many times a number must be multiplied by 10 to give the long form of the number:

$$1.2 \times 10^6 = 1.2 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \quad \text{(six tens)}$$
$$= 1{,}200{,}000$$

It is also convenient to think of the *positive exponent* as the number of places the decimal point must be moved to the *left* to obtain a number greater than 1 and less than 10. For example, if we begin with 3450 and move the decimal point three places to the left, we end up with 3.45×10^3.

In a related fashion, a negative exponent tells us how many times we must divide a number by 10 to give the long form of the number.

$$6.04 \times 10^{-4} = \frac{6.04}{10 \times 10 \times 10 \times 10} = 0.000604$$

It is convenient to think of the *negative exponent* as the number of places the decimal point must be moved to the *right* to obtain a number greater than 1 but less than 10. For example, if we begin with 0.0048 and move the decimal point three places to the right, we end up with 4.8×10^{-3}.

In the system of exponential notation, with each shift of the decimal point one place to the right, the exponent *decreases* by 1:

$$4.8 \times 10^{-3} = 48 \times 10^{-4}$$

Similarly, with each shift of the decimal point one place to the left, the exponent *increases* by 1:

$$4.8 \times 10^{-3} = 0.48 \times 10^{-2}$$

Many scientific calculators have a key labeled EXP or EE, which is used to enter numbers in exponential notation. To enter the number 5.8×10^3 on such a calculator, the key sequence is

$$\boxed{5}\ \boxed{\cdot}\ \boxed{8}\ \boxed{\text{EXP}}\ (\text{or}\ \boxed{\text{EE}})\ \boxed{3}$$

On some calculators the display will show 5.8, then a space, followed by 03, the exponent. On other calculators, a small 10 is shown with an exponent 3.

To enter a negative exponent, use the key labeled +/−. For example, to enter the number 8.6×10^{-5}, the key sequence is

$$\boxed{8}\ \boxed{\cdot}\ \boxed{6}\ \boxed{\text{EXP}}\ \boxed{+/-}\ \boxed{5}$$

When entering a number in exponential notation, do not key in the 10 if you use the EXP or EE button.

In working with exponents, it is important to recall that $10^0 = 1$. The following rules are useful for carrying exponents through calculations.

1. **Addition and Subtraction** In order to add or subtract numbers expressed in exponential notation, the powers of 10 must be the same.

$$\begin{aligned}(5.22 \times 10^4) + (3.21 \times 10^2) &= (522 \times 10^2) + (3.21 \times 10^2)\\ &= 525 \times 10^2 \quad (3 \text{ significant figures})\\ &= 5.25 \times 10^4\\ (6.25 \times 10^{-2}) - (5.77 \times 10^{-3}) &= (6.25 \times 10^{-2}) - (0.577 \times 10^{-2})\\ &= 5.67 \times 10^{-2} \quad (3 \text{ significant figures})\end{aligned}$$

When you use a calculator to add or subtract, you need not be concerned with having numbers with the same exponents because the calculator automatically takes care of this matter.

2. **Multiplication and Division** When numbers expressed in exponential notation are multiplied, the exponents are added; when numbers expressed in exponential notation are divided, the exponent of the denominator is subtracted from the exponent of the numerator.

$$\begin{aligned}(5.4 \times 10^2)(2.1 \times 10^3) &= (5.4)(2.1) \times 10^{2+3}\\ &= 11 \times 10^5\\ &= 1.1 \times 10^6\\ (1.2 \times 10^5)(3.22 \times 10^{-3}) &= (1.2)(3.22) \times 10^{5+(-3)} = 3.9 \times 10^2\\ \frac{3.2 \times 10^5}{6.5 \times 10^2} &= \frac{3.2}{6.5} \times 10^{5-2} = 0.49 \times 10^3 = 4.9 \times 10^2\\ \frac{5.7 \times 10^7}{8.5 \times 10^{-2}} &= \frac{5.7}{8.5} \times 10^{7-(-2)} = 0.67 \times 10^9 = 6.7 \times 10^8\end{aligned}$$

3. **Powers and Roots** When numbers expressed in exponential notation are raised to a power, the exponents are multiplied by the power. When the roots of numbers expressed in exponential notation are taken, the exponents are divided by the root.

$$\begin{aligned}(1.2 \times 10^5)^3 &= (1.2)^3 \times 10^{5\times 3}\\ &= 1.7 \times 10^{15}\\ \sqrt[3]{2.5 \times 10^6} &= \sqrt[3]{2.5} \times 10^{6/3}\\ &= 1.3 \times 10^2\end{aligned}$$

Scientific calculators usually have keys labeled x^2 and $\sqrt{x}$ for squaring and taking the square root of a number, respectively. To take higher powers or roots, many calculators have y^x and $\sqrt[x]{y}$ (or INV y^x) keys. For example, to perform the operation $\sqrt[3]{7.5 \times 10^{-4}}$ on such a calculator, you would key in 7.5×10^{-4}, press the $\sqrt[x]{y}$ key (or the INV and then the y^x keys), enter the root, 3, and finally press =. The result is 9.1×10^{-2}.



Sample Exercise 1

Using Exponential Notation

Perform each of the following operations, using your calculator where possible:
(**a**) Write the number 0.0054 in standard exponential notation. (**b**) $(5.0 \times 10^{-2}) + (4.7 \times 10^{-3})$ (**c**) $(5.98 \times 10^{12})(2.77 \times 10^{-5})$ (**d**) $\sqrt[4]{1.75 \times 10^{-12}}$

SOLUTION

(**a**) Because we move the decimal point three places to the right to convert 0.0054 to 5.4, the exponent is −3:

$$5.4 \times 10^{-3}$$

Scientific calculators are generally able to convert numbers to exponential notation using one or two keystrokes; frequently "SCI" for "scientific notation" will convert a number into exponential notation. Consult your instruction manual to see how this operation is accomplished on your calculator.

(**b**) To add these numbers longhand, we must convert them to the same exponent.

$$(5.0 \times 10^{-2}) + (0.47 \times 10^{-2}) = (5.0 + 0.47) \times 10^{-2} = 5.5 \times 10^{-2}$$

(**c**) Performing this operation longhand, we have

$$(5.98 \times 2.77) \times 10^{12-5} = 16.6 \times 10^{7} = 1.66 \times 10^{8}$$

(**d**) To perform this operation on a calculator, we enter the number, press the $\sqrt[x]{y}$ key (or the INV and y^x keys), enter 4, and press the = key. The result is 1.15×10^{-3}.

▶Practice Exercise

Perform the following operations:
(**a**) Write 67,000 in exponential notation, showing two significant figures.
(**b**) $(3.378 \times 10^{-3}) - (4.97 \times 10^{-5})$
(**c**) $(1.84 \times 10^{15})(7.45 \times 10^{-2})$
(**d**) $(6.67 \times 10^{-8})^3$

A.2 | Logarithms

Common Logarithms

The common, or base-10, logarithm (abbreviated log) of any number is the power to which 10 must be raised to equal the number. For example, the common logarithm of 1000 (written log 1000) is 3 because raising 10 to the third power gives 1000.

$$10^3 = 1000, \text{ therefore, } \log 1000 = 3$$

Further examples are

$$\log 10^5 = 5$$
$$\log 1 = 0 \quad \text{Remember that } 10^0 = 1$$
$$\log 10^{-2} = -2$$

In these examples the common logarithm can be obtained by inspection. However, it is not possible to obtain the logarithm of a number such as 31.25 by inspection. The logarithm of 31.25 is the number x that satisfies the following relationship:

$$10^x = 31.25$$

Most electronic calculators have a key labeled LOG that can be used to obtain logarithms. For example, on many calculators we obtain the value of log 31.25 by entering 31.25 and pressing the LOG key. We obtain the following result:

$$\log 31.25 = 1.4949$$

Notice that 31.25 is greater than 10 (10^1) and less than 100 (10^2). The value for log 31.25 is accordingly between log 10 and log 100, that is, between 1 and 2.

Significant Figures and Common Logarithms

For the common logarithm of a measured quantity, the number of digits after the decimal point equals the number of significant figures in the original number. For example, if 23.5 is a measured quantity (three significant figures), then log 23.5 = 1.371 (three significant figures after the decimal point).

Antilogarithms

The process of determining the number that corresponds to a certain logarithm is known as obtaining an *antilogarithm*. It is the reverse of taking a logarithm. For example, we saw previously that log 23.5 = 1.371. This means that the antilogarithm of 1.371 equals 23.5.

$$\log 23.5 = 1.371$$
$$\text{antilog } 1.371 = 23.5$$

The process of taking the antilog of a number is the same as raising 10 to a power equal to that number.

$$\text{antilog } 1.371 = 10^{1.371} = 23.5$$

Many calculators have a key labeled 10^x that allows you to obtain antilogs directly. On others, it will be necessary to press a key labeled INV (for *inverse*), followed by the LOG key.

Natural Logarithms

Logarithms based on the number e are called natural, or base e, logarithms (abbreviated ln). The natural log of a number is the power to which e (which has the value 2.71828...) must be raised to equal the number. For example, the natural log of 10 equals 2.303.

$$e^{2.303} = 10, \text{ therefore } \ln 10 = 2.303$$

Your calculator probably has a key labeled LN that allows you to obtain natural logarithms. For example, to obtain the natural log of 46.8, you enter 46.8 and press the LN key.

$$\ln 46.8 = 3.846$$

The natural antilog of a number is e raised to a power equal to that number. If your calculator can calculate natural logs, it will also be able to calculate natural antilogs. On some calculators there is a key labeled e^x that allows you to calculate natural antilogs directly; on others, it will be necessary to first press the INV key followed by the LN key. For example, the natural antilog of 1.679 is given by

$$\text{Natural antilog } 1.679 = e^{1.679} = 5.36$$

The relation between common and natural logarithms is as follows:

$$\ln a = 2.303 \log a$$

Notice that the factor relating the two, 2.303, is the natural log of 10, which we calculated earlier.

Mathematical Operations Using Logarithms

Because logarithms are exponents, mathematical operations involving logarithms follow the rules for the use of exponents. For example, the product of z^a and z^b (where z is any number) is given by

$$z^a \cdot z^b = z^{(a+b)}$$

Similarly, the logarithm (either common or natural) of a product equals the *sum* of the logs of the individual numbers.

$$\log ab = \log a + \log b \qquad \ln ab = \ln a + \ln b$$

For the log of a quotient,

$$\log(a/b) = \log a - \log b \qquad \ln(a/b) = \ln a - \ln b$$

Using the properties of exponents, we can also derive the rules for the logarithm of a number raised to a certain power.

$$\log a^n = n \log a \qquad \ln a^n = n \ln a$$

$$\log a^{1/n} = (1/n)\log a \qquad \ln a^{1/n} = (1/n)\ln a$$

pH Problems

One of the most frequent uses for common logarithms in general chemistry is in working pH problems. The pH is defined as $-\log[H^+]$, where $[H^+]$ is the hydrogen ion concentration of a solution. The following sample exercise illustrates this application.

Sample Exercise 2
Using Logarithms

(a) What is the pH of a solution whose hydrogen ion concentration is 0.015 *M*?
(b) If the pH of a solution is 3.80, what is its hydrogen ion concentration?

SOLUTION

(1) We are given the value of $[H^+]$. We use the LOG key of our calculator to calculate the value of $\log[H^+]$. The pH is obtained by changing the sign of the value obtained. (Be sure to change the sign *after* taking the logarithm.)

$$[H^+] = 0.015$$
$$\log[H^+] = -1.82 \quad (2 \text{ significant figures})$$
$$\text{pH} = -(-1.82) = 1.82$$

(2) To obtain the hydrogen ion concentration when given the pH, we must take the antilog of −pH.

$$\text{pH} = -\log[H^+] = 3.80$$
$$\log[H^+] = -3.80$$
$$[H^+] = \text{antilog}(-3.80) = 10^{-3.80} = 1.6 \times 10^{-4}\,M$$

Practice Exercise
Perform the following operations:
(**a**) $\log(2.5 \times 10^{-5})$
(**b**) ln 32.7
(**c**) antilog −3.47
(**d**) $e^{-1.89}$

A.3 | Quadratic Equations

An algebraic equation of the form $ax^2 + bx + c = 0$ is called a *quadratic equation*. The two solutions to such an equation are given by the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Many calculators today can calculate the solutions to a quadratic equation with one or two keystrokes. Most of the time, x corresponds to the concentration of a chemical species in solution. Only one of the solutions will be a positive number, and that is the one you should use; a "negative concentration" has no physical meaning.

Sample Exercise 3
Using the Quadratic Formula

Find the values of x that satisfy the equation $2x^2 + 4x = 1$.

SOLUTION

To solve the given equation for x, we must first put it in the form

$$ax^2 + bx + c = 0$$

and then use the quadratic formula. If

$$2x^2 + 4x = 1$$

then

$$2x^2 + 4x - 1 = 0$$

Using the quadratic formula, where $a = 2, b = 4$, and $c = -1$, we have

$$x = \frac{-4 \pm \sqrt{4^2 - 4(2)(-1)}}{2(2)}$$
$$= \frac{-4 \pm \sqrt{16 + 8}}{4} = \frac{-4 \pm \sqrt{24}}{4} = \frac{-4 \pm 4.899}{4}$$

The two solutions are

$$x = \frac{0.899}{4} = 0.225 \quad \text{and} \quad x = \frac{-8.899}{4} = -2.225$$

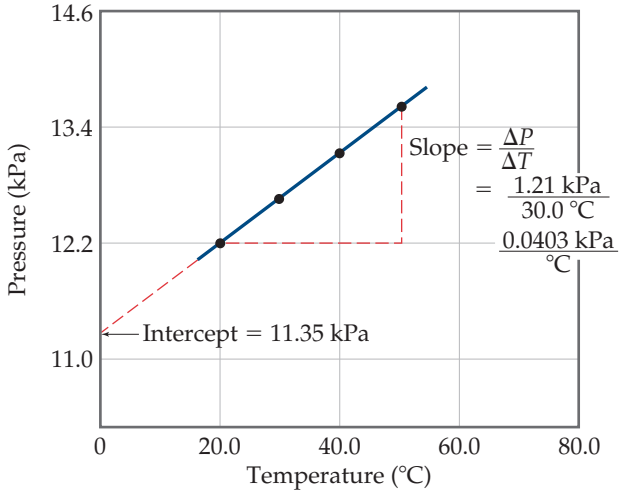
If this was a problem in which x represented a concentration, we would say $x = 0.225$ (in the appropriate units), since a negative number for concentration has no physical meaning.

A.4 | Graphs

Often the clearest way to represent the interrelationship between two variables is to graph them. Usually, the variable that is being experimentally varied, called the *independent variable*, is shown along the horizontal axis (x-axis). The variable that responds to the change in the independent variable, called the *dependent variable*,

TABLE A.1 Interrelation between Pressure and Temperature

Temperature (°C)	Pressure (kPa)
20.0	12.16
30.0	12.56
40.0	12.97
50.0	13.37



▲ **Figure A.1** **A graph of pressure versus temperature yields a straight line for the data.**

is then shown along the vertical axis (y-axis). For example, consider an experiment in which we vary the temperature of an enclosed gas and measure its pressure. The independent variable is temperature and the dependent variable is pressure. The data shown in **Table A.1** can be obtained by means of this experiment. These data are shown graphically in **Figure A.1**. The relationship between temperature and pressure is linear. The equation for any straight-line graph has the form

$$y = mx + b$$

where m is the slope of the line and b is the intercept with the y-axis. In the case of Figure A.1, we could say that the relationship between temperature and pressure takes the form

$$P = mT + b$$

where P is pressure in kPa and T is temperature in °C. As shown in Figure A.1, the slope is 0.0403 kPa/°C, and the intercept—the point where the line crosses the y-axis—is 11.35 kPa. Therefore, the equation for the line is

$$P = (0.0403 \text{ kPa/°C})T + 11.35 \text{ kPa}$$

A.5 | Standard Deviation

The standard deviation from the mean, s, is a common method for describing precision in experimentally determined data. We define the standard deviation as

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}}$$

where N is the number of measurements, $\bar{x}$ is the average (also called the mean) of the measurements, and xi represent the individual measurements. Electronic calculators with built-in statistical functions can calculate s directly by inputting the individual measurements.

A smaller value of s indicates a higher precision, meaning that the data are more closely clustered around the average. The standard deviation has statistical significance. If a large number of measurements is made, 68% of the measured values is expected to be within one standard deviation of the average, assuming only random errors are associated with the measurements.

Sample Exercise 4

Calculating an Average and Standard Deviation

The percent carbon in a sugar is measured four times: 42.01%, 42.28%, 41.79%, and 42.25%. Calculate (**a**) the average and (**b**) the standard deviation for these measurements.

SOLUTION

(**a**) The average is found by adding the quantities and dividing by the number of measurements:

$$\bar{x} = \frac{42.01 + 42.28 + 41.79 + 42.25}{4} = \frac{168.33}{4} = 42.08$$

(**b**) The standard deviation is found using the preceding equation:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}}$$

Let's tabulate the data so the calculation of $\sum_{i=1}^{N}(x_i - \bar{x})^2$ can be seen clearly.

Percent C	Difference between Measurement and Average, $(x_i - x)$	Square of Difference, $(x_i - x)^2$
42.01	$42.01 - 42.08 = -0.07$	$(-0.07)^2 = 0.005$
42.28	$42.28 - 42.08 = 0.20$	$(0.20)^2 = 0.040$
41.79	$41.79 - 42.08 = -0.29$	$(-0.29)^2 = 0.084$
42.25	$42.25 - 42.08 = 0.17$	$(0.17)^2 = 0.029$

The sum of the quantities in the last column is

$$\sum_{i=1}^{N}(x_i - \bar{x})^2 = 0.005 + 0.040 + 0.084 + 0.029 = 0.16$$

Thus, the standard deviation is

$$s = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N - 1}} = \sqrt{\frac{0.16}{4 - 1}} = \sqrt{\frac{0.16}{3}} = \sqrt{0.053} = 0.23$$

Based on these measurements, it would be appropriate to represent the measured percent carbon as 42.08 ± 0.23.

APPENDIX

B

PROPERTIES OF WATER

Density:	0.99987 g/mL at 0 °C 1.00000 g/mL at 4 °C 0.99707 g/mL at 25 °C 0.95838 g/mL at 100 °C
Heat (enthalpy) of fusion:	6.008 kJ/mol at 0 °C
Heat (enthalpy) of vaporization:	44.94 kJ/mol at 0 °C 44.02 kJ/mol at 25 °C 40.67 kJ/mol at 100 °C
Ion-product constant, K_w:	1.14×10^{-15} at 0 °C 1.01×10^{-14} at 25 °C 5.47×10^{-14} at 50 °C
Specific heat:	2.092 J/g-K = 2.092 J/g · °C for ice at −3 °C 4.184 J/g-K = 4.184 J/g · °C for water at 25 °C 1.841 J/g-K = 1.841 J/g · °C for steam at 100 °C

Vapor Pressure (kPa) at Different Temperatures

T(°C)	P	T(°C)	P	T(°C)	P	T(°C)	P
0	0.6106	21	2.486	35	5.626	92	75.59
5	0.8719	22	2.644	40	7.373	94	81.45
10	1.228	23	2.809	45	9.586	96	87.67
12	1.403	24	2.984	50	12.33	98	94.3
14	1.599	25	3.168	55	15.73	100	101.3
16	1.817	26	3.361	60	19.92	102	108.8
17	1.937	27	3.565	65	25	104	116.7
18	2.064	28	3.78	70	31.16	106	125
19	2.197	29	4.005	80	47.34	108	133.9
20	2.338	30	4.242	90	70.1	110	143.3

APPENDIX

C

THERMODYNAMIC QUANTITIES FOR SELECTED SUBSTANCES AT 298.15 K (25 °C)

Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
Aluminum			
$Al(s)$	0	0	28.32
$AlCl_3(s)$	−705.6	−630.0	109.3
$Al_2O_3(s)$	−1669.8	−1576.5	51.00
Barium			
$Ba(s)$	0	0	63.2
$BaCO_3(s)$	−1216.3	−1137.6	112.1
$BaO(s)$	−553.5	−525.1	70.42
Beryllium			
$Be(s)$	0	0	9.44
BeO(s)	−608.4	−579.1	13.77
$Be(OH)_2(s)$	−905.8	−817.9	50.21
Bromine			
$Br(g)$	111.8	82.38	174.9
$Br^-(aq)$	−120.9	−102.8	80.71
$Br_2(g)$	30.71	3.14	245.3
$Br_2(l)$	0	0	152.3
$HBr(g)$	−36.23	−53.22	198.49
Calcium			
$Ca(g)$	179.3	145.5	154.8
$Ca(s)$	0	0	41.4
$CaCO_3(s$, calcite)	−1207.1	−1128.76	92.88
$CaCl_2(s)$	−795.8	−748.1	104.6
$CaF_2(s)$	−1219.6	−1167.3	68.87
$CaO(s)$	−635.5	−604.17	39.75
$Ca(OH)_2(s)$	−986.2	−898.5	83.4
$CaSO_4(s)$	−1434.0	−1321.8	106.7
Carbon			
$C(g)$	718.4	672.9	158.0
$C(s$, diamond)	1.88	2.84	2.43
$C(s$, graphite)	0	0	5.69
$CCl_4(g)$	−106.7	−64.0	309.4
$CCl_4(l)$	−139.3	−68.6	214.4
$CF_4(g)$	−679.9	−635.1	262.3
$CH_4(g)$	−74.8	−50.8	186.3
$C_2H_2(g)$	226.77	209.2	200.8
$C_2H_4(g)$	52.30	68.11	219.4
$C_2H_6(g)$	−84.68	−32.89	229.5
$C_3H_8(g)$	−103.85	−23.47	269.9
$C_4H_{10}(g)$	−124.73	−15.71	310.0
$C_4H_{10}(l)$	−147.6	−15.0	231.0
$C_6H_6(g)$	82.9	129.7	269.2
$C_6H_6(l)$	49.0	124.5	172.8
$CH_3OH(g)$	−201.2	−161.9	237.6
$CH_3OH(l)$	−238.6	−166.23	126.8
$C_2H_5OH(g)$	−235.1	−168.5	282.7
$C_2H_5OH(l)$	−277.7	−174.76	160.7
$C_6H_{12}O_6(s)$	−1273.02	−910.4	212.1
$CO(g)$	−110.5	−137.2	197.9
$CO_2(g)$	−393.5	−394.4	213.6
$CH_3COOH(l)$	−487.0	−392.4	159.8
Cesium			
$Cs(g)$	76.50	49.53	175.6
$Cs(l)$	2.09	0.03	92.07
$Cs(s)$	0	0	85.15
$CsCl(s)$	−442.8	−414.4	101.2
Chlorine			
$Cl(g)$	121.7	105.7	165.2
$Cl^-(aq)$	−167.2	−131.2	56.5
$Cl_2(g)$	0	0	222.96
$HCl(aq)$	−167.2	−131.2	56.5
$HCl(g)$	−92.30	−95.27	186.69
Chromium			
$Cr(g)$	397.5	352.6	174.2
$Cr(s)$	0	0	23.6
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
Cobalt			
$Co(g)$	439	393	179
$Co(s)$	0	0	28.4

Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
Copper			
$Cu(g)$	338.4	298.6	166.3
$Cu(s)$	0	0	33.30
$CuCl_2(s)$	−205.9	−161.7	108.1
$CuO(s)$	−156.1	−128.3	42.59
$Cu_2O(s)$	−170.7	−147.9	92.36
Fluorine			
$F(g)$	80.0	61.9	158.7
$F^-(aq)$	−332.6	−278.8	−13.8
$F_2(g)$	0	0	202.7
$HF(g)$	−268.61	−270.70	173.51
Hydrogen			
$H(g)$	217.94	203.26	114.60
$H^+(aq)$	0	0	0
$H^+(g)$	1536.2	1517.0	108.9
$H_2(g)$	0	0	130.58
Iodine			
$I(g)$	106.60	70.16	180.66
$I^-(g)$	−55.19	−51.57	111.3
$I_2(g)$	62.25	19.37	260.57
$I_2(s)$	0	0	116.73
$HI(g)$	25.94	1.30	206.3
Iron			
$Fe(g)$	415.5	369.8	180.5
$Fe(s)$	0	0	27.15
$Fe^{2+}(aq)$	−87.86	−84.93	113.4
$Fe^{3+}(aq)$	−47.69	−10.54	293.3
$FeCl_2(s)$	−341.8	−302.3	117.9
$FeCl_3(s)$	−400	−334	142.3
$FeO(s)$	−271.9	−255.2	60.75
$Fe_2O_3(s)$	−822.16	−740.98	89.96
$Fe_3O_4(s)$	−1117.1	−1014.2	146.4
$FeS_2(s)$	−171.5	−160.1	52.92
Lead			
$Pb(s)$	0	0	68.85
$PbBr_2(s)$	−277.4	−260.7	161
$PbCO_3(s)$	−699.1	−625.5	131.0
$Pb(NO_3)_2(aq)$	−421.3	−246.9	303.3
$Pb(NO_3)_2(s)$	−451.9	—	—
$PbO(s)$	−217.3	−187.9	68.70
Lithium			
$Li(g)$	159.3	126.6	138.8
$Li(s)$	0	0	29.09
$Li^+(aq)$	−278.5	−273.4	12.2
$Li^+(g)$	685.7	648.5	133.0
$LiCl(s)$	−408.3	−384.0	59.30
Magnesium			
$Mg(g)$	147.1	112.5	148.6
$Mg(s)$	0	0	32.51
$MgCl_2(s)$	−641.6	−592.1	89.6
$MgO(s)$	−601.8	−569.6	26.8
$Mg(OH)_2(s)$	−924.7	−833.7	63.24
Manganese			
$Mn(g)$	280.7	238.5	173.6
$Mn(s)$	0	0	32.0
$MnO(s)$	−385.2	−362.9	59.7
$MnO_2(s)$	−519.6	−464.8	53.14
$MnO_4^-(aq)$	−541.4	−447.2	191.2
Mercury			
$Hg(g)$	60.83	31.76	174.89
$Hg(l)$	0	0	77.40
$HgCl_2(s)$	−230.1	−184.0	144.5
$Hg_2Cl_2(s)$	−264.9	−210.5	192.5
Nickel			
$Ni(g)$	429.7	384.5	182.1
$Ni(s)$	0	0	29.9
$NiCl_2(s)$	−305.3	−259.0	97.65
$NiO(s)$	−239.7	−211.7	37.99
Nitrogen			
$N(g)$	472.7	455.5	153.3
$N_2(g)$	0	0	191.50
$NH_3(aq)$	−80.29	−26.50	111.3
$NH_3(g)$	−46.19	−16.66	192.5
$NH_4^+(aq)$	−132.5	−79.31	113.4
$N_2H_4(g)$	95.40	159.4	238.5
$NH_4CN(s)$	0.4	—	—
$NH_4Cl(s)$	−314.4	−203.0	94.6
$NH_4NO_3(s)$	−365.6	−184.0	151
$NO(g)$	90.37	86.71	210.62
$NO_2(g)$	33.84	51.84	240.45
$N_2O(g)$	81.6	103.59	220.0
$N_2O_4(g)$	9.66	98.28	304.3
$NOCl(g)$	52.6	66.3	264
$HNO_3(aq)$	−206.6	−110.5	146
$HNO_3(g)$	−134.3	−73.94	266.4

Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
Oxygen			
$O(g)$	247.5	230.1	161.0
$O_2(g)$	0	0	205.0
$O_3(g)$	142.3	163.4	237.6
$OH^-(aq)$	−230.0	−157.3	−10.7
$H_2O(g)$	−241.82	−228.57	188.83
$H_2O(l)$	−285.83	−237.13	69.91
$H_2O_2(g)$	−136.10	−105.48	232.9
$H_2O_2(l)$	−187.8	−120.4	109.6
Phosphorus			
$P(g)$	316.4	280.0	163.2
$P_2(g)$	144.3	103.7	218.1
$P_4(g)$	58.9	24.4	280
$P_4(s$, red)	−17.46	−12.03	22.85
$P_4(s$, white)	0	0	41.08
$PCl_3(g)$	−288.07	−269.6	311.7
$PCl_3(l)$	−319.6	−272.4	217
$PF_5(g)$	−1594.4	−1520.7	300.8
$PH_3(g)$	5.4	13.4	210.2
$P_4O_6(s)$	−1640.1	—	—
$P_4O_{10}(s)$	−2940.1	−2675.2	228.9
$POCl_3(g)$	−542.2	−502.5	325
$POCl_3(l)$	−597.0	−520.9	222
$H_3PO_4(aq)$	−1288.3	−1142.6	158.2
Potassium			
$K(g)$	89.99	61.17	160.2
$K(s)$	0	0	64.67
$K^+(aq)$	−252.4	−283.3	102.5
$K^+(g)$	514.2	481.2	154.5
$KCl(s)$	−435.9	−408.3	82.7
$KClO_3(s)$	−391.2	−289.9	143.0
$KClO_3(aq)$	−349.5	−284.9	265.7
$K_2CO_3(s)$	−1150.18	−1064.58	155.44
$KNO_3(s)$	−492.70	−393.13	132.9
$K_2O(s)$	−363.2	−322.1	94.14
$KO_2(s)$	−284.5	−240.6	122.5
$K_2O_2(s)$	−495.8	−429.8	113.0
$KOH(s)$	−424.7	−378.9	78.91
$KOH(aq)$	−482.4	−440.5	91.6
Rubidium			
$Rb(g)$	85.8	55.8	170.0
$Rb(s)$	0	0	76.78
$RbCl(s)$	−430.5	−412.0	92
$RbClO_3(s)$	−392.4	−292.0	152

Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
Scandium			
$Sc(g)$	377.8	336.1	174.7
$Sc(s)$	0	0	34.6
Selenium			
$H_2Se(g)$	29.7	15.9	219.0
Silicon			
$Si(g)$	368.2	323.9	167.8
$Si(s)$	0	0	18.7
$SiC(s)$	−73.22	−70.85	16.61
$SiCl_4(l)$	−640.1	−572.8	239.3
$SiO_2(s$, quartz)	−910.9	−856.5	41.84
Silver			
$Ag(s)$	0	0	42.55
$Ag^+(aq)$	105.90	77.11	73.93
$AgCl(s)$	−127.0	−109.70	96.11
$Ag_2O(s)$	−31.05	−11.20	121.3
$AgNO_3(s)$	−124.4	−33.41	140.9
Sodium			
$Na(g)$	107.7	77.3	153.7
$Na(s)$	0	0	51.45
$Na^+(aq)$	−240.1	−261.9	59.0
$Na^+(g)$	609.3	574.3	148.0
$NaBr(aq)$	−360.6	−364.7	141.00
$NaBr(s)$	−361.4	−349.3	86.82
$Na_2CO_3(s)$	−1130.9	−1047.7	136.0
$NaCl(aq)$	−407.1	−393.0	115.5
$NaCl(g)$	−181.4	−201.3	229.8
$NaCl(s)$	−410.9	−384.0	72.33
$NaHCO_3(s)$	−947.7	−851.8	102.1
$NaNO_3(aq)$	−446.2	−372.4	207
$NaNO_3(s)$	−467.9	−367.0	116.5
$NaOH(aq)$	−469.6	−419.2	49.8
$NaOH(s)$	−425.6	−379.5	64.46
$Na_2SO_4(s)$	−1387.1	−1270.2	149.6
Strontium			
$SrO(s)$	−592.0	−561.9	54.9
$Sr(g)$	164.4	110.0	164.6
Sulfur			
$S(s$, rhombic)	0	0	31.88
$S_8(g)$	102.3	49.7	430.9
$SO_2(g)$	−296.9	−300.4	248.5
$SO_3(g)$	−395.2	−370.4	256.2
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1

Substance	ΔH_f° (kj/mol)	ΔG_f° (kj/mol)	S° (j/mol-K)
$SOCl_2(l)$	−245.6	—	—
$H_2S(g)$	−20.17	−33.01	205.6
$H_2SO_4(aq)$	−909.3	−744.5	20.1
$H_2SO_4(l)$	−814.0	−689.9	156.1
Titanium			
$Ti(g)$	468	422	180.3
$Ti(s)$	0	0	30.76
$TiCl_4(g)$	−763.2	−726.8	354.9
$TiCl_4(l)$	−804.2	−728.1	221.9
$TiO_2(s)$	−944.7	−889.4	50.29
Vanadium			
$V(g)$	514.2	453.1	182.2
$V(s)$	0	0	28.9
Zinc			
$Zn(g)$	130.7	95.2	160.9
$Zn(s)$	0	0	41.63
$ZnCl_2(s)$	−415.1	−369.4	111.5
$ZnO(s)$	−348.0	−318.2	43.9

APPENDIX

D

AQUEOUS EQUILIBRIUM CONSTANTS

TABLE D.1 Dissociation Constants for Acids at 25 °C

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Acetic acid	CH_3COOH (or $HC_2H_3O_2$)	1.8×10^{-5}		
Arsenic acid	H_3AsO_4	5.6×10^{-3}	1.0×10^{-7}	3.0×10^{-12}
Arsenous acid	H_3AsO_3	5.1×10^{-10}		
Ascorbic acid	$H_2C_6H_6O_6$	8.0×10^{-5}	1.6×10^{-12}	
Benzoic acid	C_6H_5COOH (or $HC_7H_5O_2$)	6.3×10^{-5}		
Boric acid	H_3BO_3	5.8×10^{-10}		
Butanoic acid	C_3H_7COOH (or $HC_4H_7O_2$)	1.5×10^{-5}		
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Chloroacetic acid	$CH_2ClCOOH$ (or $HC_2H_2O_2Cl$)	1.4×10^{-3}		
Chlorous acid	$HClO_2$	1.1×10^{-2}		
Citric acid	$HOOCC(OH)(CH_2COOH)_2$ (or $H_3C_6H_5O_7$)	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Cyanic acid	$HCNO$	3.5×10^{-4}		
Formic acid	$HCOOH$ (or $HCHO_2$)	1.8×10^{-4}		
Hydroazoic acid	HN_3	1.9×10^{-5}		
Hydrocyanic acid	HCN	4.9×10^{-10}		
Hydrofluoric acid	HF	6.8×10^{-4}		
Hydrogen chromate ion	$HCrO_4^-$	3.0×10^{-7}		
Hydrogen peroxide	H_2O_2	2.4×10^{-12}		
Hydrogen selenate ion	$HSeO_4^-$	2.2×10^{-2}		
Hydrogen sulfide	H_2S	9.5×10^{-8}	1×10^{-19}	
Hypobromous acid	$HBrO$	2.5×10^{-9}		
Hypochlorous acid	$HClO$	3.0×10^{-8}		
Hypoiodous acid	HIO	2.3×10^{-11}		
Iodic acid	HIO_3	1.7×10^{-1}		
Lactic acid	$CH_3CH(OH)COOH$ (or $HC_3H_5O_3$)	1.4×10^{-4}		
Malonic acid	$CH_2(COOH)_2$ (or $H_2C_3H_2O_4$)	1.5×10^{-3}	2.0×10^{-6}	
Nitrous acid	HNO_2	4.5×10^{-4}		
Oxalic acid	$(COOH)_2$ (or $H_2C_2O_4$)	5.9×10^{-2}	6.4×10^{-5}	
Paraperiodic acid	H_5IO_6	2.8×10^{-2}	5.3×10^{-9}	
Phenol	C_6H_5OH (or HC_6H_5O)	1.3×10^{-10}		
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Propionic acid	C_2H_5COOH (or $HC_3H_5O_2$)	1.3×10^{-5}		
Pyrophosphoric acid	$H_4P_2O_7$	3.0×10^{-2}	4.4×10^{-3}	2.1×10^{-7}
Selenous acid	H_2SeO_3	2.3×10^{-3}	5.3×10^{-9}	
Sulfuric acid	H_2SO_4	Strong acid	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.4×10^{-8}	
Tartaric acid	$HOOC(CHOH)_2COOH$ (or $H_2C_4H_4O_6$)	1.0×10^{-3}		

TABLE D.2 Dissociation Constants for Bases at 25 °C

Name	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	4.3×10^{-10}
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}
Ethylamine	$C_2H_5NH_2$	6.4×10^{-4}
Hydrazine	H_2NNH_2	1.3×10^{-6}
Hydroxylamine	$HONH_2$	1.1×10^{-8}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.7×10^{-9}
Trimethylamine	$(CH_3)_3N$	6.4×10^{-5}

TABLE D.3 Solubility-Product Constants for Compounds at 25 °C

Name	Formula	K_{sp}	Name	Formula	K_{sp}
Barium carbonate	$BaCO_3$	5.0×10^{-9}	Lead(II) fluoride	PbF_2	3.6×10^{-8}
Barium chromate	$BaCrO_4$	2.1×10^{-10}	Lead(II) sulfate	$PbSO_4$	6.3×10^{-7}
Barium fluoride	BaF_2	1.7×10^{-6}	Lead(II) sulfide*	PbS	3×10^{-28}
Barium oxalate	BaC_2O_4	1.6×10^{-6}	Magnesium hydroxide	$Mg(OH)_2$	1.8×10^{-11}
Barium sulfate	$BaSO_4$	1.1×10^{-10}	Magnesium carbonate	$MgCO_3$	3.5×10^{-8}
Cadmium carbonate	$CdCO_3$	1.8×10^{-14}	Magnesium oxalate	MgC_2O_4	8.6×10^{-5}
Cadmium hydroxide	$Cd(OH)_2$	2.5×10^{-14}	Manganese(II) carbonate	$MnCO_3$	5.0×10^{-10}
Cadmium sulfide*	CdS	8×10^{-28}	Manganese(II) hydroxide	$Mn(OH)_2$	1.6×10^{-13}
Calcium carbonate (calcite)	$CaCO_3$	4.5×10^{-9}	Manganese(II) sulfide*	MnS	2×10^{-53}
Calcium chromate	$CaCrO_4$	4.5×10^{-9}	Mercury(I) chloride	Hg_2Cl_2	1.2×10^{-18}
Calcium fluoride	CaF_2	3.9×10^{-11}	Mercury(I) iodide	Hg_2I_2	$1.1 \times 10^{-1.1}$
Calcium hydroxide	$Ca(OH)_2$	6.5×10^{-6}	Mercury(II) sulfide*	HgS	2×10^{-53}
Calcium phosphate	$Ca_3(PO_4)_2$	2.0×10^{-29}	Nickel(II) carbonate	$NiCO_3$	1.3×10^{-7}
Calcium sulfate	$CaSO_4$	2.4×10^{-5}	Nickel(II) hydroxide	$Ni(OH)_2$	6.0×10^{-16}
Chromium(III) hydroxide	$Cr(OH)_3$	6.7×10^{-31}	Nickel(II) sulfide*	NiS	3×10^{-20}
Cobalt(II) carbonate	$CoCO_3$	1.0×10^{-10}	Silver bromate	$AgBrO_3$	5.5×10^{-13}
Cobalt(II) hydroxide	$Co(OH)_2$	1.3×10^{-15}	Silver bromide	AgBr	5.0×10^{-13}
Cobalt(II) sulfide*	CoS	5×10^{-22}	Silver carbonate	Ag_2CO_3	8.1×10^{-12}
Copper(I) bromide	CuBr	5.3×10^{-9}	Silver chloride	AgCl	1.8×10^{-10}
Copper(II) carbonate	$CuCO_3$	2.3×10^{-10}	Silver chromate	Ag_2CrO_4	1.2×10^{-12}
Copper(II) hydroxide	$Cu(OH)_2$	4.8×10^{-20}	Silver iodide	AgI	8.3×10^{-17}
Copper(II) sulfide*	CuS	6×10^{-37}	Silver sulfate	Ag_2SO_4	1.5×10^{-5}
Iron(II) carbonate	$FeCO_3$	2.1×10^{-11}	Silver sulfide*	Ag_2S	6×10^{-51}
Iron(II) hydroxide	$Fe(OH)_2$	7.9×10^{-16}	Strontium carbonate	$SrCO_3$	9.3×10^{-10}
Lanthanum fluoride	LaF_3	2×10^{-19}	Tin(II) sulfide*	SnS	1×10^{-26}
Lanthanum iodate	$La(IO_3)_3$	7.4×10^{-14}	Zinc carbonate	$ZnCO_3$	1.0×10^{-10}
Lead(II) carbonate	$PbCO_3$	7.4×10^{-14}	Zinc hydroxide	$Zn(OH)_2$	3.0×10^{-16}
Lead(II) chloride	$PbCl_2$	1.7×10^{-5}	Zinc oxalate	ZnC_2O_4	2.7×10^{-8}
Lead(II) chromate	$PbCrO_4$	2.8×10^{-13}	Zinc sulfide*	ZnS	2×10^{-25}

* For a solubility equilibrium of the type $MS(s) + H_2O(l) \rightleftharpoons M^{2+}(aq) + HS^-(aq) + OH^-(aq)$

APPENDIX

E

STANDARD REDUCTION POTENTIALS AT 25 °C

Half-Reaction	$E°(V)$
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$AgBr(s) + e^- \longrightarrow Ag(s) + Br^-(aq)$	+0.10
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$Ag(CN)_2^-(aq) + e^- \longrightarrow Ag(s) + 2\,CN^-(aq)$	−0.31
$Ag_2CrO_4(s) + 2\,e^- \longrightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	+0.45
$AgI(s) + e^- \longrightarrow Ag(s) + I^-(aq)$	−0.15
$Ag(S_2O_3)_2^{3-}(aq) + e^- \longrightarrow Ag(s) + 2\,S_2O_3^{2-}(aq)$	+0.01
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.66
$H_3AsO_4(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_3AsO_3(aq) + H_2O(l)$	+0.56
$Ba^{2+}(aq) + 2\,e^- \longrightarrow Ba(s)$	−2.90
$BiO^+(aq) + 2\,H^+(aq) + 3\,e^- \longrightarrow Bi(s) + H_2O(l)$	+0.32
$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.07
$2\,BrO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow Br_2(l) + 6\,H_2O(l)$	+1.52
$2\,CO_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2C_2O_4(aq)$	−0.49
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.87
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$	−0.40
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.36
$2\,HClO(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow Cl_2(g) + 2\,H_2O(l)$	+1.63
$ClO^-(aq) + H_2O(l) + 2\,e^- \longrightarrow Cl^-(aq) + 2\,OH^-(aq)$	+0.89
$2\,ClO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow Cl_2(g) + 6\,H_2O(l)$	+1.47
$Co^{2+}(aq) + 2\,e^- \longrightarrow Co(s)$	−0.28
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.84
$Cr^{3+}(aq) + 3\,e^- \longrightarrow Cr(s)$	−0.74
$Cr^{3+}(aq) + e^- \longrightarrow Cr^{2+}(aq)$	−0.41
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3\,e^- \longrightarrow Cr(OH)_3(s) + 5\,OH^-(aq)$	−0.13
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.34
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Cu^+(aq) + e^- \longrightarrow Cu(s)$	+0.52
$CuI(s) + e^- \longrightarrow Cu(s) + I^-(aq)$	−0.19
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.87
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.44
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$Fe(CN)_6^{3-}(aq) + e^- \longrightarrow Fe(CN)_6^{4-}(aq)$	+0.36
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0.00

Half-Reaction	$E°(V)$
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.83
$HO_2^-(aq) + H_2O(l) + 2\,e^- \longrightarrow 3\,OH^-(aq)$	+0.88
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$	+1.78
$Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$	+0.79
$2\,Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg(l)$	+0.85
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.54
$2\,IO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow I_2(s) + 6\,H_2O(l)$	+1.20
$K^+(aq) + e^- \longrightarrow K(s)$	−2.92
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.37
$Mn^{2+}(aq) + 2\,e^- \longrightarrow Mn(s)$	−1.18
$MnO_2(s) + 4\,H^+(aq) + 2\,e^- \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	+1.23
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$MnO_4^-(aq) + 2\,H_2O(l) + 3\,e^- \longrightarrow MnO_2(s) + 4\,OH^-(aq)$	+0.59
$HNO_2(aq) + H^+(aq) + e^- \longrightarrow NO(g) + H_2O(l)$	+1.00
$N_2(g) + 4\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq) + N_2H_4(aq)$	−1.16
$N_2(g) + 5\,H^+(aq) + 4\,e^- \longrightarrow N_2H_5^+(aq)$	−0.23
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.96
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$	−0.28
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.23
$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.40
$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$	+0.68
$O_3(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow O_2(g) + H_2O(l)$	+2.07
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.13
$PbO_2(s) + HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	+1.69
$PbSO_4(s) + H^+(aq) + 2\,e^- \longrightarrow Pb(s) + HSO_4^-(aq)$	−0.36
$PtCl_4^{2-}(aq) + 2\,e^- \longrightarrow Pt(s) + 4\,Cl^-(aq)$	+0.73
$S(s) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2S(g)$	+0.14
$H_2SO_3(aq) + 4\,H^+(aq) + 4\,e^- \longrightarrow S(s) + 3\,H_2O(l)$	+0.45
$HSO_4^-(aq) + 3\,H^+(aq) + 2\,e^- \longrightarrow H_2SO_3(aq) + H_2O(l)$	+0.17
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.14
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.15
$VO_2^+(aq) + 2\,H^+(aq) + e^- \longrightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.76

ANSWERS TO SELECTED EXERCISES

Chapter 1

1.3 (**a**) Homogeneous mixture (**b**) homogeneous mixture (**c**) pure substance (**d**) homogeneous mixture. **1.4** (**a**) He (**b**) Pt (**c**) Co (**d**) Sn (**e**) Ag (**f**) antimony (**g**) lead (**h**) bromine (**i**) vanadium (**j**) mercury **1.5** C is a compound; it contains both carbon and oxygen. A is a compound; it contains at least carbon and oxygen. B is not defined by the data given; it is probably also a compound because few elements exist as white solids. **1.8** Physical properties: silvery white; lustrous; melting point = 649 °C, boiling point = 1105 °C; density at 20 °C = 1.738 g/cm^3; pounded into sheets; drawn into wires; good conductor. Chemical properties: burns in air; reacts with Cl_2. **1.9** (**a**) Physical (**b**) chemical (**c**) physical (**d**) chemical (**e**) chemical **1.10** Evaporation **1.12** (**a**) Kinetic energy (**b**) Potential energy decreases. **1.15** (**a**) 3×10^{12} m (**b**) 2.5×10^{-15} s (**c**) 5.7×10^{-5} m (**d**) 8.3×10^{3} kg **1.16** (**a**) 298 K (**b**) 383 K (**c**) 27 °C (**d**) 827 °C **1.17** (**a**) 1.62 g/mL. Tetrachloroethylene, 1.62 g/mL, is more dense than water, 1.00 g/mL; tetrachloroethylene will sink rather than float on water. (**b**) 11.7 g **1.18** (**a**) Calculated density = 0.86 g/mL. The substance is probably toluene, density = 0.866 g/mL. (**b**) 40.4 mL ethylene glycol (**c**) Yes, the graduated cylinder in Figure 1.21 will provide the appropriate level of accuracy. (**d**) 1.11×10^{3} g nickel **1.19** 4 Tg **1.21** Exact: (**b**), (**d**), and (**f**) **1.22** (**a**) 4 (**b**) 1 (**c**) 2 (**d**) 3 (**e**) 4 (**g**) 6 **1.23** (**a**) 2.04×10^{6} (**b**) 2.93×10^{-4} (**c**) -8.25×10^{4} (**d**) 9.42×10^{3} (**e**) -3.25×10^{-6} **1.24** (**a**) 43.052 (**b**) 879.30 (**c**) 2.14×10^{3} (**d**) 0.101 **1.25** 5 significant figures

1.27 (**a**) $\dfrac{2.54\text{ cm}}{1\text{ in}}$ (**b**) $\dfrac{1\text{ kg}}{2.2\text{ lb}} \times \dfrac{1\text{ g}}{1 \times 10^{-3}\text{ kg}}$

(**c**) $\dfrac{1\ \mu\text{g}}{1 \times 10^{-6}\text{ kg}}$ (**d**) $\dfrac{(12)^2\text{ in}^2}{1^2\text{ ft}^2} \times \dfrac{(2.54)^2\text{ cm}^2}{1^2\text{ in}^2}$

1.28 (**a**) 54.7 km/hr (**b**) 1.3×10^{3} gal (**c**) 46.0 m (**d**) 0.984 in/hr **1.29** (**a**) 4.32×10^{5} s (**b**) 88.5 m (**c**) \$0.499/L (**d**) 46.6km/hr (**e**) 1.420 L/s (**f**) 707.9 cm^3 **1.30** (**a**) 1.2×10^{2} L (**b**) 5×10^{2} mg (**c**) 19.9mi/gal (2×10^{1} mi/gal for 1 significant figure) (**d**) 1.81 kg **1.31** 67 kg air **1.32** \$$9 \times 10^{4}$ **1.33** (**a**) Pure element: i (**b**) mixture of elements: v, vi (**c**) pure compound: iv (**d**) mixture of an element and a compound: ii, iii **1.35** (**a**) Homogeneous mixture (**b**) Yes, brass is a solution. **1.37** Filtration **1.39** (**a**) The aluminum sphere is lightest, then nickel, then silver. (**b**) The platinum cube is smallest, then gold, then lead. **1.41** (**a**) 7.5 cm; two significant figures (sig figs) (**b**) 72 mi/hr (inner scale, two significant figures) or 115 km/hr (outer scale, three significant figures) **1.43** 464 jelly beans. The mass of an average bean has 2 decimal places and 3 sig figs. The number of beans then has 3 sig figs, by the rules for multiplication and division. **1.50** (**a**) 1.08×10^{2} J (**b**) 2.58×10^{1} cal (**c**) The kinetic energy is converted mostly to heat. **1.52** (**a**) E_k = 11 J; v = 6.6 m/s **1.55** (**a**) 28 °C (**b**) 84 °F (**c**) 567 K (**d**) 559 °C (**e**) 838 °F (**f**) 275 K **1.60** 1054 J/Btu **1.75** 8.47 g O **1.77** (**a**) Set I, 22.51; set II, 22.61. Based on the average, set I is more accurate. (**b**) The average deviation for both set I and set II is 0.02. The two sets display the same precision. **1.79** (**a**) Volume (**b**) time (**c**) length (**d**) density (**e**) temperature (**f**) speed (**g**) pressure **1.82** Substances (**b**), (**f**), and (**g**) are pure or nearly pure. **1.83** (**a**) 1.13×10^{5} quarters (**b**) 6.41×10^{5} g (**c**) \$$2.83 \times 10^{4}$ (**d**) 5.74×10^{8} stacks **1.87** The most dense liquid, acetic acid, sinks; the piece of oak wood floats on the surface of the acetic acid, in the liquid interphase. The hexane resides on top. **1.90** density of solid = 1.63 g/mL **1.93** (**a**) Density of peat = 0.13 g/cm^3,density of soil = 2.5g/cm^3. It is not correct to say that peat is "lighter" than topsoil. Volumes must be specified in order to compare masses. (**b**) Buy 16 bags of peat (more than 15 are needed). (Results to 1 significant figure are not meaningful.) **1.97** The inner diameter of the tube is 1.90 cm. **1.99** The separation with distinctly separated red and blue spots is more successful. To quantify the characteristics of the separation, calculate a reference value for each spot: distance traveled by spot/distance traveled by solvent. If the values for the two spots are fairly different, the separation is successful. **1.102** (**a**) Volume = 0.050 mL (**b**) surface area = 12.4 m^2 (**c**) 99.99% of the mercury was removed. (**d**) The spongy material weighs 17.7 mg after exposure to mercury.

Chapter 2

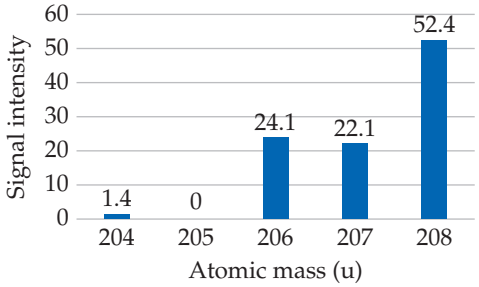
2.2 (**a**) mass O/mass C = 2.66 (**b**) mass O/mass C = 1.33 (**c**) CO **2.3** (**a**) 0.5711 g O/1 g N; 1.142 g O/1 g N; 2.284 g O/1 g N; 2.855 g O/1 g N (**b**) The numbers in part (**a**) obey the *law of multiple proportions*. Multiple proportions arise because atoms are the indivisible entities combining, as stated in Dalton's atomic theory. **2.6** The fraction of alpha particles deflected at a large angle is 2.7×10^{-9}. That is, 1 out of approximately 365 million alpha particles is deflected at a large angle. **2.9** (**a**) 0.21 nm; 2.10×102 pm (**b**) 4.76×106 W atoms (**c**) 3.88×10^{-29} m^3 **2.10** (**a**) Proton, neutron, electron (**b**) proton = 1+, neutron = 0, electron = 1− (**c**) The neutron is most massive. (The neutron and proton have very similar masses.) (**d**) The electron is least massive. **2.11** (**a**) 15 protons, 15 electrons, 17 neutrons (**b**) ^{32}S (**c**) ^{33}P (**d**) ^{33}P **2.12** (**a**) Atomic number is the number of protons in the nucleus of an atom. Mass number is the total number of nuclear particles, protons plus neutrons, in an atom. (**b**) mass number **2.13** (**a**) ^{84}Kr: 36 p, 48 n, 36 e (**b**) ^{200}Hg: 80 p, 120 n, 80 e (**c**) ^{59}Co: 27 p, 32 n, 27 e (**d**) ^{55}Mn: 25 p, 30 n, 25 e (**e**) ^{239}U: 92 p, 147 n, 92 e (**f**) ^{181}Ta: 73 p, 108 n, 73 e

2.14

Symbol	^{159}Tb	^{63}Cu	^{95}Mo	^{79}Se	^{85}Rb
Protons	65	29	42	34	37
Neutrons	94	34	53	45	48
Electrons	65	29	42	34	37
Mass no.	159	63	95	79	85

2.15 (**a**) $^{178}_{72}$Hf (**b**) $^{201}_{80}$Hg (**c**) $^{187}_{75}$Re (**d**) $^{40}_{20}$Ca **2.17** (**a**) $^{12}_{6}$C (**b**) Atomic weights are average atomic masses, the sum of the mass of each naturally occurring isotope of an element times its fractional abundance. Each B atom will have the mass of one of the naturally occurring isotopes, while the "atomic weight" is an average value. **2.18** 55.84 u **2.19** (**a**) In Thomson's cathode ray tube, the charged particles are electrons. In a mass spectrometer, the charged particles are positively charged ions (cations). (**b**) The *x*-axis label is atomic mass (or particle mass), and the *y*-axis label is signal intensity. (**c**) The Cl^{2+} ion will be deflected more. **2.20** (**a**) average atomic mass = 207.22 u

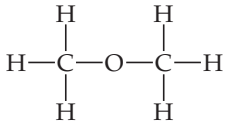
(**b**)



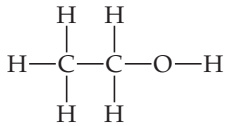
2.22 (**a**) Rn, 86 (nonmetal) (**b**) Te, 52 (metalloid) (**c**) Cd, 48, (metal) (**d**) Cr, 24 (metal) (**e**) Ba, 56 (metal) (**f**) Se, 34, (nonmetal) (**g**) S, 16, (nonmetal) **2.25** (**a**) C_4H_{10} is the molecular formula for both compounds. (**b**) C_2H_5 is the empirical formula for both compounds. (**c**) structural **2.26** From left to right: molecular, N_2H_4, empirical, NH_2; molecular, N_2H_2, empirical, NH, molecular and empirical, NH_3 **2.27** (**a**) $AlBr_3$ (**b**) C_4H_5 (**c**) C_2H_4O (**d**) P_2O_5 (**e**) C_3H_2Cl (**f**) BNH_2 **2.28** (**a**) 6 (**b**) 10 (**c**) 12

2.29

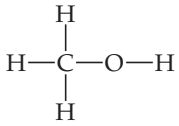
(**a**) C_2H_6O,



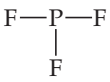
(**b**) C_2H_6O,



(**c**) CH_4O,



(**d**) PF_3,



2.31 Molecular: (**a**) $HClO_4$ (**b**) CH_3OCH_3 (**d**) H_2S (**g**) PCl_5 (**h**) $P(OH)_3$ Ionic: (**c**) $Mg(NO_3)_2$ (**e**) $TiCl_4$ (**f**) K_2O_2

2.32

Symbol	$^{58}Fe^{2+}$	$^{118}Sn^{4+}$	$^{130}Te^{2-}$	$^{90}Zr^{2+}$
Protons	26	50	52	40
Neutrons	32	68	78	50
Electrons	24	46	54	38
Net charge	2+	4+	2−	2+

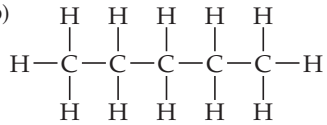
2.33 (**a**) Be^{2+} (**b**) Rb^+ (**c**) AS^{3-} (**d**) In^+ (**e**) At^- **2.34** (**a**) GaF_3, gallium(III) fluoride (**b**) LiH, lithium hydride (**c**) AlI_3, aluminum iodide (**d**) K_2S, potassium sulfide **2.35** (**a**) $Fe(OH)_3$ (**b**) $CsNO_3$ (**c**) $V(CH_3COO)_2$ (**d**) Li_3PO_4 (**e**) In_2O_3

2.36

Ion	K^+	NH_4^+	Mg^{2+}	Fe^{3+}
Cl^-	KCl	NH_4Cl	$MgCl_2$	$FeCl_3$
OH^-	KOH	NH_4OH	$Mg(OH)_2$	$Fe(OH)_3$
CO_3^{2-}	K_2CO_3	$(NH_4)_2CO_3$	$MgCO_3$	$Fe_2(CO_3)_3$
PO_4^{3-}	K_3PO_4	$(NH_4)_3PO_4$	$Mg_3(PO_4)_2$	$FePO_4$

2.38 (**a**) CrO_4^{2-} (**b**) Br^- (**c**) NO_2^- (**d**) SO_3^{2-} (**e**) MnO_4^- **2.39** (**a**) calcium, 2+; oxide, 2− (**b**) sodium, 1+; sulfate, 2− (**c**) potassium, 1+; perchlorate, 1− (**d**) iron, 2+, nitrate, 1− (**e**) chromium, 3+; hydroxide, 1− **2.40** (**a**) lithium oxide (**b**) iron(III) chloride (ferric chloride) (**c**) sodium hypochlorite (**d**) calcium sulfite (**e**) copper(II) hydroxide (cupric hydroxide) (**f**) iron(II) nitrate (ferrous nitrate) (**g**) calcium acetate (**h**) chromium(III) carbonate (chromic carbonate) (**i**) potassium chromate (**j**) ammonium sulfate **2.41** (**a**) $Al(OH)_3$ (**b**) K_2SO_4 (**c**) Cu_2O (**d**) $Zn(NO_3)_2$ (**e**) $HgBr_2$ (**f**) $Fe_2(CO_3)_3$ (**g**) NaBrO **2.42** (**a**) Bromic acid (**b**) hydrobromic acid (**c**) phosphoric acid (**d**) HClO (**e**) HIO_3 (**f**) H_2SO_3 **2.43** (**a**) Sulfur hexafluoride (**b**) iodine pentafluoride (**c**) xenon trioxide (**d**) N_2O_4 (**e**) HCN (**f**) P_4S_6 **2.44** (**a**) $ZnCO_3$, ZnO, CO_2 (**b**) HF, SiO_2, SiF_4, H_2O (**c**) SO_2, H_2O, H_2SO_3 (**d**) PH_3 (**e**) $HClO_4$, Cd, $Cd(ClO_4)_2$ (**f**) VBr_3 **2.46** (**a**) A hydrocarbon is a compound composed of the elements hydrogen and carbon only.

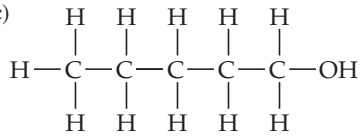
(**b**)



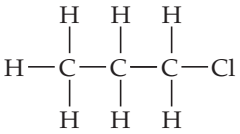
molecular and empirical formulas, C_5H_{12}

2.47 (**a**) A functional group is a group of specific atoms that are constant from one molecule to the next. (**b**) —OH

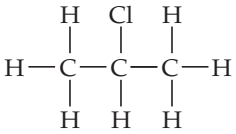
(**c**)



2.48 (a, b)



1-chloropropane



2-chloropropane

2.49 (**a**) (−) (**b**) increase (**c**) decrease **2.52** The particle is an ion. $^{32}_{16}S^{2-}$ **2.54** Formula: IF_5; name: iodine pentafluoride; the compound is molecular. **2.56** Only $Ca(NO_3)_2$, calcium nitrate, is consistent with the diagram. **2.58** (**a**) In the presence of an electric field, there is electrostatic attraction between the negatively charged oil drops and the positively charged plate as well as electrostatic repulsion between the negatively charged oil drops and the negatively charged plate. These electrostatic forces oppose the force of gravity and change the rate of fall of the drops. (**b**) Each individual drop has a different number of electrons associated with it. If the combined electrostatic forces are greater than the force of gravity, the drop moves up. **2.61** The neutron was the most difficult to be discovered because it does not carry any charge. **2.75** (**a**) Po, chalcogens (metal) (**b**) Sr, alkaline earth metals (metal) (**c**) Ne, noble gases (nonmetal) (**d**) Rb, alkaline metals (metal) (**e**) Br, halogens (nonmetal) **2.98** (**a**) 2 protons, 1 neutron, 2 electrons (**b**) tritium, ^3H, is more massive. (**c**) A precision of 1×10^{-27} g would be required to differentiate between $^3H^+$ and $^3He^+$. **2.100** Arrangement A, 4.1×10^{14} atoms/cm^2 (**b**) Arrangement B, 4.7×10^{14} atoms/cm^2 (**c**) The ratio of atoms going from arrangement B to arrangement A is 1.2 to 1. In three dimensions, arrangement B leads to a greater density for Rb metal. **2.104** (**a**) $^{36}_{18}Ar$, $^{38}_{18}Ar$, $^{40}_{18}Ar$, (**b**) All isotopes are atoms of the same element, argon, with the same atomic number, 18 protons in the nucleus and 18 electrons. We expect their electron arrangements to be the same and their chemical properties to be very similar. Each has a different number of neutrons, a different mass number, and a different atomic mass. **2.106** (**a**) $^{63}_{29}Cu$ 29 protons, 34 neutrons; $^{65}_{29}Cu$ 29 protons, 36 neutrons (**b**) $^{63}_{29}Cu = 69\%$, $^{65}_{29}Cu = 30\%$. **2.109** (**a**) 5 significant figures (**b**) An electron is 0.05444% of the mass of an ^1H atom.

2.116 (**a**) Silver (I) chloride, 1+ (**b**) Titanium (IV) chloride 4+ (**c**) Iridium (III) chloride, 3+ (**d**) Lithium chloride, 1+ **2.119** (**a**) Perbromate ion (**b**) selenite ion (**c**) AsO_4^{3-} (**d**) $HTeO_4^-$ **2.122** (**a**) Potassium nitrate (**b**) sodium carbonate (**c**) calcium oxide (**d**) hydrochloric acid (**e**) magnesium sulfate (**f**) magnesium hydroxide

Chapter 3

3.4 (**a**) False (**b**) true (**c**) false
3.5 (**a**) $SiCl_4(l) + 4\,H_2O(l) \longrightarrow Si(OH)_4(s) + 4\,HCl(aq)$
(**b**) $6\,CO_2(g) + 6\,H_2O \longrightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$
(**c**) $2\,Al(OH)_3(s) + 3\,H_2SO_4(l) \longrightarrow Al_2(SO_4)_3(s) + 6\,H_2O(l)$
(**d**) $2\,H_3PO_4(aq) \longrightarrow H_4P_2O_7(aq) + H_2O(l)$
3.6 (**a**) $CaS(s) + 2\,H_2O(l) \longrightarrow Ca(HS)_2(s) + Ca(OH)_2(aq)$
(**b**) $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$
(**c**) $FeCl_3(s) + 3\,Na_2CO_3(aq) \longrightarrow Fe_2(CO_3)_6(s) + 6\,NaCl(aq)$
(**d**) $4\,FeS_2(s) + 11\,O_2(g) \longrightarrow 2\,Fe_2O_3(s) + 8\,SO_2(g)$
3.7 (**a**) $2\,KCN(g) + H_2SO_4(aq) \longrightarrow 2\,HCN(aq) + K_2SO_4(aq)$
(**b**) $4\,NH_4NO_2(aq) + 3\,KOH(aq) \longrightarrow 5\,NH_3(g) + 2\,H_2O(l) + 3\,KNO_3(aq)$ (**c**) $Fe_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Fe(s) + 3\,H_2O(g)$
(**d**) $CH_3COOH(l) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) + 2\,H_2O(l)$
3.11 (**a**) LiCl. (**b**) solid (**c**) 2 **3.12** (**a**) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$
(**b**) $BaCO_3(s) \xrightarrow{\Delta} BaO(s) + CO_2(g)$
(**c**) $C_8H_8(l) + 10\,O_2(g) \longrightarrow 8\,CO_2(g) + 4\,H_2O(l)$
(**d**) $C_2H_6O(g) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$
3.13 (**a**) $C_7H_{16}(s) + 11\,O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(l)$ combustion
(**b**) $Li_3N(s) + BN(s) \longrightarrow Li_3BN_2(s)$ combination
(**c**) $Zn(OH)_2(s) \longrightarrow ZnO(s) + H_2O(l)$ decomposition
(**d**) $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$ decomposition
3.17 (**a**) 349.2 u (**b**) 79.5 u (**c**) 175.9 u (**d**) 122.5 u (**e**) 128.8 u (**f**) 284 u (**g**) 117.3 u **3.18** (**a**) 31.58% (**b**) 26.67% (**c**) 21.19% (**d**) 28.57% (**e**) 9.94% (**f**) 19.16% **3.19** (**a**) 79.2% (**b**) 63.2% (**c**) 64.6% **3.23** (**a**) False (**b**) true (**c**) false (**d**) true **3.24** 197 g gold contains 1 mol of atom; 0.5 mol BCl_3 contains 2.0 mol atoms; 6.0×10^{23} CCl_4 molecules contains 5 mol of atoms. **3.25** (**a**) 35.9 g $C_{12}H_{22}O_{11}$ (**b**) 0.75766 mol $Zn(NO_3)_2$ (**c**) 6.0×10^{17} CH_3CH_2OH molecules (**d**) 2.47×10^{23} N atoms **3.26** (**a**) 0.373 g $(NH_4)_3PO_4$ (**b**) 5.737×10^{-3} mol Cl^- (**c**) 0.248 g $C_8H_{10}N_4O_2$ (**d**) 387 g cholesterol/mol **3.27** (**a**) Molar mass = 83.0 g/mol (**b**) 1.09×10^{-5} mol saccharin (**c**) 6.56×10^{18} saccharin molecules (**d**) 4.59×10^{19} C atoms **3.28** (**a**) 2.500×10^{21} H atoms (**b**) 2.083×10^{20} $C_6H_{12}O_6$ molecules (**c**) 3.460×10^{-4} mol $C_6H_{12}O_6$ (**d**) 0.06227 g $C_6H_{12}O_6$ **3.29** 3.2×10^{-8} mol C_2H_3Cl/L; 1.9×10^{16} molecules/L **3.33** (**a**) C_3H_6O (**b**) NiO (**c**) $K_2Cr_2O_7$ **3.34** (**a**) C_5H_7N (**b**) NaOH (**c**) N_2H_8S **3.35** 31 g/mol **3.36** (**a**) C_6H_6 (**b**) H_2O_2 **3.37** (**a**) Empirical formula, CH; molecular formula, C_8H_8 (**b**) empirical formula, $C_4H_5N_2O$; molecular formula, $C_8H_{10}N_4O_2$ (**c**) empirical formula and molecular formula, $NaC_5H_8O_4N$ **3.38** (**a**) C_7H_8 (**b**) The empirical and molecular formulas are $C_{10}H_{20}O$. **3.39** Empirical formula, C_4H_8O; molecular formula, $C_8H_{16}O_2$ **3.40** $x = 10$; $Na_2CO_3 \cdot 10\,H_2O$ **3.45** (**a**) 2.40 mol HF (**b**) 5.25 g NaF (**c**) 0.610 g Na_2SiO_3 **3.46** (**a**) $Al(OH)_3(s) + 3\,HCl(aq) \longrightarrow AlCl_3(aq) + 3\,H_2O(l)$
(**b**) 0.701 g HCl (**c**) 0.855 g $AlCl_3$; 0.347 g H_2O
(**d**) Mass of reactants = 0.500 g + 0.701 g = 1.201 g;
mass of products = 0.855 g + 0.347 g = 1.202 g.
Mass is conserved, within the precision of the data.
3.47 (**a**) $Al_2S_3(s) + 6\,H_2O(l) \longrightarrow 2\,Al(OH)_3(s) + 3\,H_2S(g)$
(**b**) 14.7 g $Al(OH)_3$ **3.48** (**a**) 2.25 mol N_2 (**b**) 15.5 g NaN_3 (**c**) 548 g NaN_3 **3.49** (**a**) 5.50×10^{-3} mol Al (**b**) 1.47 g $AlBr_3$ **3.50** 416.8 g. **3.54** (**a**) The *limiting reactant* determines the maximum number of product moles resulting from a chemical reaction; any other reactant is an *excess reactant*. (**b**) The limiting reactant regulates the amount of products because it is completely used up during the reaction; no more product can be made when one of the reactants is unavailable. (**c**) Combining ratios are molecule and mole ratios. Since different molecules have different masses, comparing initial masses of reactants will not provide a comparison of numbers of molecules or moles. **3.55** (**a**) $2\,C_2H_5OH + 6\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$ [This equation corresponds to the mixture of reactants in the box, but it does not have the simplest ratio of coefficients. Divide all coefficients by 2 to obtain $C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O$] (**b**) C_2H_5OH limits (**c**) If the reaction goes to completion, there will be four molecules of CO_2, six molecules of H_2O, zero molecules of C_2H_5OH and one molecule of O_2. **3.56** NaOH is the limiting reactant; 0.925 mol Na_2CO_3 can be produced; 0.075 mol CO_2 remains. **3.57** (**a**) $NaHCO_3$ is the limiting reactant. (**b**) 0.524 g CO_2 (**c**) 0.238 g citric acid remains **3.58** 0.00 g $AgNO_3$ (limiting reactant), 1.94 g Na_2CO_3, 4.06 g Ag_2CO_3, 2.50 g $NaNO_3$ **3.59** (**a**) The theoretical yield is 60.3 g C_6H_5Br. (**b**) 70.1% yield **3.60** 28 g S_8 actual yield **3.61** Equation (**a**) best fits the diagram. **3.63** (**a**) NO_2 (**b**) No, because we have no way of knowing whether the empirical and molecular formulas are the same. NO_2 represents the simplest ratio of atoms in a molecule but not the only possible molecular formula. **3.65** (**a**) $C_2H_5NO_2$ (**b**) 75.0 g/mol (**c**) 1.332 mol glycine (**d**) Mass %N in glycine is 18.7%. **3.67** (**a**) $N_2 + 3H_2 \longrightarrow 2\,NH_3$. (**b**) H_2 is the limiting reactant. (**c**) 6 NH_3 molecules can be made. (**d**) One N_2 molecule is left over. **3.107** (**a**) $CH_3COCH_3(l) + 4\,O_2(g) \longrightarrow 3\,CO_2(g) + 3\,H_2O(l)$ (**b**) $Hg_2CO_3(s) \longrightarrow CO_2(g) + H_gO(s) + Hg(l)$
(**c**) $SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$ **3.111** (**a**) 4.8×10^{-20} g CdSe (**b**) 150 Cd atoms (**c**) 8.4×10^{-19} g CdSe (**d**) 2.6×10^3 Cd atom **3.115** $C_8H_8O_3$ **3.119** (**a**) 1.19×10^{-5} mol NaI (**b**) 8.1×10^{-3} g NaI **3.123** 7.5 mol H_2 and 4.5 mol N_2 present initially **3.128** 6.46×10^{24} O atoms **3.132** (**a**) $2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$ (**b**) 3.95×10^1 g NO, 6.05×10^1 g NO_2

Chapter 4

4.2 (**a**) False. Electrolyte solutions conduct electricity because *ions* are moving through the solution. Because ions are mobile in solution, the added presence of uncharged molecules does not inhibit conductivity. **4.3** Statement (**b**) is most correct.
4.4 (**a**) $Li_2CO_3(aq) \longrightarrow 2\,Li^+(aq) + CO_3^{2-}(aq)$
(**b**) $(NH_4)_3PO_4(aq) \longrightarrow 3\,NH_4^+(aq) + PO_4^{3-}(aq)$
(**c**) $Na_2Cr_2O_7(aq) \longrightarrow 2\,Na^+(aq) + Cr_2O_7^{2-}(aq)$
(**d**) $NaPF_6(aq) \longrightarrow Na^+(aq) + PF_6^-(aq)$
4.5 H^+ and CO_3^{2-} ions; $H_2CO_3(aq) \rightleftharpoons 2\,H^+(aq) + CO_3^{2-}(aq)$
4.7 (**a**) Insoluble (**b**) soluble (**c**) soluble (**d**) soluble (**e**) insoluble
4.8 (**a**) $Ca(CH_3COO)_2(aq) + 2\,NaOH(aq) \longrightarrow Ca(OH)_2(s) + 2\,NaCH_3COO(aq)$ (**b**) No precipitate
(**c**) $3\,Na_2S(aq) + 2\,FeCl_3(aq) \longrightarrow Fe_2S_3(s) + 6\,NaCl(aq)$
4.10 Only Pb^{2+} could be present. **4.11** (**a**) True (**b**) false (**c**) false (**d**) true (**e**) false **4.13** (**a**) False. H_2SO_4 is a diprotic acid; it has two ionizable hydrogen atoms. (**b**) False. HCl is a strong acid. (**c**) False. CH_3OH is a molecular nonelectrolyte. **4.14** (**a**) Acid, mixture of ions and molecules (weak electrolyte) (**b**) none of the above, entirely molecules (nonelectrolyte) (**c**) salt, entirely ions (strong electrolyte) (**d**) base, entirely ions (strong electrolyte) **4.15** (**a**) HF, weak electrolyte (**b**) C_6H_5COOH, weak electrolyte (**c**) C_6H_6, nonelectrolyte (**d**) $CoCl_3$, strong electrolyte (**e**) $AgNO_3$, strong electrolyte
4.16 (**a**) $2\,HBr(aq) + Ca(OH)_2(aq) \longrightarrow CaBr(aq) + 2\,H_2O(l)$;
$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$;
(**b**) $Cu(OH)_2(s) + 2\,HClO_4(aq) \longrightarrow Cu(ClO_4)_2(aq) + 2\,H_2O(l)$;
$Cu(OH)_2(s) + 2\,H^+(aq) \longrightarrow 2\,H_2O(l) + Cu^{2+}(aq)$
(**c**) $Al(OH)_3(s) + 3\,HNO_3(aq) \longrightarrow Al(NO_3)_3(aq) + 3\,H_2O(l)$;
$Al(OH)_3(s) + 3\,H^+(aq) \longrightarrow 3\,H_2O(l) + Al^{3+}(aq)$
4.17 (**a**) $CdS(s) + H_2SO_4(aq) \longrightarrow CdSO_4(aq) + H_2S(g)$;
$CdS(s) + 2H^+(aq) \longrightarrow H_2S(g) + Cd^{2+}(aq)$

(**b**) $MgCO_3(s) + 2\,HClO_4(aq) \longrightarrow Mg(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$; $MgCO_3(s) + 2\,H^+(aq) \longrightarrow H_2O(l) + CO_2(g) + Mg^{2+}(aq)$ **4.18** (**a**) $MgCO_3(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$; $MgCO_3(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$; $MgO(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$; $MgO(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l)$; $Mg(OH)_2(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,H_2O(l)$ (**b**) We can distinguish magnesium carbonate, $MgCO_3(s)$, because its reaction with acid produces $CO_2(g)$, which appears as bubbles. The other two compounds are indistinguishable, because the products of the two reactions are exactly the same. **4.20** Metals in region A are most easily oxidized. Nonmetals in region D are least easily oxidized. **4.22** (**a**) +6 (**b**) +4 (**c**) +5 (**d**) +5 (**e**) +4 (**f**) +2 **4.23** (**a**) $N_2 \longrightarrow 2\,NH_3$, N is reduced; $3\,H_2 \longrightarrow 2\,NH_3$, H is oxidized (**b**) $Fe^{2+} \longrightarrow Fe$, Fe is reduced; $Al \longrightarrow Al^{3+}$, Al is oxidized (**c**) $Cl_2 \longrightarrow 2\,Cl^-$, Cl is reduced; $2\,I^- \longrightarrow I_2$, I is oxidized (**d**) $S^{2-} \longrightarrow SO_4^{2-}$, S is oxidized; $H_2O_2 \longrightarrow H_2O$, O is reduced

4.24 (**a**) $Mn(s) + H_2SO_4(aq) \longrightarrow MnSO_4(aq) + H_2(g)$; $Mn(s) + 2\,H^+(aq) \longrightarrow Mn^{2+}(aq) + H_2(g)$ (**b**) $2\,Cr(s) + 6\,HBr(aq) \longrightarrow 2\,CrBr_3(aq) + 3\,H_2(g)$; $2\,Cr(s) + 6\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,H_2(g)$ (**c**) $Sn(s) + 2\,HCl(aq) \longrightarrow SnCl_2(aq) + H_2(g)$; $Sn(s) + 2\,H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g)$ (**d**) $2\,Al(s) + 6\,HCOOH(aq) \longrightarrow 2\,Al(HCOO)_3(aq) + 3\,H_2(g)$; $2\,Al(s) + 6\,HCOOH(aq) \longrightarrow 2\,Al^{3+}(aq) + 6\,HCOO^-(aq) + 3\,H_2(g)$ **4.25** (**a**) $Fe(s) + Cu(NO_3)_2(aq) \longrightarrow Fe(NO_3)_2(aq) + Cu(s)$ (**b**) NR (**c**) $Sn(s) + 2\,HBr(aq) \longrightarrow SnBr_2(aq) + H_2(g)$ (**d**) NR (**e**) $2\,Al(s) + 3\,CoSO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3\,Co(s)$ **4.27** (**a**) 1.17 *M* $ZnCl_2$ (**b**) 0.158 mol H^+ (**c**) 58.3 mL of 6.00 *M* NaOH **4.28** 16 g $Na^+(aq)$ **4.29** BAC of 0.08 = 0.02 *M* CH_3CH_2OH (alcohol) **4.30** (**a**) 0.15 *M* Na_2CO_3 has the highest Na^+ concentration. (**b**) 20.0 mL of 0.15 *M* $NaHCO_3$ has more Na^+ ions. **4.31** (**a**) 1.05 *M* K^+, 0.35 *M* PO_4^{3-} (**b**) 5×10^{-4} *M* Cu^{2+}, 1×10^{-3} *M* Cl^- (**c**) 0.0184 *M* CH_3CH_2OH (**d**) 0.082 *M* Na^+, 0.041 *M* CO_3^{2-}, 0.236 *M* K^+, 0.118 *M* SO_4^{2-}

4.32 (**a**) 16.9 mL 14.8 *M* NH_3 (**b**) 0.296 *M* NH_3 **4.33** (**a**) The ratio of drug molecules to cancer cells is 4.5×10^6 **4.34** 1.398 *M* CH_3COOH **4.36** (**a**) 20.0 mL of 0.15 *M* HCl (**b**) 0.224 g KCl (**c**) The KCl reagent is virtually free relative to the HCl solution. The KCl analysis is more cost-effective. **4.37** (**a**) 38.0 mL of 0.115 *M* $HClO_4$ (**b**) 769 mL of 0.128 *M* HCl (**c**) 0.408 *M* $AgNO_3$ (**d**) 0.275 g KOH **4.38** 27 g $NaHCO_3$ **4.39** (**a**) Molar mass of metal hydroxide is 103 g/mol. (**b**) Rb^+

4.40 (**a**) $3\,NaOH(aq) + AlCl_3(aq) \longrightarrow Al(OH)_3(s) + 3\,NaCl(aq)$ (**b**) $Al(OH)_3$ (**c**) $AlCl_3$ is the limiting reagent. (**d**) 0.70 g $Al(OH)_3$ (**e**) 0.124 *M* Na^+, 0.106 *M* Cl^-, and 0.018 *M* OH^-.

4.41 91.39% $Mg(OH)_2$ **4.42** Diagram (**c**) represents Li_2SO_4

4.46 $BaCl_2$ **4.48** Platinum will neither be oxidized by nor dissolve in any of the three available solutions. Lead is oxidized by and will dissolve in the nitric acid solution, but not the nickel nitrate solution. Zinc is oxidized by and will dissolve in both nitric acid and nickel nitrate solutions. **4.50** The "water-splitting" reaction is (**c**), a redox reaction. **4.60** (**a**) K^+, SO_4^{2-} (**b**) Li^+, NO_3^- (**c**) NH_4^+, Cl^- **4.69** (**a**) False (**b**) false **4.75** (**a**) i. $Zn(s) + Cd^{2+}(aq) \longrightarrow Cd(s) + Zn^{2+}(aq)$; ii. $Cd(s) + Ni^{2+}(aq) \longrightarrow Ni(s) + Cd^{2+}(aq)$ (**b**) The elements chromium, iron, and cobalt more closely define the position of cadmium in the activity series. (**c**) Place an iron strip in $CdCl_2(aq)$. If Cd(s) is deposited, Cd is less active than Fe; if there is no reaction, Cd is more active than Fe. Do the same test with Co if Cd is less active than Fe or with Cr if Cd is more active than Fe. **4.77** (**a**) Extensive; it represents the amount of substances in a solution. The more the number of substances present in a solution, the larger the number of moles. (**b**) No. Concentration is an intensive property. It is the ratio of the amount of solute, in terms of number of moles, present in a certain quantity of solvent or solution. One cannot determine the number of moles of Zn^{2+} in a 0.1 *M* $ZnCl_2$ solution if the quantity of the solution is not given. **4.82** (**a**) 316 g ethanol (**b**) 401 mL ethanol **4.95** (**a**) $UO_2(s) + 4\,HF(aq) \longrightarrow UF_4(s) + H_2O$; $UF_4(s) + F_2(g) \longrightarrow UF_6(s)$ (**b**) Step 1 (**c**) Step 2 **4.99** (**a**) $Al(OH)_3(s) + 3\,H^+(aq) \longrightarrow Al^{3+}(aq) + 3\,H_2O(l)$ (**b**) $Mg(OH)_2(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,H_2O(l)$ (**c**) $MgCO_3(s) + 2\,H^+(aq) \longrightarrow Mg^{2+}(aq) + H_2O(l) + CO_2(g)$ (**d**) $NaAl(CO_3)(OH)_2(s) + 4\,H^+(aq) \longrightarrow Na^+(aq) + Al^{3+}(aq) + 3\,H_2O(l) + CO_2(g)$ (**e**) $CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$ [In (**c**), (**d**) and (**e**), one could also write the equation for formation of bicarbonate, e.g., $MgCO_3(s) + H^+(aq) \longrightarrow Mg^{2+} + HCO_3^-(aq)$.] **4.103** 415 mL H_3PO_4 **4.106** (**a**) 0.854 *M* CsOH (**b**) $CsOH(aq) + HI(aq) \longrightarrow CsI(aq) + H_2O(l)$ (**c**) 0.38 *M* HI **4.112** (**a**) $Zn(OH)_2(s) + H_2SO_4(aq) \longrightarrow 2\,H_2O(l) + ZnSO_4(aq)$ (**b**) $Zn(OH)_2$ is the limiting reactant. (**c**) 0 mol $Zn(OH)_2$, 0.026 mol of H_2SO_4, 0.0901 mol $ZnSO_4$ are present. **4.115** (**a**) +5 (**b**) silver arsenate (**c**) 5.22% As

Chapter 5

5.3 $w = 2.6 \times 10^{-18}$ J. **5.4** (**a**) Gravity; work is done because the force of gravity is opposed and the book is lifted. (**b**) Gas spring force; Work is done because the force of the pump is opposed as the gas is compressed into it. **5.6** (**a**) Matter cannot leave or enter a closed system. (**b**) Neither matter nor energy can leave or enter an isolated system. (**c**) Any part of the universe not part of the system is called the surroundings. **5.7** (**a**) According to the first law of thermodynamics, energy is conserved. (**b**) The *internal energy* (**E**) of a system is the sum of all the kinetic and potential energies of the system components. (**c**) The internal energy of a closed system increases when work is done on the system and when heat is transferred to the system. **5.8** (**a**) $\Delta E = -0.077$ kJ, endothermic (**b**) $\Delta E = -22.1$ kJ, exothermic **5.9** (**a**) Since no work is done by the system in case (2), the gas will absorb most of the energy as heat; the case (2) gas will have the higher temperature. (**b**) In case (1) energy will be used to do work on the surroundings ($-w$), but some will be absorbed as heat ($+q$). In case (2) $w = 0$ and q is (+). (**c**) ΔE is greater for case (2) because the entire 100 J increases the internal energy of the system rather than a part of the energy doing work on the surroundings. **5.10** (**a**) A *state function* is a property that depends only on the physical state (pressure, temperature, etc.) of the system, not on the route used to get to the current state. (**b**) Internal energy is a state function; heat is not a state function. (**c**) Volume is a state function. The volume of a system depends only on conditions (pressure, temperature, amount of substance), not the route or method used to establish that volume. **5.12** $w = 203$ J **5.13** (**a**) As $\Delta E = q + w$, measuring ΔE generally requires a means to measure both q and w. While, at constant pressure, the measured heat q_p is identical to the change in enthalpy ΔH. (**b**) E is a property of a thermodynamic system; it only depends on its conditions, e.g. its temperature and pressure. Heat q is not a property of a system, q describes energy transferred to or from the system. We can equate change in internal energy, ΔE, with heat only for the specific conditions of constant volume and no work. (**c**) The process is exothermic. **5.15** $\Delta E = 1.47$ kJ; $\Delta H = 0.824$ kJ **5.16**(**a**) $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -890$ kJ

(**b**)

$CH_4(g) + 2\,O_2(g)$

$\Delta H = -890$ kJ

$CO_2(g) + 2H_2O(l)$

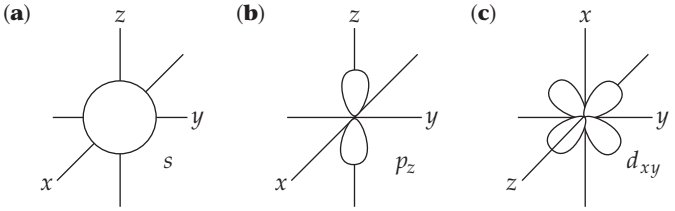
5.17 (**a**) $\Delta H^0_{rxn} = -435.88$ kJ/mol (**b**) 2 H(g) has the higher enthalpy. **5.18** (**a**) Exothermic (**b**) −87.9 kJ heat transferred (**c**) 15.7 g MgO produced (**d**) 602 kJ heat absorbed **5.19** (**a**)−29.5 kJ (**b**) −4.11 kJ (**c**) 60.6 J **5.20** (**a**) $\Delta H = 726.5$ kJ (**b**) $\Delta H = -1453$ kJ (**c**) The exothermic forward reaction is more likely to be thermodynamically favored. (**d**) Vaporization is endothermic. If the product were $H_2O(g)$, the reaction would be more endothermic and would have a less negative ΔH. **5.22** (**a**) $C_m/C_s = MM$ (**b**) $C_m = 24.3$ J/mol-K (**c**) To calculate heat capacity from specific heat, the mass of the particular piece of aluminum component must be known. **5.23** (**a**) 4.184 J (**b**) 75.4 J (**c**) 1548 J/K (**d**) 452 kJ **5.24** (**a**) 2.66×10^3 J (**b**) It will require more heat to increase the temperature of one mole of octane, $C_8H_{18}(l)$, by a certain amount than to increase the temperature of one mole of water, $H_2O(l)$, by the same amount. **5.25** (**a**) $\Delta H = -19.024$ kJ (**b**) $\Delta H = -57.37$ kJ/mol **5.26** (**a**) $C_6H_4O_2(s) + 6O_2(g) \longrightarrow 2H_2O(l) + 6CO_2(g)$ (**b**) $\Delta H_{rxn} = -25.44$ kJ/g quinone or –2750 kJ/mol. **5.27** (**a**) Heat capacity of the complete calorimeter = 18.46 kJ/°C (**b**) 5.36 °C **5.30** $\Delta H = -1300.0$ kJ **5.31** $\Delta H = -2.49 \times 10^3$ kJ **5.33** (**a**) *Standard conditions* for enthalpy changes are $P = 1$ atm and some common temperature, usually 298 K. (**b**) *Enthalpy of formation* is the enthalpy change that occurs when a compound is formed from its component elements. (**c**) *Standard enthalpy of formation*, ΔH°_f, is the enthalpy change that accompanies formation of one mole of a substance from elements in their standard states.

5.34 (**a**) $\frac{1}{2}N_2(g) + O_2(g) \longrightarrow NO_2(g)$, $\Delta H^\circ_f = 33.84$ kJ
(**b**) $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g)$, $\Delta H^\circ_f = -395.2$ kJ
(**c**) $Na(s) + \frac{1}{2}Br_2(l) \longrightarrow NaBr(s)$, $\Delta H^\circ_f = -361.4$ kJ
(**d**) $Pb(s) + N_2(g) + 3O_2(g) \longrightarrow Pb(NO_3)_2(s)$, $\Delta H^\circ_f = -451.9$ kJ
5.35 $\Delta H^\circ_{rxn} = -847.6$ kJ **5.36** (**a**) $\Delta H^\circ_{rxn} = -196.6$ kJ
(**b**) $\Delta H^\circ_{rxn} = 37.1$ kJ (**c**) $\Delta H^\circ_{rxn} = -976.94$ kJ (**d**) $\Delta H^\circ_{rxn} = -68.3$ kJ
5.37 $\Delta H^\circ_f = -248$ kJ
5.38 (**a**) $C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$
(**b**) $\Delta H^\circ_f = -259.5$kJ
5.39 (**a**) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$
(**b**) $\Delta H^\circ_{rxn} = -1234.8$ kJ (**c**) 2.11×10^4 kJ/L heat produced
(**d**) 0.071284 g CO_2/kJ heat emitted **5.41** (**a**) $+\Delta H$ (**b**) $-\Delta H$ (**c**) $+\Delta H$ (**d**) $+\Delta H$ **5.42** (**a**) $\Delta H = -103$ kJ (**b**) $\Delta H = -1295$ kJ **5.43** (**a**) ΔH for the reaction is 192.9 kJ. D(Br—Br) = 193 kJ (**b**) The difference between the value calculated in part (**a**) and the value from Table 5.4 is zero, to three significant figures. **5.44** (**a**) ΔH for the reaction calculated using bond enthalpies is −485 kJ. (**b**) The estimate from part (**a**) is less negative or larger than the true reaction enthalpy. (**c**) ΔH for the reaction calculated using enthalpies of formation is −572 kJ. **5.45** (**a**) *Fuel value* is the amount of energy produced when 1 g of a substance (fuel) is combusted. (**b**) 5 g of fat (**c**) These products of metabolism are expelled as waste via the alimentary tract, $H_2O(l)$ primarily in urine and feces, and $CO_2(g)$ as gas when breathing. **5.46** (**a**) 228 cal/ serving (**b**) Potassium is not metabolized by the body, so it does not contribute to the calorie content of the food. **5.47** 59.7 Cal **5.48** (**a**) $\Delta H_{comb} = -1850$ kJ/mol C_3H_4, −1926 kJ/mol C_3H_6, −2044 kJ/mol C_3H_8 (**b**) $\Delta H_{comb} = -4.616 \times 10^4$ kJ/kg C_3H_4, -4.578×10^4 kJ/kg C_3H_6, -4.635×10^4 kJ/kg C_3H_8 (**c**) These three substances yield nearly identical quantities of heat per unit mass, but propane is marginally higher than the other two. **5.49** (**a**) $E_{el} = 1.8 \times 10^2$ J (**b**) If the spheres are released, they will move away from each other. (**c**) v = 19 m/s **5.52** (**a**) (iii) (**b**) none of them (**c**) all of them **5.55** (**a**) The sign of w is (+). (**b**) The sign of q is (−). (**c**) The sign of w is positive and the sign of q is negative, so we cannot absolutely determine the sign of ΔE. It is likely that the heat lost is much smaller than the work done on the system, so the sign of ΔE is probably positive. **5.58** (**a**) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$. Since $\Delta V = 0$, $w = 0$. (**b**) $\Delta H = \Delta H_f = 90.37$ kJ. The definition of a formation reaction is one where elements combine to form one mole of a single product. The enthalpy change for such a reaction is the enthalpy of formation. **5.61** (**a**) $E_{el} = -1.0 \times 10^{-18}$ J (**b**) $\Delta E_{el} = 7.7 \times 10^{-19}$ J (**c**) The two objects carry opposite charges; they attract each other. As they move farther apart, their energy increases. **5.62** (**a**) $F_{el} = -4.4 \times 10^{-9}$ N (**b**) $F_g = 1.9 \times 10^{-48}$ N (**c**) The electrostatic force is 2.3×10^{39} times larger than the gravitational force. Both forces are attractive, that is, they point in the same direction. **5.73** (**a**) $w = 7.4$ kJ (**b**) $\Delta E = -476.2$ kJ (**c**) Since the value of Δn is negative, the quantity $(-P\Delta V)$ is positive. We add a positive quantity to ΔH to calculate ΔE, so ΔE must be larger. **5.87** Yes, because internal energy is a state function. **5.105** The spontaneous air bag reaction is probably exothermic, with $-\Delta H$ and thus $-q$. When the bag inflates, work is done by the system, so the sign of w is also negative. **5.108** $\Delta H = -11.73$ kJ; $\Delta E = -14.21$ kJ **5.110** 1.8×10^4 bricks **5.113** (**a**) $\Delta H^0_{rxn} = -11.73$ KJ (**b**) 39.7 g Fe needed **5.117** (**a**) $\Delta H^0_{rxn} = 82$ KJ/mol (**b**) 1-hexene has greater enthalpy than cyclohexane. (**c**) 1-hexene will have the larger combustion enthalpy. **5.120** If all work is used to increase the man's potential energy, the stair climbing uses 70 Cal and will not compensate for the extra order of 245 Cal fries. (More than 70 Cal will be required to climb the stairs because some energy is used to move limbs and some will be lost as heat.) **5.125** (**a**) 1.479×10^{-18} J/molecule (**b**) 1×10^{-15} J/photon. The X-ray has approximately 1000 times more energy than is produced by the combustion of 1 molecule of $CH_4(g)$. **5.127** (**a**) $\Delta H°$ for neutralization of the acids is: HNO_3, −55.8 kJ; HCl, −56.1 kJ; NH_4^+, −4.1 kJ. (**b**) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ is the net ionic equation for the first two reactions. $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$ (**c**) The $\Delta H°$ values for the first two reactions are nearly identical, −55.8 kJ and −56.1 kJ. Because spectator ions do not change during a reaction and these two reactions have the same net ionic equation, it is not surprising that they have the same $\Delta H°$. (**d**) Strong acids are more likely than weak acids to donate H^+. Neutralization of the two strong acids is energetically favorable, while the third reaction is barely so. NH_4^+ is likely a weak acid. **5.129** (**a**) $\Delta H° = -65.7$ kJ (**b**) $\Delta H°$ for the complete molecular equation will be the same as $\Delta H°$ for the net ionic equation. Since the overall enthalpy change is the enthalpy of products minus the enthalpy of reactants, the contributions of spectator ions cancel. (**c**) ΔH°_f for $AgNO_3(aq)$ is −100.4 kJ/mol.

Chapter 6

6.2 (**a**) True (**b**) False. Ultraviolet light has shorter wavelengths than visible light. (**c**) False. X-rays travel at the same speed as microwaves. (**d**) False. Electromagnetic radiation and sound waves travel at different speeds. **6.3** Wavelength of X-rays < ultraviolet < green light < red light < infrared < radio waves **6.4** (**a**) 10^7 1/cm (**b**) 2×10^4 1/cm (**c**) 10 1/cm **6.5** (**a**) 3.0×10^{13} s^{-1} (**b**) 5.45×10^{-7} m = 545 nm. (**c**) The radiation in (**b**) is visible; the radiation in (**a**) is not. (**d**) 1.50×10^4 m **6.6** 4.6×10^{14} s^{-1}; red. **6.8** (iv) **6.9** (**a**) 1.95×10^{-19} J (**b**) 4.81×10^{-19} J (**c**) 328 nm **6.10** (**a**) $\lambda = 3.0$ mm, $E = 6.6 \times 10^{-23}$ J, $\lambda = 3.0$ nm, $E = 6.6 \times 10^{-16}$ J (**b**) The 3.0 mm photon is in the microwave region and the 0.3 nm photon is in the x-ray region. The x-ray photon has the greater energy. **6.11** (**a**) 6.11×10^{-19} J/photon (**b**) 368 kJ/mol (**c**) 1.64×10^{15} photons (**d**) 368 kJ/mol **6.12** (**a**) The $\sim 1 \times 10^{-6}$ m radiation is in the infrared portion of the spectrum.
(**b**) 8.1×10^{16} photons/s **6.13** (**a**) $\nu = 1.09 \times 10^{15}$ 1/s
(**b**) $\lambda = 275$ nm (**c**) $E_{240} = 8.28 \times 10^{-19}$ J. The excess energy of the 240-nm photon is converted into the kinetic energy of the emitted electron. $\nu = 4.82 \times 10^5$ m/s. **6.15** When an electron in a hydrogen atom transitions from $n = 1$ to $n = 3$, the atom "expands". **6.16** (**a**) Emitted (**b**) emitted (**c**) emitted **6.17** (**a**) $E_3 = -2.42 \times 10^{-19}$ J; $E_6 = -6.06 \times 10^{-20}$ J; $\Delta E = -1.82 \times 10^{-19}$ J; $\lambda = 1090$ nm
(**b**) infrared **6.18** (**a**) (ii) (**b**) $n_i = 3$, $n_f = 2$; $\lambda = 6.56 \times 10^{-7}$ m; this is the red line at 656 nm. $n_i = 4$, $n_f = 2$; $\lambda = 4.86 \times 10^{-7}$ m; this is

the blue-green line at 486 nm. $n_i = 5$, $n_f = 2$; $\lambda = 4.34 \times 10^{-7}$ m; this is the blue-violet line at 434 nm. **6.19** (**a**) Ultraviolet region (**b**) $n_i = 5$, $n_f = 1$ **6.20** The order of decreasing energy of light absorbed is: $n = 1$ to $n = 3$; $n = 2$ to $n = 5$; $n = 3$ to $n = 7$; $n = 4$ to $n = 8$ **6.23** (**a**) $\lambda = 5.6 \times 10^{-37}$ m (**b**) $\lambda = 2.65 \times 10^{-34}$ m (**c**) $\lambda = 2.3 \times 10^{-13}$ m (**d**) $\lambda = 1.51 \times 10^{-11}$ m **6.24** 3.16×10^3 m/s **6.25** (**a**) $\Delta x \geq 4 \times 10^{-27}$ m (**b**) $\Delta x \geq 3 \times 10^{-10}$ m **6.27** (**a**) False (**b**) false **6.28** (**a**) $n = 4$, $l = 3, 2, 1, 0$ (**b**) $l = 2$, $m_l = -2, -1, 0, 1, 2$ (**c**) $m_l = 2$, $l \geq 2$ or $l = 2, 3$ or 4 **6.29** (**a**) 3*p*: $n = 3$, $l = 1$ (**b**) 2*s*: $n = 2$, $l = 0$ (**c**) 4*f*: $n = 4$, $l = 3$ (**d**) 5*d*: $n = 5$, $l = 2$ **6.30** (**a**) 3, 2, 1, 0, −1, −2, −3 (**b**) $\frac{1}{2}$, $-\frac{1}{2}$ **6.31** (**a**) Impossible, 1*p* (**b**) possible (**c**) possible (**d**) impossible, 2*d* **6.33**



6.34 (**a**) The hydrogen atom 1*s* and 2*s* orbitals have the same overall spherical shape, but the 2*s* orbital has a larger radial extension and one more node than the 1*s* orbital. (**b**) A single 2*p* orbital is directional in that its electron density is concentrated along one of the three Cartesian axes of the atom. The $d_{x^2-y^2}$ orbital has electron density along both the *x*- and *y*-axes, while the p_x orbital has density only along the *x*-axis. (**c**) The average distance of an electron from the nucleus in a 3*s* orbital is greater than for an electron in a 2*s* orbital. (**d**) $1s < 2p < 3d < 4f < 6s$ **6.36** (**a**) For the He^+ ion, the 2*s* and 2*p* orbitals have the same energy. (**b**) Yes. In a helium atom, the 2*s* orbital is lower in energy than the 2*p* orbital. **6.37** (**a**) No. Both configurations follow the Pauli exclusion principle. (**b**) No. Both configurations follow Hund's rule. (**c**) No. In the absence of a magnetic field, we cannot say which configuration has the lower energy. **6.38** (**a**) 2 (**b**) 6 (**c**) 10 (**d**) 2 **6.40** (**a**) "Valence electrons" are those involved in chemical bonding. They are part or all of the outer-shell electrons listed after the core. (**b**) "Core electrons" are inner-shell electrons that have the electron configuration of the nearest noble-gas element. (**c**) Each box represents an orbital. (**d**) Each half-arrow in an orbital diagram represents an electron. The direction of the half-arrow represents electron spin. **6.41** (**a**) Cs, $[Xe]6s^1$ (**b**) Ni, $[Ar]4s^23d^8$ (**c**) Se, $[Ar]4s^23d^{10}4p^4$ (**d**) Cd, $[Kr]5s^24d^{10}$ (**e**) U, $[Rn]5f^36d^17s^2$ (**f**) Pb, $[Xe]6s^24f^{14}5d^{10}6p^2$ **6.42** (**a**) Be, 0 unpaired electrons (**b**) O, 2 unpaired electrons (**c**) Cr, 6 unpaired electrons (**d**) Te, 2 unpaired electrons **6.43** (**a**) The 4*s* subshell would fill before the 3*d*. (**b**) The *s* subshell can hold only 2 electrons. (**c**) The third electron would fill the 2*s* subshell before the 3*s*. **6.45** (**a**) 0.1 m or 10 cm (**b**) No. Visible radiation has wavelengths much shorter than 0.1 m. (**c**) Energy and wavelength are inversely proportional. Photons of the longer 0.1-m radiation have less energy than visible photons. (**d**) Radiation with $\lambda = 0.1$ m is in the low-energy portion of the microwave region. The appliance is probably a microwave oven. **6.48** (**a**) Increase (**b**) decrease **6.52** (**a**) $l = 1$ (**b**) $3p_y$ (**c**) (iii) **6.90** (**a**) $\lambda_A = 3.6 \times 10^{-8}$ m, $\lambda_B = 8.0 \times 10^{-8}$ m (**b**) $\nu_A = 8.4 \times 10^{15}$ s^{-1}, $\nu_B = 3.7 \times 10^{15}$ s^{-1} (**c**) A, ultraviolet; B, ultraviolet **6.93** 3.9 hr **6.95** 8.835×10^{19} photons **6.100** (**a**) Lines with $n_f = 1$ lie in the ultraviolet, lines with $n_f = 2$ lie in the visible and lines with $n_f = 3$ lie near the infrared. Lines with $n_f = 4$ will have smaller energy differences and longer wavelengths and lie in the infrared. (**b**) $n_i = 5$, $\Delta E = -4.905 \times 10^{-20}$ J; $\lambda = 4050$ nm; $n_i = 6$, $\Delta E = -7.569 \times 10^{-20}$ J, $\lambda = 2624$ nm; $n_i = 7$, $\Delta E = -9.176 \times 10^{-20}$ J, $\lambda = 2165$ nm **6.104** $\lambda = 12.3$ pm

6.108 (**a**) The nodal plane of the p_z orbital is the *xy*-plane. (**b**) The two nodal planes of the d_{xy} orbital are the ones where $x = 0$ and $y = 0$. These are the *yz*- and *xz*-planes. (**c**) The two nodal planes of the $d_{x^2-y^2}$ orbital are the ones that bisect the *x*- and *y*-axes and contain the *z*-axis. **6.110** (**a**) Cl:$[Ne]3s^2\,3p^5$, 1 unpaired electron (**b**) Al:$[Ne]3s^2\,3p^1$, 1 unpaired electron (**c**) Zr:$[Kr]5s^2\,4d^2$, 2 unpaired electrons (**d**) As:$[Ar]4s^2\,3d^{10}\,4p^3$, 3 unpaired electrons (**e**) Sb:$[Kr]5s^2\,4d^{10}\,5p^3$, 3 unpaired electrons (f) W:$[Xe]6s^2\,4f^{14}\,5d^4$, 4 unpaired electrons **6.113** (**a**) 1.7×10^{28} photons (**b**) 34 s **6.117** (**a**) Bohr's theory was based on the Rutherford nuclear model of the atom: a dense positive charge at the center and a diffuse negative charge surrounding it. Bohr's theory then specified the nature of the diffuse negative charge. The prevailing theory before the nuclear model was Thomson's plum pudding model: discrete electrons scattered about a diffuse positive charge cloud. Bohr's theory could not have been based on the Thomson model of the atom. (**b**) De Broglie's hypothesis is that electrons exhibit both particle and wave properties. Thomson's conclusion that electrons have mass is a particle property, while the nature of cathode rays is a wave property. De Broglie's hypothesis actually rationalizes these two seemingly contradictory observations about the properties of electrons.

Chapter 7

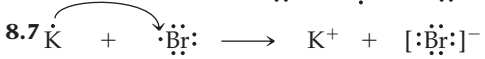
7.3 (**a**) Of the elements listed, only Fe was known before 1700. (**b**) The seven metals known in ancient times, Fe, Cu, Ag, Sn, Au, Hg, and Pb, are mostly near the bottom of the activity series, Table 4.5. **7.5** For elements N, O, P, and S, O and S have the largest effective nuclear charge; N and P have the smallest effective nuclear charge. **7.6** (**a**) For both Na and K, $Z_{eff} = 1$. (**b**) For both Na and K, $Z_{eff} = 2.2$. (**c**) Slater's rules give values closer to the detailed calculations: Na, 2.51; K, 3.49. (**d**) Both approximations give the same value of Z_{eff} for Na and K; neither accounts for the gradual increase in Z_{eff} moving down a group. (**e**) Following the trend from detailed calculations, we predict a Z_{eff} value of approximately 4.5. **7.7** The $n = 2$ electrons in F experience a greater effective nuclear charge and thus have a greater probability of being closer to the nucleus. **7.10** Quantity (**b**) must be measured to determine the bonding atomic radius of an atom. **7.11** (**a**) 137 pm (**b**) The distance between W atoms will decrease. **7.12** From the bonding atomic radii, P—Cl = 107 + 102 pm = 209 pm. It is very close to the experimental values of 204 pm in PCl_3. **7.13** (**a**) As > Kr > Ar (**b**) Rb > Cd > Te (**c**) Cu > Cl > C **7.14** (**a**) False (**b**) true (**c**) false **7.15** H^-: He, Ca^{2+}: Ar, In^{3+}: Pd, Pd ($[Kr]4d^{10}$, irregular), Ge^{2+}: Zn **7.16** (**a**) Na^+ (**b**) F^-, $Z_{eff} = 7$; Na^+, $Z_{eff} = 9$ (**c**) S = 4.15; F^-, $Z_{eff} = 4.85$; Na^+, $Z_{eff} = 6.85$ (**d**) For isoelectronic ions, as nuclear charge (*Z*) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases. **7.18** $Cl(g) \longrightarrow Cl^+(g) + e^-$; $Cl^+(g) \longrightarrow Cl^{2+}(g) + e^-$; $Cl^{2+}(g) \longrightarrow Cl^{3+}(g) + e^-$. The process for the first ionization energy requires the least amount of energy. **7.19** Of these three elements, Li has the highest second ionization energy. Both Li^+ and K^+ have the stable electron configurations of noble gases, but the unshielded 1*s* electron of Li^+ is much closer to the nucleus and requires more energy to remove. **7.20** (**a**) The smaller the atom, the larger its first ionization energy. (**b**) Of the nonradioactive elements, He has the largest and Cs has the smallest first ionization energy. **7.21** (**a**) Br (**b**) Ca (**c**) Rb (**d**) Pb (**e**) Al **7.22** (**a**) Cu^{2+}: [Ar] $3d^9$ (**b**) Ca^{2+}: [Ar], noble gas configuration (**c**) N^{3-}: [Ne], noble gas configuration (**d**) Ru^{2+}: $[Kr]4d^6$ (**e**) H^-: [He], noble gas configuration **7.23** Zn^{2+}, $[Ar]3d^{10}$; Cd^{2+}, $[Kr]4d^{10}$; Hg^{2+}, $[Xe]4f^{14}6d^{10}$ **7.25** Second electron affinity of Cl: $Cl^- + 1e^- \longrightarrow Cl^{2-}(g)$. We predict that the second electron affinity of chlorine will be positive. It is probably not possible to directly measure this quantity, because a positive value indicates that Cl^{2-} ion is unstable and will not form.

7.26 The electron affinity of I will be negative. The electron-electron repulsions created by adding an electron to an I^- ion causes the electron affinity of I^- to be a positive value. **7.27** (**a**) Ionization energy (I_1) of Ne: $Ne(g) \longrightarrow Ne^+(g) + 1\ e^-$; $[He]2s^22p^6 \longrightarrow [He]2s^22p^5$; electron affinity ($E_1$) of F: $F(g) + 1\ e^- \longrightarrow F^-(g)$; $[He]2s^22p^5 \longrightarrow [He]2s^22p^6$. (**b**) I_1 of Ne is positive; E_1 of F is negative. (**c**) One process is apparently the reverse of the other, with one important difference. Ne has a greater Z and Z_{eff}, so we expect I_1 for Ne to be somewhat greater in magnitude and opposite in sign to E_1 for F. **7.29** (**a**) Decrease (**b**) Increase (**c**) The smaller the first ionization energy of an element, the greater the metallic character of that element. The trends in (**a**) and (**b**) are the opposite of the trends in ionization energy. **7.30** Agree. When forming ions, all metals form cations. The only nonmetallic element that forms cations is the metalloid Sb, which is likely to have significant metallic character. **7.31** Ionic: ZnO, K_2O, TiO_2; molecular: SO_2, SiO_2, OF_2. Ionic compounds are formed by combining a metal and a nonmetal; molecular compounds are formed by two or more nonmetals. **7.32** ZrO will react more readily with $HCl(aq)$. **7.33** (**a**) Dichlorine heptoxide (**b**) $2\ Cl_2(g) + 7\ O_2(g) \longrightarrow 2\ Cl_2O_7(l)$ (**c**) Cl_2O_7 is an acidic oxide, so it will be more reactive to base, OH^-. (**d**) The oxidation state of Cl in Cl_2O_7 is +7; the corresponding electron configuration for Cl is $[He]2s^22p^6$ or [Ne]. **7.34** (**a**) $BCl_3(l) + 3\ H_2O(l) \longrightarrow B(OH)_3(aq) + 3\ HCl(aq)$ (**b**) $CoO\ (s) + 2\ HNO_3\ (aq) \longrightarrow Co(NO_3)_2\ (aq) + H_2O(l)$ (**c**) $P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$
(**d**) $CO_2(g) + Ba(OH)_2(aq) \longrightarrow BaCO_3(s) + H_2O(l)$
7.36 (**a**) The first and second ionization energies of calcium are less than those of beryllium. (**b**) The first ionization energy of calcium is higher than that of rubidium. **7.37** (**a**) $2\ K(s) + Cl_2(g) \longrightarrow 2\ KCl(s)$
(**b**) $SrO(s) + H_2O(l) \longrightarrow Sr(OH)_2(aq)$
(**c**) $4\ Li(s) + O_2(g) \longrightarrow 2\ Li_2O(s)$ (**d**) $2\ Na(s) + S(l) \longrightarrow Na_2S(s)$
7.38 (**a**) The reactions of the alkali metals with hydrogen and with a halogen are redox reactions. Both hydrogen and the halogen gain electrons and are reduced. (The alkali metal loses electrons and is oxidized.) $Ca(s) + F_2(g) \longrightarrow CaF_2(s)$; $Ca(s) + H_2(g) \longrightarrow CaH_2(s)$.
(**b**) The oxidation number of Ca in both products is +2. The electron configuration is that of Ar, $[Ne]3s^23p^6$. **7.40** (**a**) Br, $[Ar]4s^24p^5$; Cl, $[Ne]3s^23p^5$ (**b**) Br and Cl are in the same group, and both adopt a 1− ionic charge. (**c**) The ionization energy of Br is smaller than that of Cl, because the 4*p* valence electrons in Br are farther from to the nucleus and less tightly held than the 3*p* electrons of Cl. (**d**) Both react slowly with water to form HX + HOX. (**e**) The electron affinity of Br is less negative than that of Cl, because the electron added to the 4*p* orbital in Br is farther from the nucleus and less tightly held than the electron added to the 3*p* orbital of Cl. (**f**) The atomic radius of Br is larger than that of Cl, because the 4*p* valence electrons in Br are farther from the nucleus and less tightly held than the 3*p* electrons of Cl. **7.41** (**a**) The term *inert* was dropped because it no longer described all the Group 18 elements. (**b**) In the 1960s, scientists discovered that Xe would react with substances having a strong tendency to remove electrons, such as F_2. Thus, Xe could not be categorized as an "inert" gas. (**c**) The group is now called the noble gases. **7.42** (**a**) $P_4(s) + 6\ Cl_2(g) \longrightarrow 4\ PCl_3(l)$ (**b**) $2Na(s) + 2H_2O(l) \longrightarrow H_2(g) + 2\ NaOH(aq)$ (**c**) $2HBr(g) + Cl_2(g) \longrightarrow 2HCl(g) + Br_2$
(**d**) $AlCl_3(s) + 3NaOH(aq) \longrightarrow Al(OH)_3(s) + 3NaCl(aq)$ **7.44** The largest brown sphere is Br^-, the intermediate blue one is Br, and the smallest red one is F. **7.47** (**a**) The bonding atomic radius of A, r_A, is $d_1/2$; $r_x = d_2 - (d_1/2)$. (**b**) The length of the X—X bond is $2r_x$ or $2d_2 - d_1$. **7.50** (**a**) $X + 2F_2 \longrightarrow XF_4$ (**b**) X in the diagram has about the same bonding radius as F, so it is likely to be a nonmetal. If X were a metal, the compound would be ionic and the charge on X would be 4+. The bonding (ionic) radius of X^{4+} would be much smaller than that of fluorine. **7.51** (**a**) The results are 2, 8, 18, 32. (**b**) The atomic numbers of the noble gases are 2, 10, 18, 36, 54, and 86. The differences between sequential pairs of these atomic numbers is 8, 8, 18, 18, and 32. These differences correspond to the results in (**a**). They represent the filling of new subshells when moving across the next row of the periodic chart. (**c**) The Pauli exclusion principle is the source of the "2". **7.63** (**a**) Cl < S < K (**b**) $K^+ < Cl^- < S^{2-}$ (**c**) The neutral K atom has the largest radius because the *n*-value of its outer electron is larger than the *n*-value of valence electrons in S and Cl. The K^+ ion is smallest because, in an isoelectronic series, the ion with the largest Z has the smallest ionic radius. **7.65** (**a**) Cl^- is larger than Ar because the two are isoelectronic and Ar has the larger Z and Z_{eff}. (**b**) P^{3-} is larger than S^{2-} because the two ions are isoelectronic and S^{2-} has the larger Z and Z_{eff}. (**c**) K^+ is larger than Na^+ because for particles with like charges, size increases going down a family. (**d**) F^- is larger than F because the increase in electron repulsions that accompany addition of an electron causes the electron cloud to expand. **7.88** Up to $Z = 82$, there are three instances where atomic weights are reversed relative to atomic numbers: Ar and K; Co and Ni; Te and I. **7.90** (**a**) 5+ (**b**) 4.8+ (**c**) Shielding is greater for 3*p* electrons, owing to penetration by 3*s* electrons, so Z_{eff} for 3*p* electrons is less than that for 3*s* electrons. (**d**) The first electron lost is a 3*p* electron because it has a smaller Z_{eff} and experiences less attraction for the nucleus than a 3*s* electron does. **7.94** (**a**) The P—Cl distance is 194 pm. (**b**) The predicted P—Cl bond length is 209 pm. **7.96** (**a**) Chalcogens, −2; halogens, −1. (**b**) The family with the larger value is: atomic radii, chalcogens; ionic radii of the most common oxidation state, chalcogens; first ionization energy, halogens; second ionization energy, halogens **7.100** *C*: $1s^22s^22p^2$. I_1 through I_4 represent loss of the 2*p* and 2*s* electrons in the outer shell of the atom. The values of I_1–I_4 increase as expected. I_5 and I_6 represent loss of the 1*s* core electrons. These 1*s* electrons are much closer to the nucleus and experience the full nuclear charge, so the values of I_5 and I_6 are significantly greater than I_1–I_4. **7.105** (**a**) Mg^{2+} (**b**) Cu^{2+} (**c**) Pb^{2+}
7.108 (**a**) For both H and the alkali metals, the added electron will complete an *ns* subshell, so shielding and repulsion effects will be similar. For the halogens, the electron is added to an *np* subshell, so the energy change is likely to be quite different. (**b**) True. The electron configuration of H is $1s^1$. The single 1*s* electron experiences no repulsion from other electrons and feels the full unshielded nuclear charge. The outer electrons of all other elements that form compounds are shielded by a spherical inner core of electrons and are less strongly attracted to the nucleus, resulting in larger bonding atomic radii. (**c**) Both H and the halogens have large ionization energies. The relatively large effective nuclear charge experienced by *np* electrons of the halogens is similar to the unshielded nuclear charge experienced by the H 1*s* electron. For the alkali metals, the *ns* electron being removed is effectively shielded by the core electrons, so ionization energies are low. (**d**) ionization energy of hydride, $H^-(g) \longrightarrow H(g) + 1e^-$ (**e**) electron affinity of hydrogen, $H(g) + 1\ e^- \longrightarrow H^-(g)$. The value for the ionization energy of hydride is equal in magnitude but opposite in sign to the electron affinity of hydrogen. **7.111** The most likely product is (**iii**). **7.116** Electron configuration, $[Rn]7s^25f^{14}6d^{10}7p^5$; first ionization energy, 805 kJ/mol; electron affinity, −235 kJ/mol; atomic size, 1.65 Å; common oxidation state, −1. **7.119** (**a**) Li, $[He]2s^1$; $Z_{eff} \approx 1+$ (**b**) $I_1 \approx 5.45 \times 10^{-19}$ J/atom ≈ 328 kJ/mol (**c**) The estimated value of 328 kJ/mol is less than the Table 7.4 value of 520 kJ/mol. Our estimate for Z_{eff} was a lower limit; the [He] core electrons do not perfectly shield the 2*s* electron from the nuclear charge. (**d**) Based on the experimental ionization energy, $Z_{eff} = 1.26$. This value is greater than the estimate from part (**a**) but agrees well with the "Slater" value of 1.3 and is consistent with the explanation in part (c). **7.122** (**a**) Mg_3N_2 (**b**) $Mg_3N_2(s) + 3\ H_2O(l) \longrightarrow 3\ MgO(s) + 2\ NH_3(g)$;

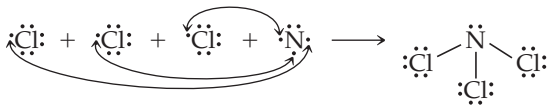
the driving force is the production of $NH_3(g)$. (**c**) 17% Mg_3N_2 (**d**) 3 $Mg(s)$ + 2 $NH_3(g)$ ⟶ $Mg_3N_2(s)$ + 3 $H_2(g)$. NH_3 is the limiting reactant and 0.46 g H_2 is formed. (**e**) $\Delta H^\circ_{rxn} = -368.70$ kJ

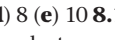
Chapter 8

8.3 (**a**) $1s^2 2s^2 2p^6 3s^2 3p^5$ (**b**) seven (**c**) The 3*s* and 3*p* electrons are valence electrons. **8.4** (**a**)  (**b**)  (**c**)  (**d**) 

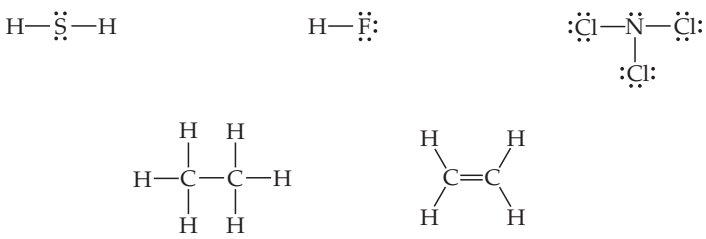
8.7 

(**b**) one (**c**) K loses an electron. **8.8** (**a**) $AlCl_3$ (**b**) MgO (**c**) $ZnCl_2$ (**d**) Li_2O **8.9** (**a**) Be^{2+}: $1s^2$ = [He], noble-gas configuration (**b**) Mn^{2+}: [Ar] $3d^5$ (**c**) Cd^{2+}: [Kr] $4d^{10}$ (**d**) Fe^{3+}: [Ar] $3d^5$ (**e**) Tl^+: [Xe] $4f^{14}5d^{10}6s^2$ (**f**) At^-: [Xe] $4f^{14}5d^{10}6s^2 6p^6$ = [Rn], noble-gas configuration **8.10** (**a**) Endothermic (**b**) $NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ (**c**) Salts like NaCl, that have singly charged ions, will have smaller lattice energies compared with salts like CaO, that have doubly charged ions. **8.11** (**a**) Na^+, 1+; Ca^{2+}, 2+ (**b**) F^-, 1−; O^{2-}, 2− (**c**) CaO will have the larger lattice energy. (**d**) We expect the lattice energy of ScN to be slightly less than 8.10×10^3 kJ **8.12** (**a**) K—F, 271 pm; Na—Cl, 283 pm; Na—Br, 298 pm; Li—Cl, 257 pm (**b**) LiCl > KF > NaCl > NaBr (**c**) From Table 8.2: LiCl, 1030 kJ; KF, 808 kJ; NaCl, 788 kJ; NaBr, 732 kJ. The predictions from ionic radii are correct. **8.13** Statement (**a**) is the best explanation. **8.15**



(**a**) 5 (**b**) 1 (**c**) 8 (**d**) 8 (**e**) 10 **8.16** (**a**)  (**b**) four bonding electrons (two bonding electron pairs) (**c**) An O═O double bond is shorter than an O—O single bond. The greater the number of shared electron pairs between two atoms, the shorter the distance between the atoms.

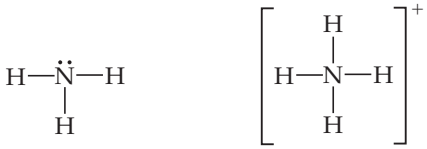
8.17



8.18

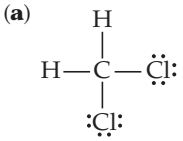
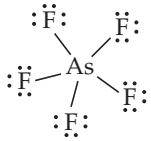


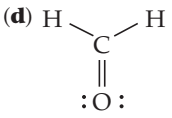
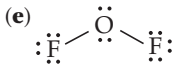
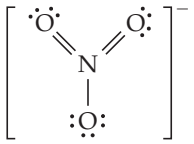
8.19



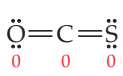
8.21 Statement (**b**) is false. **8.22** (**a**) Mg (**b**) S (**c**) C (**d**) As **8.23** The bonds in (**a**), (**b**) and (**d**) are polar. The more electronegative atom in each polar bond is: (**a**) O, (**b**) F (**d**) Cl. **8.24** (**a**) The calculated charge on H and Br is 0.12*e*. (**b**) Decrease **8.25** (**a**) SiF_4, molecular, silicon tetrachloride; LaF_3, ionic, lanthanum(III) fluoride (**b**) $FeCl_2$, ionic, iron(II) chloride; $ReCl_6$, molecular (metal in high oxidation state), rhenium hexachloride. (**c**) $PbCl_4$, molecular (by contrast to the distinctly ionic RbCl), lead tetrachloride; RbCl, ionic, rubidium chloride

8.27

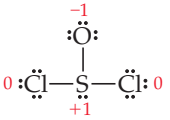
(**a**)  (**b**)  (**c**) 

(**d**)  (**e**)  (**f**) 

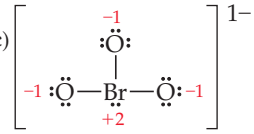
8.28 Statement (**b**) is most true. Keep in mind that when it is necessary to place more than an octet of electrons around an atom in order to minimize formal charge, there may not be a "best" Lewis structure. **8.29** Formal charges are shown on the Lewis structures; oxidation numbers are listed below each structure.

(**a**) 

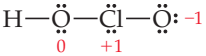
O, −2; C, +4; S, −2

(**b**) 

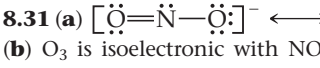
S, +4; Cl, −1; O, −2

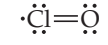
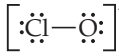
(**c**) 

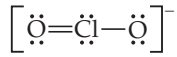
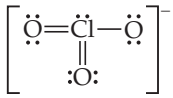
Br, +5; O, −2

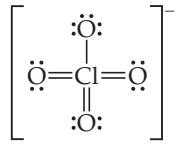
(**d**) 

Cl, +3; H, +1; O, −2

8.31 (**a**)  (**b**) O_3 is isoelectronic with NO_2^-; both have 18 valence electrons. (**c**) Since each N—O bond has partial double-bond character, the N—O bond length in NO_2^- should be shorter than an N—O single bond but longer than an N═O double bond. **8.34** Assume that the dominant structure is the one that minimizes formal charge. Following this guideline, only ClO^- obeys the octet rule. ClO, ClO_2^-, ClO_3^-, and ClO_4^- do not obey the octet rule.

ClO,  ClO^-, 

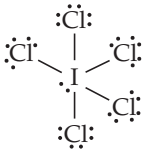
ClO_2^-,  ClO_3^-, 

ClO_4^-, 

8.35

(**a**) 

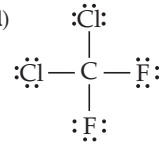
Does not obey the octet rule. H has 2 electrons.

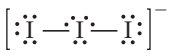
(**b**) 

Does not obey the octet rule. Central I has 12 electrons.

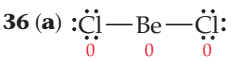
(**c**) 

Does not obey the octet rule. N has only 7 electrons.

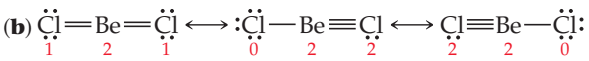
(d) 

(e) 

Does not obey the octet rule. Central I has 10 electrons.

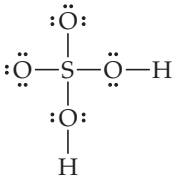
8. 36 (a) 

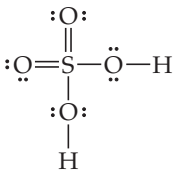
This structure violates the octet rule.

(b) 

(c) Formal charges are minimized on the structure that violates the octet rule; this form is probably dominant.

8.37 32 e^-, 16 e^- pr

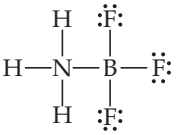
(a) 

(b) 

8.39 **(a)** $\Delta H = -304$ kJ **(b)** $\Delta H = -82$ kJ **(c)** $\Delta H = -467$ kJ **8.40** **(a)** False **(b)** false **(c)** false **(d)** false **(e)** false **8.41** The Ca—O bond will be stronger than the Na—Cl bond, because the ion charges are greater. **8.43** **(a)** Group 14 **(b)** Group 2 **(c)** Group 15 **8.46** **(a)** Ru **(b)** $[Kr]5s^24d^6$. **8.49** **(a)** Four **(b)** In order of increasing bond length: 3 < 1 < 2 **(c)** Bond 3 is the strongest C—C bond in the hydrocarbon molecule. For the same pair of bonded atoms, the greater the number of shared pairs of electrons, the shorter and stronger the bond. **8.61** The lattice energy of RbCl(*s*) is +692 kJ / mol. **8.74** The more electron pairs shared by the atoms, the shorter the bond. Thus, the bond length of O_2 is shorter than that of H_2O_2. **8.75** **(a)** AsF_5 is an exception to the octet rule. **(b)** BCl_3 is an exception to the octet rule. **8.83** **(a)** CH_2, 6 e^-, 3 e^- pr H—C—H 2 CH_2, → C_2H_4. **(b)** The product of this reaction, C_2H_4, contains a C—C double bond, with a typical bond length of 134 pm. **8.84** A double C—O bond **8.92** **(a)** B—O. The most polar bond will be formed by the two elements with the greatest difference in electronegativity. **(b)** As—I. These elements have the two largest covalent radii among this group of elements. **(c)** BCI_3. B has three valence electron and participates in three covalent bonds. The Octet rule is satisfied by all three chlorine atoms. **(d)** O. O has 6 valence electrons and it needs to participate in two covalent bonds in order to satisfy the octet rule. **8.97** **(a)** +1 **(b)** −1 **(c)** +1 (assuming the odd electron is on N) **(d)** 0 **(e)** +3 **8.100** **(a)** False. One possible example is ozone O_3. **(b)** False. O_3 does not have an odd electron. **8.103** **(a)** Ti^{2+}, $[Ar]3d^2$; Ca, $[Ar]4s^2$. **(b)** Ca has no unpaired electrons and Ti^{2+} has two. **(c)** In order to be isoelectronic with Ca^{2+}, Ti would have a 4+ charge. **8.109** **(a)** Potassium peroxide is K_2O_2. **(b)** 14 e^-, 7 e^- pairs **(c)**  **(d)** Based on the Lewis structure, it is a single bond in the peroxide ion, whereas a double bond for the oxygen molecule. Therefore, the O—O in peroxide ion is longer than that of the oxygen molecule.

8.114

(a) NH_3BF_3, 32 e^-, 16 e^- pr **(b)** $\overset{\delta+}{B}—\overset{\delta-}{N}$

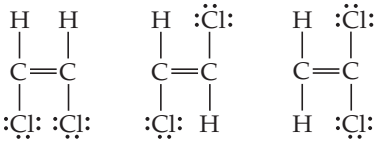


(c) Chlorine is less electronegative and less electron withdrawing than fluorine. The B—N bond in NH_3BCl_3 is less polar than the B—N bond in NH_3BF_3.

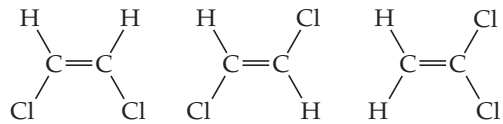
Chapter 9

9.2 **(a)** 1 **(b)** 2 **(c)** 9 **(d)** 5 **9.3** **(a)** i, trigonal planar; ii, tetrahedral; iii, trigonal bipyramidal **(b)** i, 0; ii, 1; iii, 2 **(c)** N and P **(d)** Cl (or Br or I). This T-shaped molecular geometry arises from a trigonal-bipyramidal electron-domain geometry with 2 nonbonding domains. Assuming each F atom has 3 nonbonding domains and forms only single bonds with A, A must have 7 valence electrons and be in or below the third row of the periodic table to produce these electron-domain and molecular geometries. **9.4** **(a)** 1, less than 109.5°; 2, close to 120°; 3, less than 109.5° **(b)** 4, close to 120° **(c)** 5, close to 120°; 6, close to 180° **(d)** 7, less than 109.5°; 8, close to 120° **9.6** **(a)** In a linear AB_2 molecule, there can be either 0 or 3 nonbonding electron pairs. **(b)** three **(c)** yes **9.7** **(a)** Octahedral **(b)** octahedral **(c)** square planar **9.8** **(a)** No effect **(b)** no effect **(c)** 2 nonbonding pairs on the central O influence the molecular shape. **(d)** no effect **(e)** no effect **9.9** **(a)** Tetrahedral, tetrahedral **(b)** trigonal bipyramidal, T-shaped **(c)** octahedral, square pyramidal **(d)** octahedral, square planar **9.10** **(a)** Linear, linear **(b)** trigonal bipyramidal, trigonal bipyramidal **(c)** trigonal planar, bent **(d)** linear, linear **(e)** trigonal bipyridimal, seesaw **(f)** octahedral, square pyridimal **9.11** **(a)** NH_4^+ has zero nonbonding electron pairs on N and the largest bond angles. **(b)** NH_2^- has two nonbonding electron pairs on N and the smallest bond angles. **9.12** **(a)** Although both ions have 4 bonding electron domains, the 6 total domains around Br require octahedral domain geometry and square-planar molecular geometry, while the 4 total domains about B lead to tetrahedral domain and molecular geometry. **(b)** The angles will vary as $H_2O > H_2S > H_2Se$. The less electronegative the central atom, the larger the nonbonding electron domain, and the greater the effect of repulsive forces on adjacent bonding domains. The less electronegative the central atom, the greater the deviation from ideal tetrahedral angles. **9.15** **(a)** No. CS_2 does not have a dipole moment. **(b)** Yes. The net dipole moment vector points along the O—S—O angle bisector. **9.16** **(a)** Nonpolar. The polar B—F bonds are arranged in a symmetrical trigonal planar geometry. **(b)** No. The added nonbonding electron pair requires that the electron domain geometry is tetrahedral and the shape is a trigonal pyramid. **(c)** Yes. In BF_2Cl, the bond dipoles do not cancel. **9.17** **(a)** IF **(d)** PCl_3 and **(f)** IF_5 are polar.

9.18 **(a)** Lewis structures



Molecular geometries



Polar Nonpolar Polar

(b) The middle isomer has a zero net dipole moment. **(c)** C_2H_3Cl has only one isomer, and it has a dipole moment. **9.22** **(a)** False **(b)** true **(c)** false **(d)** false **9.23** **(a)** B, $[He]2s^22p^1$ **(b)** F, $[He]2s^22p^5$ **(c)** sp^2 **(d)** A single 2*p* orbital is unhybridized. It lies perpendicular to the trigonal plane of the sp^2 hybrid orbitals. **9.24** **(a)** sp^3 **(b)** sp^3d^2 **(c)** sp^3 **(d)** sp^2 **9.25** Left, no hybrid orbitals discussed in this chapter form angles

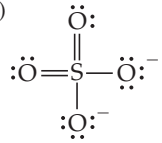
of 90° with each other; *p* atomic orbitals are perpendicular to each other; center, 109.5°, sp^3; right, 120°, sp^2

9.28 (**a**) 

(**b**) 

(**c**) A σ bond is generally stronger than a π bond because there is more extensive orbital overlap. (**d**) No. Overlap of two *s* orbitals results in electron density along the internuclear axis, while a π bond has none. **9.29** (**a**) 18 valence electrons (**b**) 10 valence electrons make σ bonds. (**c**) 2 valence electrons make π bonds. (**d**) 6 valence electrons are nonbonding. (**e**) Both carbon atoms in the molecule are sp^2 hybridized. **9.31** (**a**) In a localized π bond, the electron density is concentrated between the two atoms forming the bond. In a delocalized π bond, the electron density is spread over all the atoms that contribute *p* orbitals to the network. (**b**) The existence of more than one resonance form is a good indication that a molecule will have delocalized π bonding. (**c**) delocalized

9.32

(**a**) 

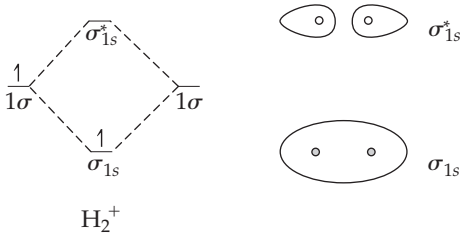
(**b**) sp^3

(**c**) Yes, there are five equivalent resonance structures of the type shown in (a).

(**d**) There are four electrons in the π system of the molecule.

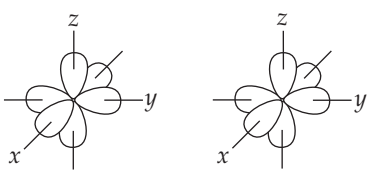
9.33 (**a**) Linear (**b**) The two central C atoms each have trigonal planar geometry with ~120° bond angles about them. The C and O atoms lie in a plane with the H atoms free to rotate in and out of this plane. (**c**) The molecule is planar with ~120° bond angles about the two N atoms. **9.35** (**a**) Hybrid orbitals are mixtures of atomic orbitals from a single atom and remain localized on that atom. Molecular orbitals are combinations of atomic orbitals from two or more atoms and are delocalized over at least two atoms. (**b**) Each MO can hold a maximum of two electrons. (**c**) Antibonding molecular orbitals can have electrons in them.

9.36

(**a**) 

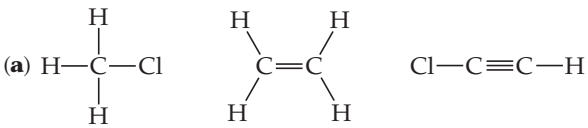
(**b**) There is one electron in H_2^+. (**c**) $\sigma_{1s}{}^1$ (**d**) BO $= \frac{1}{2}$ (**e**) Fall apart. If the single electron in H_2^+ is excited to the σ^*_{1s} orbital, its energy is higher than the energy of an H 1*s* atomic orbital and H_2^+ will decompose into a hydrogen atom and a hydrogen ion. (**f**) Statement (**i**) is correct.

9.38



(**a**) 1 σ bond (**b**) 2 π bonds (**c**) 1 σ^* and 2 π^* **9.39** (**a**) When comparing the same two bonded atoms, as bond order increases, bond energy increases. As bond order increases, bond length decreases. When comparing different bonded nuclei, there are no simple relationships. (**b**) Be_2 is not expected to exist; it has a bond order of zero and is not energetically favored over isolated Be atoms. Be_2^+ has a bond order of 0.5 and is slightly lower in energy than isolated Be atoms. It will probably exist under special experimental conditions. **9.40** (**a**) Diamagnetic (**b**) F_2, O_2^{2+} **9.41** (**a**) B_2^+, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\pi_{2p}{}^1$, increase (**b**) Li_2^+, $\sigma_{1s}{}^2\sigma^*_{1s}{}^2\sigma_{2s}{}^1$, increase (**c**) N_2^+, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\pi_{2p}{}^4\sigma_{2p}{}^1$, increase (**d**) Ne_2^{2+}, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\sigma_{2p}{}^2\pi_{2p}{}^4\pi^*_{2p}{}^4$, decrease **9.42** CN, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\sigma_{2p}{}^2\pi_{2p}{}^3$, bond order $= 2.5$; CN^+, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\sigma_{2p}{}^2\pi_{2p}{}^2$, bond order $= 2.0$; CN^-, $\sigma_{2s}{}^2\sigma^*_{2s}{}^2\sigma_{2p}{}^2\pi_{2p}{}^4$, bond order $= 3.0$. (**a**) CN^- (**b**) CN, CN^+ **9.43** (**a**) 3*s*, $3p_x$, $3p_y$, $3p_z$ (**b**) π_{3p} (**c**) 2 (**d**) If the MO diagram for P_2 is similar to that of N_2, P_2 will have no unpaired electrons and be diamagnetic. **9.44** Removing an atom from the equatorial plane of the trigonal bipyramid in Figure 9.3 creates a seesaw shape. **9.46** (**a**) Two electron-domain geometries, linear and trigonal bipyramidal (**b**) one electron-domain geometry, trigonal bipyramidal (**c**) one electron-domain geometry, octahedral (**d**) one electron domain geometry, octahedral (**e**) one electron domain geometry, octahedral (**f**) one electron-domain geometry, trigonal bipyramidal (This triangular pyramid is an unusual molecular geometry not listed in Table 9.3. It could occur if the equatorial substituents on the trigonal bipyramid were extremely bulky, causing the nonbonding electron pair to occupy an axial position.) **9.48** (**a**) Zero. Moving from left to right along the x-axis of the plot, the distance between the Cl atoms increases. At very large separation, the potential energy of interaction approaches zero. (**b**) The Cl—Cl bond distance is approximately 200 pm. The Cl—Cl bond energy is approximately 240 kJ/mol. (**c**) Weaker. Under extreme pressure, the Cl—Cl bond gets shorter. The potential energy of the atom pair increases and the bond gets weaker. **9.54** (**a**) i, Two *s* atomic orbitals; ii, two *p* atomic orbitals overlapping end to end; iii, two *p* atomic orbitals overlapping side to side (**b**) i, σ-type MO; ii, σ-type MO; iii, π-type MO (**c**) i, antibonding; ii, bonding; iii, antibonding (**d**) i, the nodal plane is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. ii, there are two nodal planes; both are perpendicular to the interatomic axis. One is left of the left atom and the second is right of the right atom. iii, there are two nodal planes; one is between the atom centers, perpendicular to the interatomic axis and equidistant from each atom. The second contains the interatomic axis and is perpendicular to the first. **9.57** A molecule with tetrahedral molecular geometry has an atom at each vertex of the tetrahedron. A trigonal-pyramidal molecule has one vertex of the tetrahedron occupied by a nonbonding electron pair rather than an atom. **9.68** A bond dipole is the asymmetric charge distribution between two bonded atoms with unequal electronegativities. A molecular dipole moment is the three-dimensional sum of all the bond dipoles in a molecule. **9.73** (**a**) True (**b**) false (**c**) true (**d**) false (**e**) true

9.79

(**a**) 

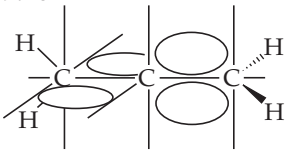
(**b**) sp^3, sp^2, *sp* (**c**) nonplanar, planar, planar (**d**) 4 σ,0 π; 5 σ, 1 π; 3 σ, 2 π **9.82** (**a**) ~109° bond angles about the leftmost C, sp^3; ~120° bond angles about the right-hand C, sp^2. (**b**) The doubly bonded O can be viewed as sp^2, the other as sp^3; the bond angle of the sp^3 O is somewhat less than 109.5°. (**c**) Seven σ bonds, one π bond. **9.96** (**a**) PF_4^-, BrF_4^- and ClF_4^- (**b**) AlF_4^- (**c**) BrF_4^- (**d**) PF_4^- and ClF_4^+

9.99

Molecule	Electron-Domain Geometry	Hybridization of Central Atom	Dipole Moment? Yes or No
CO_2	Linear	sp	No
NH_3	Tetrahedral	sp^3	Yes
CH_4	Tetrahedral	sp^3	No
BH_3	Trigonal planar	sp^2	No
SF_4	Trigonal bipyramidal	Not applicable	Yes
SF_6	Octahedral	Not applicable	No
H_2CO	Trigonal planar	sp^2	Yes
PF_5	Trigonal bipyramidal	Not applicable	No
XeF_2	Trigonal bipyramidal	Not applicable	No

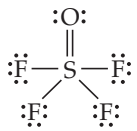
9.100 (**a**) 5 σ bonds (**b**) 2 σ bonds 2 π bonds (**c**) 3 σ bonds 3 π bonds (**d**) 2 σ bonds 1 π bond

9.107

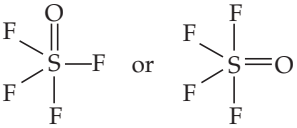


(**a**) The molecule is nonplanar. (**b**) Allene has no dipole moment. (**c**) The bonding in allene would not be described as delocalized. The π electron clouds of the two adjacent C=C are mutually perpendicular, so there is no overlap and no delocalization of π electrons. **9.110** (**a**) All O atoms have sp^2 hybridization. (**b**) The two σ bonds are formed by overlap of sp^2 hybrid orbitals, the π bond is formed by overlap of atomic p orbitals, one nonbonded pair is in a p atomic orbital and the other five nonbonded pairs are in sp^2 hybrid orbitals. (**c**) unhybridized p atomic orbitals (**d**) four, two from the π bond and two from the nonbonded pair in the p atomic orbital **9.113** (**a**) Ground state, $\sigma_{2s}^2\sigma^*_{2s}^2\pi_{2p}^4\sigma_{2p}^2$; excited state, $\sigma_{2s}^2\sigma^*_{2s}^2\pi_{2p}^4\sigma_{2s}^1\pi^*_{2p}^1$ (**b**) paramagnetic (**c**) σ_{2p} to π^*_{2p} (**d**) 7.0×10^2 kJ/mol (**e**) The bond order of the N—N bond in the first excited state is smaller and the bond is weaker than in the ground state. The silicon analogs would have the same hybridization as the C compounds. Silicon, which is in the row below C, has a larger bonding atomic radius and atomic orbitals than C. The close approach of Si atoms required to form strong, stable π bonds in Si_2H_4 and Si_2H_2 is not possible and these Si analogs do not readily form. **9.117** The yellow curcumin has the larger HOMO-LUMO gap because it absorbs visible violet light and appears yellow. **9.123** (**a**) $2\ SF_4(g) + O_2(g) \longrightarrow 2\ OSF_4(g)$

(**b**)



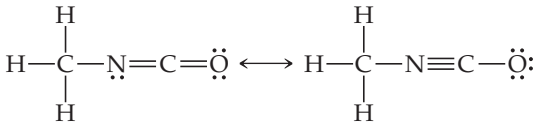
(**c**) $\Delta H = -551$ kJ, exothermic (**d**) The electron-domain geometry is trigonal bipyramidal. The O atom can be either equatorial or axial.



(**e**) In the structure on the left, there are 3 equatorial and 1 axial fluorine atoms. In the structure on the right, there are 2 equatorial and 2 axial fluorine atoms. **9.126** (**a**) 8462 kJ/mol (**b**) 8778 kJ/mol (**c**) Because the π electrons are delocalized, the molecule has a lower overall energy than that predicted for the presence of localized C—C and C=C bonds.

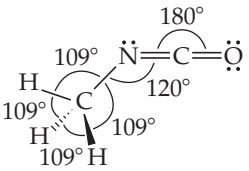
9.130

(**a**)



(The structure on the right does not minimize formal charges and will make a minor contribution to the true structure.)

(**b**)



Both resonance structures predict the same bond angles. (**c**) The two extreme Lewis structures predict different bond lengths. These bond length estimates assume that the structure minimizing formal charge makes a larger contribution to the true structure. C—O, 1.28 Å; C=N, 1.33 Å; C—N, 1.43 Å; C—H, 1.07 Å (**d**) The molecule will have a dipole moment. The C=N and C=O bond dipoles are opposite each other, but they are not equal. And, there are nonbonding electron pairs that are not directly opposite each other and will not cancel.

Chapter 10

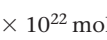
10.2 Statement (**c**) is false. Gaseous molecules are so far apart that there is no barrier to mixing, regardless of the identity of the molecules. **10.10** The action in (**c**) would double the pressure **10.27** $X_{CO_2} = 0.000407$ **10.29** $P_{CO_2} = 91.0$ kPa **10.33** The root-mean-square speed of Rn is approximately 7.5 times slower than that of He. **10.36** Statements (**a**) and (**d**) are true. **10.40** (**a**) Non-ideal-gas behavior is observed at very high pressures and low temperatures. (**b**) The real volumes of gas molecules and attractive intermolecular forces between molecules cause gases to behave nonideally. **10.44** It would be much easier to drink from a straw on Mars. When a straw is placed in a glass of liquid, the atmosphere exerts equal pressure inside and outside the straw. When we drink through a straw, we withdraw air, thereby reducing the pressure on the liquid inside. If only 709 Pa is exerted on the liquid in the glass, a very small reduction in pressure inside the straw will cause the liquid to rise. **10.46** At the same temperature, volume and the lower pressure, the container would have half as many particles as at the higher pressure. **10.48** For a fixed amount of ideal gas at constant volume, if the pressure is doubled, the temperature also doubles. **10.50** (**a**) $P_{red} < P_{yellow} < P_{blue}$ (**b**) $P_{red} = 28.4$ kPa; $P_{yellow} = 42.6$ kPa; $P_{blue} = 71.0$ kPa **10.52** (**a**) Curve B is helium. (**b**) Curve B corresponds to the higher temperature. (**c**) The root mean square speed is highest. **10.54** The $NH_4Cl(s)$ ring will form at location a. **10.57** (**a**) 14.72 bar (**b**) 14.52 atm (**c**) 213.5 lb/in^2 **10.58** (**a**) 1.72 m (**b**) 1.96 atm **10.59** (**a**) 1.084 atm (**b**) 823.7 mm Hg (**c**) 1.098×10^5 Pa (**d**) 1.098 bar (**e**) 15.93 psi **10.60** (**i**) 0.31 atm (ii) 1.88 atm (iii) 0.136 atm **10.62** (**a**) Boyle's Law, $PV =$ constant or $P_1V_1 = P_2V_2$, at constant V, $P_1/P_2 = 1$; Charles' Law, $V/T =$ constant or $V_1/T_1 = V_2/T_2$, at constant V, $T_1/T_2 = 1$; then $P_1/T_1 = P_2/T_2$ or $P/T =$ constant. Amonton's law is that pressure and Kelvin temperature are directly proportional at constant volume. (**b**) 239.2 kPa **10.63** (**a**) STP stands for standard temperature, 0 °C (or 273 K), and standard pressure, 101.3 kPa. (**b**) 22.4 L (**c**) 24.5 L (**d**) 0.08315 L-bar/mol-K **10.65** Flask A contains the gas with a molar mass of 28 g/mol and flask B contains the gas with a molar mass of 56 g/mol.

10.66

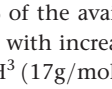
P	*V*	*n*	*T*
303.98 kPa	3.00 L	1.500 mol	73.1 K
50.663 kPa	0.750 L	1.52×10^{-2} mol	300 K
101.33 kPa	83.1 L	0.333 mol	300 K
2.478×10^{6} kPa	0.750 L	0.750 mol	298 K

10.67 (**a**) 5.15×10^{22} molecules (**b**) 6.5 kg air **10.69** (**a**) 16.72 MPa (**b**) 1.91×10^{3} L **10.71** 567.4 kPa **10.73** (**a**) 29.8 g Cl_2 (**b**) 9.42 L (**c**) 501 K (**d**) 231.3 kPa **10.74** (**a**) 1×10^{-2} mol O_2 (**b**) The roach needs 72% of the available O_2 in the jar. **10.75** The density of a gas increases with increasing molar mass. The order of increasing density is: NH^3 (17g/mol) < O_2(32g/mol) < HCl (36.5g/mol) Ar (40g/mol) **10.76** (**c**) Because the helium atoms are of lower mass than the average air molecule, the helium gas is less dense than air. The balloon thus weighs less than the air displaced by its volume. **10.78** molar mass = 89.4 g/mol **10.80** (**a**) 8.47 L CO_2 (**b**) 12.4 L O_2 **10.81** 0.0786 g Zn **10.83** 5.1×10^{-7} g Mg **10.84** (**a**) When the stopcock is opened, the volume occupied by $N_2(g)$ increases from 2.0 L to 5.0 L. $P_{N_2} = 40.53$ kPa (**b**) When the gases mix, the volume of $O_2(g)$ increases from 3.0 L to 5.0 L. $P_{O_2} = 121.6$ kPa (**c**) $P_t = 162.1$ kPa **10.85** (**a**) $P_t = 495.5$ kPa (**b**) $P_{H_2} = 49.6$ kPa, $P_{O_2} = 99.3$ kPa, $P_{N_2} = 346.5$ kPa **10.87** $P_{CO_2} = 45.04$ kPa, $P_t = 95.70$ kPa **10.89** $P_t = 250.27$ *kPa* **10.91** (**a**) Decrease (**b**) increase (**c**) decrease **10.93** (**a**) Average kinetic energy of the molecules increases. (**b**) Root mean square speed of the molecules increases. (**c**) Strength of an average impact with the container walls increases. (**d**) Total collisions of molecules with walls per second increases. **10.95** (**a**) In order of increasing speed and decreasing molar mass: Ar < HCl, < O_2 < CO < CH_4 (**b**) $u_{rms} = 515$ m/s (**c**) The most probable speed of an argon atom in the stratosphere is 337 m/s. **10.97** The order of increasing rate of effusion is $^2H^{37}Cl < {}^1H^{37}Cl < {}^2H^{35}Cl < {}^1H^{35}Cl$. **10.98** As_4S_6 **10.100** Statement (**b**) is true. **10.101** (**a**) $P = 495.48$ kPa (**b**) $P = 475.21$ kPa (**c**) Qualitatively, molecular attractions are more important as the amount of free space decreases and the number of molecular collisions increases. Molecular volume is a larger part of the total volume as the container volume decreases. **10.102** From the value of *b* for Xe, the nonbonding radius is 272 pm. From Figure 7.7, the bonding atomic radius of Xe is 140 pm. We expect the bonding radius of an atom to be smaller than its nonbonding radius, but our calculated value is nearly twice as large. **10.104** $V_f = 2.2$ mm^3 **10.106** $P = 74.7$ Pa **10.108** (**a**) 5.73 mol $C_3H_8(g)$ (**b**) 2.68×10^{2} mol $C_3H_8(l)$ (**c**) The ratio of moles liquid to moles gas is 47. Many more molecules and moles of liquid fit in a container of fixed volume because there is much less space between molecules in the liquid phase. **10.110** (**a**) Molar mass of the unknown gas is 100.4 g/mol (**b**) We assume that the gases behave ideally, and that *P, V* and *T* are constant. **10.112** (**a**) 0.00378 mol O_2 (**b**) 0.0345 g C_8H_{18} **10.114** 0.552 g H_2 **10.116** (**a**) Molar mass of the unknown gas is 50.46 g/mol (**b**) The ratio d/P varies with pressure because of the finite volumes of gas molecules and attractive intermolecular forces. **10.118** $T_2 = 687$ °C **10.120** (**a**) More significant (**b**) less significant **10.122** (**a**) At STP, argon atoms occupy 0.0359% of the total volume. (**b**) At 20.27 MPa pressure and 0 °C, argon atoms occupy 7.19% of the total volume. **10.124** (**a**) The molecular formula of cyclopropane is C_3H_6. (**b**) Although the molar masses of Ar and C_3H_6 are similar, we expect intermolecular attractions to be more significant for the more complex C_3H_6 molecules, and that C_3H_6 will deviate more from ideal behavior at the conditions listed. If the pressure is high enough for the volume correction in the van der Waals equation to dominate behavior, the larger C_3H_6 molecules definitely deviate more than Ar atoms from ideal behavior. (**c**) Cyclopropane would effuse through a pinhole slower than methane, because it has the greater molar mass. **10.126** (**a**) 44.58% C, 6.596% H, 16.44% Cl, 32.38% N (**b**) $C_8H_{14}N_5Cl$ (**c**) Molar mass of the compound is required in order to determine molecular formula when the empirical formula is known. **10.128** (**a**) $NH_3(g)$ remains after reaction. (**b**) 96.97 kPa (**c**) 7.33 g NH_4Cl

10.130

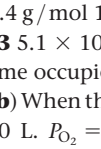
(**a**) 

(**b**) ClO_2 is very reactive because it is an odd-electron molecule. Adding an electron pairs the odd electron and completes the octet of Cl. ClO_2 has a strong tendency to gain an electron and be reduced.

(**c**) 

(**d**) The bond angle is less than 109°. (**e**) 11.2 g ClO_2

10.132 (**a**) $P_{IF_3} = 52.18$ kPa (**b**) $X_{IF_5} = 0.544$

(**c**) 

(**d**) Total mass in the flask is 20.00 g; mass is conserved.

Chapter 11

11.4 (**a**) The molar volumes of Cl_2 and NH_3 are nearly the same because they are both gases. (**b**) On cooling to 160 K, both compounds condense from the gas phase to the solid-state, so we expect a significant decrease in the molar volume. (**c**) The molar volumes are 0.0351 L/mol Cl_2 and 0.0203 L/mol NH_3 (**d**) Solid-state molar volumes are not as similar as those in the gaseous state, because most of the empty space is gone and molecular characteristics determine properties. $Cl_2(s)$ is heavier, has a longer bond distance and weaker intermolecular forces, so it has a significantly larger molar volume than $NH_3(s)$. (**e**) There is little empty space between molecules in the liquid state, so we expect their molar volumes to be closer to those in the solid state than those in the gaseous state. **11.10** (**a**) A molecule must contain H atoms, bound to either N, O, or F atoms, in order to participate in hydrogen bonding with like molecules. (**b**) CH_3NH_2 and CH_3OH **11.22** (**a**) 14.3 kJ (**b**) 25.1 kJ **11.23** (**a**) False (**b**) true (**c**) false (**d**) true **11.30** (**a**) The critical point is the temperature and pressure beyond which the gas and liquid phases are indistinguishable. (**b**) The line that separates the gas and liquid phases ends at the critical point because at conditions beyond the critical temperature and pressure, there is no distinction between gas and liquid. In experimental terms a gas cannot be liquefied at temperatures higher than the critical temperature, regardless of pressure. At conditions beyond the critical point, a substance is known as a supercritical fluid. **11.32** (**a**) 24 K (**b**) Neon sublimes at pressures less than the triple point pressure, approximately 50.7 kPa. (**c**) No **11.35** In a nematic liquid crystalline phase, molecules are aligned along their long axes, but the molecular ends are not aligned. Molecules are free to translate in all dimensions, but they cannot tumble or rotate out of the molecular plane, or the order of the nematic phase is lost and the sample becomes an ordinary liquid. In an ordinary liquid, molecules are randomly oriented and free to move in any direction. No **11.39** (**a**) The diagram best describes a liquid. (**b**) In the diagram, particles are close together, mostly touching, but there is no regular arrangement or order. This rules out a gaseous sample, where the particles are far apart, and a crystalline solid, which has a regular repeating structure in all three directions. **11.42** In its final state, methane is a gas at 185 °C. **11.44**

(**a**) Propanol can engage in hydrogen bonding. (**b**) While both molecules are somewhat polar, we expect propanol to have a larger dipole moment because of its O–H bond. (**c**) Propanol boils at 97.2 °C, while ethyl methyl ether boils at 10.8 °C. The stronger intermolecular forces in propanol cause it to have the higher boiling point. **11.47** (**a**) Solid < liquid < gas (**b**) gas < liquid < solid (**c**) Matter in the gaseous state is most easily compressed because particles are far apart and there is much empty space. **11.48** (**a**) It increases. Kinetic energy is the energy of motion. As melting occurs, the motion of atoms relative to each other increases. (**b**) It increases somewhat. The density of liquid lead is less than the density of solid lead. The smaller density means a greater sample volume and greater average distance between atoms in three dimensions. **11.50** (**a**) London dispersion forces (**b**) dipole–dipole forces (**c**) hydrogen bonding **11.51** (**a**) SO_2, London dispersion forces (**b**) NH_3, London dispersion, dipole–dipole, and hydrogen-bonding (N—H bonds) forces (**c**) BCl_3, non-polar covalent molecule **11.52** (**a**) In order of increasing polarizability: $CH_4 < SiH_4 < SiCl_4 < GeCl_4 < GeBr_4$ (**b**) The magnitudes of London dispersion forces and thus the boiling points of molecules increase as polarizability increases. The order of increasing boiling points is the order of increasing polarizability given in (a). **11.53** (**a**) CH_3CH_2OH (**b**) $N(CH_3)_3$ (**c**) CH_2Br_2 **11.54** Both rodlike butane molecules and spherical 2-methylpropane molecules experience dispersion forces. The larger contact surface between butane molecules facilitates stronger forces and produces a higher boiling point. **11.57** (**a**) Replacing a hydroxyl hydrogen with a CH_3 group eliminates hydrogen bonding in that part of the molecule. This reduces the strength of intermolecular forces and leads to a lower boiling point. (**b**) $CH_3OCH_2CH_2OCH_3$ is a larger, more polarizable molecule with stronger London dispersion forces and thus a higher boiling point.

11.58

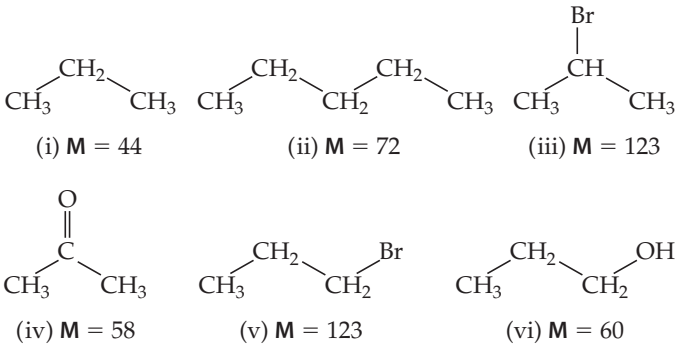
Physical Property	H_2O	H_2S
Normal boiling point, °C	100.00	−60.7
Normal melting point, °C	0.00	−85.5

(**a**) Based on its much higher normal melting point and boiling point, H_2O has much stronger intermolecular forces. (**b**) H_2O has hydrogen bonding, while H_2S has dipole–dipole forces. Both molecules have London dispersion forces. **11.59** SO_4^{2-} has a greater negative charge than BF_4^-, so ion–ion electrostatic attractions are greater in sulfate salts and they are less likely to form liquids. **11.60** (**a**) As temperature increases, surface tension decreases; they are inversely related. (**b**) As temperature increases, viscosity decreases; they are inversely related. (**c**) The same attractive forces that cause surface molecules to be difficult to separate (high surface tension) cause molecules elsewhere in the sample to resist movement relative to each other (high viscosity). **11.61** (**a**) Diagram (ii) shows stronger adhesive forces between the surface and the liquid. (**b**) Diagram (**i**) represents water on a nonpolar surface. (**c**) Diagram (ii) represents water on a polar surface. **11.62** (**a**) The three molecules have similar structures and experience the same types of intermolecular forces. As molar mass increases, the strength of dispersion forces increases and the boiling points, surface tension, and viscosities all increase. (**b**) Ethylene glycol has an —OH group at both ends of the molecule. This greatly increases the possibilities for hydrogen bonding; the overall intermolecular attractive forces are greater and the viscosity of ethylene glycol is much greater. (**c**) Water has the highest surface tension but lowest viscosity because it is the smallest molecule in the series. There is no hydrocarbon chain to inhibit their strong attraction to molecules in the interior of the drop, resulting in high surface tension. The absence of an alkyl chain also means the molecules can move around each other easily, resulting in the low viscosity. **11.63** (**a**) Fusion, endothermic (**b**) vaporization, endotermic (**c**) condensation exothermic (**d**) condensation exothermic **11.64** (**a**) vaporization (l) → (g) (**b**) endothermic (**c**) Same numerical value. **11.65** 2.3×10^3 g H_2O **11.68** Properties (**c**) intermolecular attractive forces, (**d**) temperature and (**e**) density of the liquid affect vapor pressure of a liquid.

11.69 (**a**) $CBr_4 < CHBr_3 < CH_2Br_2 < CH_2Cl_2 < CH_3Cl < CH_4$. (**b**) $CH_4 < CH_3Cl < CH_2Cl_2 < CH_2Br_2 < CHBr_3 < CBr_4$ (**c**) By analogy to attractive forces in HCl, the trend will be dominated by dispersion forces, even though four of the molecules are polar. The order of increasing boiling point is the order of increasing molar mass and increasing strength of dispersion forces. **11.70** (**a**) The temperature of the water in the two pans is the same. (**b**) Vapor pressure does not depend on either volume or surface area of the liquid. At the same temperature, the vapor pressures of water in the two containers are the same. **11.71** (**a**) Approximately 40 °C (**b**) approximately 7 kPa (**c**) approximately 50 °C (**d**) approximately 51 kPa **11.73** (**a**) $H_2O(g)$ will condense to $H_2O(s)$ at approximately 530 Pa; at a higher pressure, perhaps 500 kPa or so, $H_2O(s)$ will melt to form $H_2O(l)$. (**b**) At 100 °C and 50.7 kPa, water is in the vapor phase. As it cools, water vapor condenses to the liquid at approximately 82 °C, the temperature where the vapor pressure of liquid water is 50.7 kPa. Further cooling results in freezing at approximately 0 °C. The freezing point of water increases with decreasing pressure, so at 50.7 kPa the freezing temperature is very slightly above 0 °C. **11.75** (**a**) Methane on the surface of Titan is likely to exist in both solid and liquid forms. (**b**) As pressure decreases upon moving away from the surface of Titan, $CH_4(l)$ (at −178 °C) will vaporize to $CH_4(g)$, and $CH_4(s)$ (at temperatures below −180 °C) will sublime to $CH_4(g)$. **11.77** (**a**) True (**b**) false (**c**) true (**d**) false (**e**) false (**f**) true **11.78** Because order is maintained in at least one dimension, the molecules in a liquid-crystalline phase are not totally free to change orientation. This makes the liquid-crystalline phase more resistant to flow, more viscous, than the isotropic liquid. **11.79** Melting provides kinetic energy sufficient to disrupt molecular alignment in one dimension in the solid, producing a smectic phase with ordering in two dimensions. Additional heating of the smectic phase provides kinetic energy sufficient to disrupt alignment in another dimension, producing a nematic phase with one-dimensional order. **11.80** (**a**) Decrease (**b**) increase (**c**) increase (**d**) increase (**e**) increase (**f**) increase (**g**) increase **11.83** (**a**) The *trans* isomer will have stronger intermolecular hydrogen bonding, but the *cis* isomer will have stronger intramolecular hydrogen bonding. (**b**) The *trans* isomer melts at 287 °C and the *cis* isomer melts at 135 °C. **11.85** (**a**) All of these compounds exhibit dispersion interactions. (**b**)) All of these compounds are polar and exhibit dipole–dipole interactions. (**c**) Only methanoic acid and ethanoic acid exhibit hydrogen bonding. (**d**) Methanoic acid and ethanoic acid both exhibit hydrogen bonding, but ethanoic acid has a higher molecular weight. Thus, it has a higher total intermolecular force resulting in a higher boiling point. (**e**) Ethanal does not exhibit hydrogen bonding and it has the lowest molecular weight. Therefore, it has the lowest boiling point. **11.88** A plot of number of carbon atoms versus boiling point indicates that the boiling point of C_8H_{18} is approximately 130 °C. The more carbon atoms in the hydrocarbon, the longer the chain, the more polarizable the electron cloud, the higher the boiling point. **11.90** (**a**) Evaporation is an endothermic process. The heat required to vaporize sweat is absorbed from your body, helping to keep it cool. (**b**) The vacuum pump reduces the pressure of the atmosphere above the water until atmospheric pressure equals the vapor pressure of water and the water boils. Boiling is an endothermic process, and the temperature drops if the system is not able to absorb heat from the surroundings fast enough. As the temperature of the water decreases, the water freezes. **11.95** At low Antarctic temperatures,

molecules in the liquid crystalline phase have less kinetic energy due to temperature, and the applied voltage may not be sufficient to overcome orienting forces among the ends of molecules. If some or all of the molecules do not rotate when the voltage is applied, the display will not function properly.

11.99

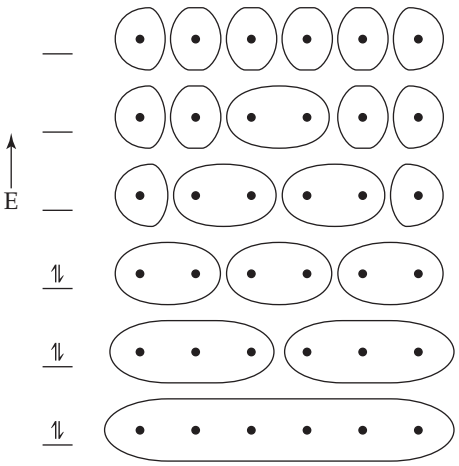


(**a**) Molar mass: Compounds (**i**) and (ii) have similar rodlike structures. The longer chain in (ii) leads to greater molar mass, stronger London dispersion forces, and higher heat of vaporization. (**b**) Molecular shape: Compounds (iii) and (v) have the same chemical formula and molar mass but different molecular shapes. The more rodlike shape of (v) leads to more contact between molecules, stronger dispersion forces, and higher heat of vaporization. (**c**) Molecular polarity: Compound (iv) has a smaller molar mass than (ii) but a larger heat of vaporization, which must be due to the presence of dipole–dipole forces. (**d**) Hydrogen bonding interactions: Molecules (v) and (vi) have similar structures. Even though (v) has larger molar mass and dispersion forces, hydrogen bonding causes (vi) to have the higher heat of vaporization. **11.103** P(hexane vapor) = 25,278 Pa

Chapter 12

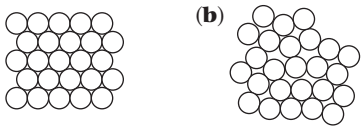
12.14 Copper. A body-centered cubic structure has more empty space than a face-centered cubic one. The more empty space, the less dense the solid. We expect the element with the highest density, copper, to adopt the face-centered cubic structure.

12.20



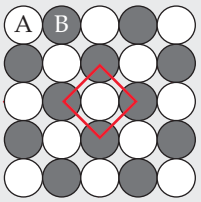
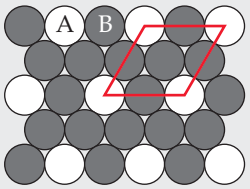
(**a**) Six AOs require six MOs (**b**) zero nodes in the lowest energy orbital (**c**) five nodes in highest energy orbital (**d**) two nodes in the HOMO (**e**) three nodes in the LUMO (**f**) The HOMO-LUMO energy gap for the six-atom diagram is smaller than the one for the four-atom diagram. In general, the more atoms in the chain, the smaller the HOMO-LUMO energy gap. **12.21** (**a**) Ag is more ductile. Cr has stronger metallic bonding, a stiffer lattice, and is less susceptible to distortion. (**b**) Zn is more ductile. Ge is a metalloid semi-conductor solid with a stiffer lattice than metallic Zn. **12.46** 2.47×10^5 Au atoms **12.48** The red-orange compound is more likely to be a semiconductor and the white one an insulator. The red-orange compound absorbs light in the visible spectrum (red-orange is reflected, so blue-green is absorbed), while the white compound does not. This indicates that the red-orange compound has a lower energy electron transition than the white one. Semiconductors have lower energy electron transitions than insulators. **12.52** (**a**) The structure is hexagonal close-packed. (**b**) The coordination number, CN, is twelve. (**c**) CN(1) = 9, CN(2) = 6. **12.54** Fragment (**b**) is more likely to give rise to electrical conductivity. Arrangement (**b**) has a delocalized π system, in which electrons are free to move. Mobile electrons are required for electrical conductivity. **12.56** We expect linear polymer (**a**), with ordered regions, to be more crystalline and to have a higher melting point than branched polymer (**b**). **12.57** Statement (**b**) is the best explanation. **12.58** (**a**) Hydrogen bonding, dipole–dipole forces, London dispersion forces (**b**) covalent chemical bonds (**c**) ionic bonds (**d**) metallic bonds **12.59** (**a**) Covalent-network (**b**) metallic (**c**) ionic (**d**) molecular (**e**) molecular (**f**) ionic **12.61** Metallic, because of its melting point, conductivity, and insolubility in water

12.62 (**a**) (**b**)



Crystalline Amorphous

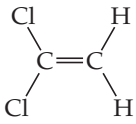
12.64

Two-dimensional structure	**(i)**	**(ii)**
(**a**) unit cell		
(**b**) γ, a, b	$\lambda = 90°$, $a = b$	$\lambda = 120°$, $a = b$
(**c**) lattice type	square	hexagonal

12.65 Tetragonal **12.66** (**e**) Triclinic and rhombohedral **12.67** (**b**) 2 **12.68** (**a**) Primitive hexagonal unit cell (**b**) NiAs **12.70** (**a**) Structure types A and C have equally dense packing and are more densely packed than structure type B. (**b**) Structure type B is least densely packed. **12.72** (**a**) The radius of an Rh atom is 135 pm. (**b**) The density of Rh is 12.4 g/cm^3. **12.73** (**a**) The radius of a Ca atom is 197.6 pm. (**b**) The density of Ca is 1.526 g/cm^3 **12.75** (**a**) 4 Al atoms per unit cell (**b**) coordination number = 12 (**c**) $a = 4.04 \times 10^{-8}$ cm (**d**) density = 2.71 g/cm^3 **12.77** Statement (**b**) is false. **12.78** (**a**) Interstitial alloy (**b**) substitutional alloy (**c**) intermetallic compound **12.79** (**a**) True (**b**) false (**c**) false **12.80** (**a**) Nickel or palladium, substitutional alloy (**b**) copper, substitutional alloy (**c**) silver, substitutional alloy **12.82** (**a**) True (**b**) false (**c**) false (**d**) false**12.84** The order of increasing melting points is La < Hf < Ta < W. Moving from La to W, the number of valence electrons, occupancy of the bonding band, and strength of

metallic bonding increase. Stronger metallic bonding requires more energy to break bonds and mobilize atoms, resulting in higher melting points from La to W. **12.86** (**a**) $SrTiO_3$ (**b**) Six (**c**) Each Sr atom is coordinated to a total of twelve O atoms in the eight unit cells that contain the Sr atom. **12.87** The density of PbS is 7.60 g/cm^3. **12.88** (**a**) 2.90 g/cm^3 (**b**) We expect As^{3-} to have a larger ionic radius than P^{3-}, so BAs will occupy a larger volume and the unit cell edge will be longer. (**c**) The density of BAs is 5.21 g/cm^3. The greater mass of As accounts for the greater density of BAs. **12.89** (**a**) Cs^+ and I^- have the most similar radii and will adopt the CsCl-type structure. The radii of Na^+ and I^- are somewhat different; NaI will adopt the NaCl-type structure. The radii of Cu^+ and I^- are very different; CuI has the ZnS-type structure. (**b**) CsI, 8; NaI, 6; CuI, 4 **12.90** (**a**) 6 (**b**) 3 (**c**) 6 **12.91** (**a**) False (**b**) true **12.92** (**a**) Ionic solids are much more likely to dissolve in water. (**b**) Covalent-network solids can become considerably better conductors of electricity via chemical substitution. **12.93** (**a**) CdS (**b**) GaN (**c**) GaAs **12.94** Ge or Si (Ge is closer to Ga in bonding atomic radius.) **12.95** (**a**) A 1.1 eV photon corresponds to a wavelength of 1.1×10^{-6} *M* (**b**) According to the figure, Si can absorb all wavelengths in the visible portion of the solar spectrum. (**c**) Si absorbs wavelengths less than 1100 nm. This corresponds to approximately 80–90% of the total area under the curve. **12.96** The emitted light has a wavelength of 365 nm. This is radiation in the ultraviolet region of the electromagnetic spectrum. **12.97** The band gap is approximately 2.09 eV, which corresponds to a wavelength of 593 nm. **12.99** (**a**) A monomer is a small molecule with low molecular mass that can be joined with other monomers to form a polymer. They are the repeating units of a polymer. (**b**) ethene (also known as ethylene) **12.100** Reasonable values for a polymer's molecular weight are 10,000 u, 100,000 u, and 1,000,000 u.

12.101



12.102





12.104 (**a**) Flexibility of the molecular chains causes flexibility of the bulk polymer. Flexibility is enhanced by molecular features that inhibit order, such as branching, and diminished by features that encourage order, such as cross-linking or delocalized π electron density. (**b**) Less flexible **12.105** Low degree of crystallinity **12.106** If a solid has nanoscale dimensions of 1–10 nm, there may not be enough atoms contributing atomic orbitals to produce continuous energy bands of molecular orbitals. **12.107** (**a**) False. As particle size decreases, the band gap increases. (**b**) False. As particle size decreases, wavelength decreases. **12.109** Statement (**b**) is correct. **12.116** 3 Ni atoms, 1 Al atom; 6 Nb atoms, 2 Sn atoms; 1 Sm atom, 5 Co atoms. In each case, the atom ratio matches the empirical formula given in the exercise. **12.118** The wavelength that corresponds to a photon with this energy is 477 nm. **12.120** (**a**) Zinc sulfide, ZnS (**b**) covalent (**c**) In the solid, each Si is bound to four C atoms in a tetrahedral arrangement, and each C is bound to four Si atoms in a tetrahedral arrangement, producing an extended three-dimensional network. SiC is high-melting because melting requires breaking covalent Si—C bonds, which takes a huge amount of thermal energy. It is hard because the three-dimensional lattice resists any deformation that would weaken the Si—C bonding network. **12.127** The distance between planes in crystalline silicon is 313 pm. **12.133** (**a**) 109° (**b**) 120° (**c**) atomic *p* orbitals **12.137** (**a**) 2.50×10^{22} Si atoms (To 1 sig fig, the result is 2×10^{22} Si atoms.) (**b**) 1.29×10^{-3} mg P (1.29 μg P) **12.139** 63 Si atoms

Chapter 13

13.4 Very soluble (**b**) ΔH_{mix} will be the largest negative number. In order for ΔH_{soln} to be negative, the magnitude of ΔH_{mix} must be greater than the magnitude of ($\Delta H_{solute} + \Delta H_{solvent}$). **13.6** (**a**) ΔH_{soln} is nearly zero. Because the solute and solvent in this case experience very similar London dispersion forces, the energy required to separate them individually and the energy released when they are mixed are approximately equal. $\Delta H_{mix} \approx -(\Delta H_{solute} + \Delta H_{solvent})$. (**b**) The entropy of the system increases when benzene and toluene form a solution. The change involves taking two pure liquids and forming a (homogeneous) mixture. The result is an increase in randomness or disorder. From part (**a**), the enthalpy of mixing is nearly zero, so the increase in entropy is the driving force for mixing in all proportions. **13.12** Toluene, $C_6H_5CH_3$, is the best solvent for nonpolar solutes. Without polar groups or nonbonding electron pairs, it forms only dispersion interactions with itself and other molecules. **13.16** $S_{H_2} = 2.0 \times 10^{-3}$ *M*, $S_{Ar} = 3.5 \times 10^{-3}$ *M* **13.30** (**a**) $X_{Eth} = 0.2812$ (**b**) $P_{soln} = 31.7$ kPa (**c**) X_{Eth} in vapor = 0.472 **13.34** Molar mass of lysozyme = 1.39×10^4 g **13.40** (**a**) < (**b**) < (**c**) **13.42** (**a**) No (**b**) The ionic solid with the smaller lattice energy will be more soluble in water. **13.46** Vitamin B_6 is more water soluble. Vitamin E is more fat soluble. **13.48** (**a**) Yes, the *molarity* changes with a change in temperature. (**b**) No, *molality* does not change with change in temperature. **13.50** The volume inside the balloon will be 0.5 L, assuming perfect osmosis across the semipermeable membrane. **13.52** (**a**) False (**b**) false (**c**) true **13.53** (**a**) Dispersion (**b**) hydrogen bonding (**c**) ion–dipole (**d**) dipole–dipole **13.55** (**a**) ΔH_{solute} (**b**) ΔH_{mix} **13.57** (**a**) Supersaturated (**b**) The bits of glass scraped from the vessel act as a seed crystal, which provides a nucleus of already aligned molecules, so that ordering of the dissolved particles is more facile. The excess alum is crystallizing out. (**c**) 86 g alum form **13.58** (**a**) Saturated (**b**) unsaturated (**c**) saturated (**d**) unsaturated **13.59** (**a**) We expect the liquids water and glycerol to be miscible in all proportions. (**b**) Hydrogen bonding, dipole-dipole forces, London dispersion forces **13.61** (**a**) Carbon tetrachloride (**b**) water **13.62** (**a**) CCl_4 is more soluble because dispersion forces among nonpolar CCl_4 molecules are similar to dispersion forces in hexane. (**b**) C_6H_6 is a nonpolar hydrocarbon and will be more soluble in the similarly nonpolar hexane. (**c**) The long, rodlike hydrocarbon chain of octanoic acid forms strong dispersion interactions and causes it to be more soluble in hexane. **13.63** (**a**) False (**b**) true (**c**) false (**d**) true **13.65** (**a**) 1.60% of $NaNO_3$ (**b**) 28.6 ppm **13.66**(**a**) $X_{C_2H_5OH} = 0.0192$ (**b**) 4.76% C_2H_5OH by mass (**c**) 1.09 *m* C_2H_5OH **13.67** (**a**) 8.63×10^{-3} *M* $Mg(NO_3)_2$ (**b**) 1.25 M $LiClO_4 \cdot 3H_2O$ (**c**) 0.375 *M* HNO_3 **13.68** (**a**) 2.56 *m* C_6H_6 (**b**) 0.858 *m* NaCl **13.69** (**a**) 50.01% H_2SO_4 by mass (**b**) $X_{H_2SO_4} = 0.155$ (**c**) 10.20 *m* H_2SO_4 (**d**) 7.112 *M* H_2SO_4 **13.70** (**a**) $X_{CH_3OH} = 0.244$ (**b**) 7.85 *m* CH_3OH (**c**) 4.94 *M* CH_3OH **13.72** (**a**) 0.0900 mol $SrBr_2$ (**b**) 1.40×10^{-2} mol KCl (**c**) 8.63 g $C_6H_{12}O_6$ **13.73** (**a**) Weigh out 1.3 g KBr, dissolve in water, dilute with stirring to 0.75 L. (**b**) Weigh out 2.62 g KBr, dissolve it in 122.38 g H_2O to make exactly 125 g of 0.180 *m* solution. (**c**) Dissolve 244 g KBr in water, dilute with stirring to 1.85 L. (**d**) Weigh 10.1 g KBr, dissolve it in a small amount of water, and dilute to 0.568 L. **13.75** 21% HNO_3 by mass **13.76** (**a**) 8.23 *m* Zn (**b**) 45.3 *M* Zn **13.77** (**a**) 4.66 kPa (**b**) 1.8×10^{-3} *M* CO_2 **13.78** (**a**) False (**b**) true (**c**) true (**d**) false **13.79** The vapor pressure of the first solution, $C_6H_{12}O_6$ (*aq*), is 3.10 kPa. The vapor

pressure of the second solution, $C_{12}H_{22}O_{11}$ (*aq*), is 3.14 kPa. Generally, the less concentrated solution, the one with fewer moles of solute per kilogram of solvent, will have the higher vapor pressure. **13.81** (**a**) P_{H_2O} = 24.85 kPa (**b**) 78.9 g $C_3H_8O_2$ **13.83** (**a**) Because KCl is a strong electrolyte, one mole of KCl produces twice as many dissolved particles as one mole of the molecular solute urea. Freezing-point depression is directly related to total moles of dissolved particles. The 0.10 *m* KCl has more dissolved particles so its freezing point is lower than that of 0.10 *m* $CO(NH_2)_2$. (b) In solutions of strong electrolytes like KCl, ion pairing reduces the effective number of particles in solution, decreasing the change in freezing point. The actual freezing point is then higher than the calculated freezing point for a 0.10 *m* solution. (**b**) In solutions of strong electrolytes like NaCl, ion pairing reduces the effective number of particles in solution, decreasing the change in boiling point. The actual boiling point is then lower than the calculated boiling point for a 0.10 *m* solution. **13.85** 0.130 *m* urea < 0.080 *m* KBr < 0.070 *m* $Mg(NO_2)_2$ **13.86** (**a**) $T_f = -115.0\,°C$, $T_b = 78.7\,°C$ (**b**) $T_f = -67.3\,°C$, $T_b = 64.2\,°C$ (**c**) $T_f = -0.4\,°C$, $T_b = 100.1\,°C$ (**d**) $T_f = -0.6\,°C$, $T_b = 100.2\,°C$ **13.87** 667 g $C_2H_6O_2$ **13.89** Π = 7.15 kPa **13.90** The approximate molar mass of adrenaline is 1.8×10^2 g. **13.93** $i = 2.8$ **13.94** (**a**) No. In the gaseous state, particles are far apart and intermolecular attractive forces are small. When two gases combine, all terms in Equation 13.1 are essentially zero and the mixture is always homogeneous. (**b**) To determine whether Faraday's dispersion is a true solution or a colloid, shine a beam of light on it. If light is scattered, the dispersion is a colloid. **13.95** Choice (**d**), $CH_3(CH_2)_{11}COONa$, is the best emulsifying agent. The long hydrocarbon chain will interact with the hydrophobic component, while the ionic end will interact with the hydrophilic component, as well as stabilize the colloid. **13.96** (**a**) No. The hydrophobic or hydrophilic nature of the protein will determine which electrolyte at which concentration will be the most effective precipitating agent. (**b**) Stronger. If a protein has been "salted out", protein-protein interactions are stronger than protein-solvent interactions and solid protein forms. (**c**) The first hypothesis seems plausible, since ion-dipole interactions among electrolytes and water molecules are stronger than dipole–dipole and hydrogen bonding interactions between water and protein molecules. But, we also know that ions adsorb on the surface of a hydrophobic colloid; the second hypothesis also seems plausible. If we could measure the charge and adsorbed water content of protein molecules as a function of salt concentration, then we could distinguish between these two hypotheses. **13.97** (**a**) Hydrochloride (**b**) free base (**c**) 0.492 *M* free base (**d**) 7.36 *M* hydrochloride (**e**) 275 mL of 12.0 *M* HCl **13.100** (**a**) $k_{Rn} = 7.17 \times 10^{-3}$mol/L-kPa (**b**) P_{Rn} = 23 Pa; $S_{Rn} = 1.6 \times 10^{-6}\,M$ **13.103** (**a**) 2.69 *m* LiBr (**b**) $X_{LiBr} = 0.0994$ (**c**) 81.1% LiBr by mass **13.105** $X_{H_2O} = 0.95$; 0.0263 mol ions; 0.0132 mol NaCl; 0.769 g NaCl **13.108** (**a**) − 0.6 °C (**b**) −0.4 °C **13.111** (**a**), CF_4, 1.7×10^{-4} *m*; $CClF_3$, 9×10^{-4} *m*; CCl_2F_2, 2.3×10^{-2} *m*; $CHClF_2$, 3.5×10^{-2} *m* (**b**) dipole moment (**c**) 3.9×10^{-4} mol O_2 **13.114** (**a**) The central atom and the number of electron-pair domains about it are: (**i**) Cl, 4; (ii) B, 4; (iii) P, 6; (iv) Al, 4; (v) B, 4 (**b**) tetrahedral (**c**) The central P atom in anion (iii) has an expanded octet. As drawn, the central Cl atom in anion (**i**) also has an expanded octet. Note that multiple resonance structures for ClO_4^- can be drawn, including one where Cl obeys the octet rule. The structure shown in this exercise is one that minimizes formal charge. (**d**) BARF **13.118** (**a**) P_t = 56.34 kPa (**b**) Endothermic. Repulsive forces lead to an overall lowering of the energy of the system. $\Delta H_{soln} > 0$.

Chapter 14

14.2 (**a**) *Reaction rate* is the change in the amount of products or reactants in a given amount of time. (**b**) Rates depend on concentration of reactants, surface area of reactants, temperature, and activation energy/presence of catalyst. (**c**) No. The stoichiometry of the reaction (mole ratios of reactants and products) must be known to relate rate of disappearance of reactants to rate of appearance of products.**14.12** (**a**) Rate = $k[N_2O_5]$ (**b**) Rate = $2.06 \times 10^{-4}\,M/s$ (**c**) When the concentration of N_2O_5 triples,the rate of the reaction triples. (**d**) When the concentration of N_2O_5 is reduced by 10 %, the rate of the reaction is reduced by 10%. **14.19** (**a**) A graph of ln[A] versus time yields a straight line for a first-order reaction. (**b**) On a graph of ln[A] versus time, the rate constant is the (–slope) of the straight line. **14.20**(**a**) $k = 3.2 \times 10^{-6}s^{-1}(0.28\,d^{-1})$ (**b**) $t_{1/2} = 2.2 \times 10^2$ s (3.7 min) **14.21** (**a**) P = 4 kPa (**b**) t = 51 s **14.26** (**a**) The energy of the collision and the orientation of the molecules when they collide determine whether a reaction will occur. (**b**) The rate constant usually increases with an increase in reaction temperature. (**c**) The fraction of molecules with energy greater than the activation energy changes most dramatically with temperature. Frequency of collision and the orientation factor are lumped into the frequency factor, A, which is considered to be constant with temperature. **14.47** The rate of the combustion reaction in the cylinder depends on the surface area of the droplets in the spray. The smaller the droplets, the greater the surface area exposed to oxygen, the faster the combustion reaction. In the case of a clogged injector, larger droplets lead to slower combustion. Uneven combustion in the various cylinders can cause the engine to run roughly and decrease fuel economy. **14.49** Equation (iv) (**b**) rate = $-\Delta[B]/\Delta t = \frac{1}{2}\Delta[A]/\Delta t$ **14.55** (1) Total potential energy of the reactants (2) E_a, activation energy of the reaction (3) ΔE, net energy change for the reaction (4) total potential energy of the products **14.58** (**a**) $NO_2 + F_2 \longrightarrow NO_2F + F$; $NO_2 + F \longrightarrow NO_2F$ (**b**) $2NO_2 + F_2 \longrightarrow 2NO_2F$ (**c**) F (atomic fluorine) is the intermediate (**d**) rate = $k[NO_2][F_2]$ **14. 61** (**a**) Net reaction: $AB + AC \longrightarrow BA_2 + C$ (**b**) A is the intermediate. (**c**) A_2 is the catalyst.

14.64

Time (min)	Mol A	(a) Mol B	[A] (mol/L)	Δ[A] (mol/L)	(b) Rate (M/s)
0	0.065	0.000	0.65		
10	0.051	0.014	0.51	−0.14	2.3×10^{-4}
20	0.042	0.023	0.42	−0.09	1.5×10^{-4}
30	0.036	0.029	0.36	−0.06	1.0×10^{-4}
40	0.031	0.034	0.31	−0.05	0.8×10^{-4}

(**c**) $\Delta[B]_{avg}/\Delta t = 1.3 \times 10^{-4}\,M/s$

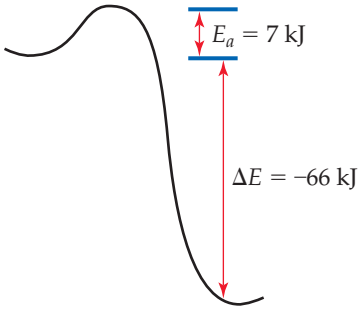
14.65
(**a**)

Time (s)	Time Interval (s)	Concentration (M)	Δ*M*	Rate (M/s)
0		0.0165		
2,000	2,000	0.0110	−0.0055	28×10^{-7}
5,000	3,000	0.00591	−0.0051	17×10^{-7}
8,000	3,000	0.00314	−0.00277	9.3×10^{-7}
12,000	4,000	0.00137	−0.00177	4.43×10^{-7}
15,000	3,000	0.00074	−0.00063	2.1×10^{-7}

(**b**) The average rate of reaction is $1.05 \times 10^{-6}\,M/s$ (**c**) The average rate between t = 2000 and t = 12,000 s ($9.63 \times 10^{-7}M/s$) is greater than the average rate between t = 8,000 and t = 15,000 s

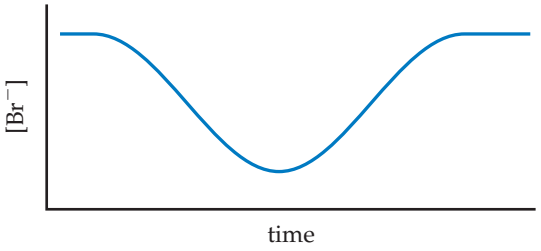
$(3.43 \times 10^{-7} M/s)$. (**d**) From the slopes of the tangents to the graph, the rates are $12 \times 10^{-7} M/s$ at 5000 s, $5.8 \times 10^{-7} M/s$ at 8000 s. **14.66** (**a**) $-\Delta[CO]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[H_2]/\Delta t$; $-\Delta[H_2O]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[H_2]\Delta t$ (**b**) $-\Delta[NO]/\Delta t = \Delta[NOCl]/\Delta t$; $-\Delta[Cl_2]/\Delta t = \Delta[NOCl]/2\,\Delta t$ (**c**) $-\Delta[CO_4]/\Delta t = \Delta[CO_2]/\Delta t = \Delta[H_2O]/2\,\Delta t$; $-\Delta[O_2]/\Delta t = 2\Delta[CO_2]/\Delta t = \Delta[H_2O]/\Delta t$ (**d**) $-\Delta[N_2O_4]/\Delta t = \Delta[NO_2]/\Delta t$ **14.67** (**a**) $-\Delta[O_2]/\Delta t = 0.25$ mol/s; $\Delta[H_2O]/\Delta t = 0.5$ mol/s (**b**) P_{total} decreases by 30 kPa/min. **14.68** (**a**) If [B] doubles, there is no change in the rate or the rate constant. (**b**) The reaction is third order in A, zero order in B, and third order overall. (**c**) units of $k = M^{-2}s^{-1}$ **14.70** (**a**) $5.2 \times 10^2 M^{-1}s^{-1}$ (**b**) If $[OH^-]$ is cut in half, the rate decreases by a factor of ½. (**c**) If both $[OH^-]$ and $[C_2H_5Cl]$ are cut in half, the rate decreases by a factor of ¼. **14.71** (**a**) Rate $= k[OCl^-][I^-]$ (**b**) $k = 60\,M^{-1}s^{-1}$. (**c**) Rate $= 6.0 \times 10^{-5}\,M/s$ **14.72** (**a**) Rate $= k[BF_3][NH_3]$ (**b**) The reaction is second order overall. (**c**) $k_{avg} = 3.41\,M^{-1}s^{-1}$ (**d**) $0.170\,M/s$ **14.73** (**a**) Rate $= k[NO]^2[Br_2]$ (**b**) $k_{avg} = 1.2 \times 10^4\,M^{-2}s^{-1}$ (**c**) $\frac{1}{2}\Delta[NOBr]/\Delta t = -\Delta[Br_2]/\Delta t$ (**d**) $-\Delta[Br_2]/\Delta t = 8.4\,M/s$ **14.77** Plot $(\ln P_{SO_2Cl_2})$ versus time, $k = -\text{slope} = 2.19 \times 10^{-5}s^{-1}$ **14.78** (**a**) The plot of $1/[A]$ versus time is linear, the reaction is second order in [A]. (**b**) 281 seconds (**c**) $t_{1/2} = 38$ min **14.79** (**a**) The plot of $1/[NO_2]$ versus time is linear, so the reaction is second order in NO_2. (**b**) $k = \text{slope} = 10\,M^{-1}s^{-1}$ (**c**) rate at $0.200\,M = 0.400\,M/s$, rate at $0.100\,M = 0.100\,M/s$; rate at $0.050\,M = 0.025\,M/s$ **14.81** $f = 1.81 \times 10^{-2}$. At 300 K, approximately 2 out of 100 molecules have this kinetic energy.

14.82 (**a**)



(**b**) E_a(reverse) = 73 kJ **14.83** (**a**) False (**b**) false (**c**) true **14.84** The order of slowest reaction to fastest reaction is: rate (**b**) < rate (**c**) < rate (**a**) **14.85** (**a**) $k = 1.1\ s^{-1}$ (**b**) $k = 13\ s^{-1}$ (**c**) The method in parts (**a**) and (**b**) assumes that the collision model and thus the Arrhenius equation describe the kinetics of the reactions. That is, activation energy is constant over the temperature range under consideration. **14.86** A plot of ln k versus $1/T$ has a slope of -5.64×10^3; $E_a = -R(\text{slope}) = 47.5$ kJ/mol **14.87** (**a**) An *elementary reaction* is a process that occurs as a single event; the order is given by the coefficients in the balanced equation for the reaction. (**b**) A *unimolecular* elementary reaction involves only one reactant molecule; a *bimolecular* elementary reaction involves two reactant molecules. (**c**) A *reaction mechanism* is a series of elementary reactions that describes how an overall reaction occurs and explains the experimentally determined rate law. (**d**) A *rate-determining step* is the slow step in a reaction mechanism. It limits the overall reaction rate. **14.88** (**a**) Bimolecular, rate $= k[H_2O][CN^-]$ (**b**) bimolecular, rate $= k[CH_3Cl][OH^-]$ (**c**) unimolecular, rate $= k[N_2O_4]$ **14.89** (**a**) Two intermediates, B and C. (**b**) three transition states (**c**) C ⟶ D is fastest. (**d**) ΔE is positive. **14.90** (**a**) $H_2(g) + 2\,ICl(g) \rightarrow I_2(g) + 2\,HCl(g)$ (**b**) HI is the intermediate. (**c**) If the first step is slow, the observed rate law is rate $= k[H_2][ICI]$. **14.91** (**a**) The two-step mechanism is consistent with the data, assuming that the second step is rate determining. (**b**) No. The linear plot guarantees that the overall rate law will include $[NO]^2$. Since the data were obtained at constant $[Cl_2]$, we have no information about reaction order with respect to $[Cl_2]$. **14.92** (**a**) A catalyst is a substance that changes (usually increases) the speed of a chemical reaction without undergoing a permanent chemical change itself. (**b**) A homogeneous catalyst is in the same phase as the reactants, while a hetereogeneous catalyst is in a different phase. (**c**) A catalyst has no effect on the overall enthalpy change for a reaction, but it does affect activation energy. It can also affect the frequency factor.

14.93



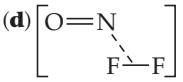
14.94 (**a**) Multiply the coefficients in the first reaction by 2 and sum. (**b**) NO_2(**g**) is a catalyst. (**c**) NO(**g**) is an intermediate. (**d**) This is a homogeneous catalysis. **14.95** (**a**) Use of chemically stable supports makes it possible to obtain very large surface areas per unit mass of the precious metal catalyst because the metal can be deposited in a very thin, even monomolecular, layer on the surface of the support. (**b**) The greater the surface area of the catalyst, the more reaction sites, the greater the rate of the catalyzed reaction. **14.96** To put two D atoms on a single carbon, it is necessary that one of the already existing C—H bonds in ethylene be broken while the molecule is adsorbed, so that the H atom moves off as an adsorbed atom and is replaced by a D atom. This requires a larger activation energy than simply adsorbing C_2H_4 and adding one D atom to each carbon. **14.97** The enzyme lowers the activation energy of the reaction by 44 kJ/mol. **14.98** (**a**) The catalyzed reaction is approximately 10,000,000 times faster at 25 °C (**b**) The catalyzed reaction is 180,000 times faster at 125 °C. **14.101** (**a**) Rate $= 4.7 \times 10^{-5}\,M/s$ (b, c) $k = 0.84\,M^{-2}s^{-1}$ (**d**) If the [NO] is increased by a factor of 1.8, the rate would increase by a factor of 3.2. **14.105** (**a**) The reaction is second order in C_2F_4. (**b**) 889 seconds **14.109** (**a**) The half-life of cobalt-60 is 5.29 years, that of iron-59 is 44.7 days. (**b**) Iron-59 decays at a faster rate. (**c**) 0.13 mg remains after three half-lives. (**d**) 0.925 mg remains after five days. **14.113** (**a**) The plot of $1/[C_5H_6]$ versus time is linear and the reaction is second order. (**b**) $k = 0.167\,M^{-1}\,s^{-1}$ **14.116** (**a**) When the two elementary reactions are added, $N_2O_2(g)$ appears on both sides and cancels, resulting in the overall reaction. $2\,NO(g) + H_2(g) \longrightarrow N_2O(g) + H_2O(g)$ (**b**) First reaction, $-[NO]/\Delta t = k[NO]^2$, second reaction, $-[H_2]/\Delta t = k[H_2][N_2O_2]$ (**c**) N_2O_2 is the intermediate. (**d**) Because $[H_2]$ appears in the rate law, the second step must be slow relative to the first. **14.119** (**a**) $Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$ (**b**) Cl(**g**), CCl_3(**g**) (**c**) reaction 1, unimolecular; reaction 2, bimolecular; reaction 3, bimolecular (**d**) Reaction 2 is rate determining. (**e**) Rate $= k[CHCl_3][Cl_2]^{1/2}$. **14.124** The enzyme must lower the activation energy by 22 kJ in order to make it useful. **14.129** (**a**) $k = 8 \times 10^7\,M^{-1}s^{-1}$

(**b**) :Ṅ═Ö:

:Ö═Ṅ—F̈: ⟷ (:Ö̇—N═F̈)

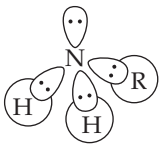
(**c**) NOF is bent with a bond angle of approximately 120°

(**d**)



(**e**) The electron-deficient NO molecule is attracted to electron-rich F_2 so the driving force for formation of the transition state is greater than simple random collisions.

14.132 (**a**)



(**b**) A reactant that is attracted to the lone pair of electrons on nitrogen will produce a tetrahedral intermediate. This can be a moiety with a full, partial, or even transient positive charge.

Chapter 15

15.2 (**a**) $K = 0.1$ (**b**) At equilibrium, the partial pressure of A is greater than the partial pressure of B. **15.17** $K_c = 10.5$ **15.18** (**a**) $[NO] = 0.050$, $[N_2] = 0.010$, $[H_2O] = 0.150$ (**b**) $K_c = 9.0 \times 10^2$ **15.32** (**a**) Endothermic (**b**) The equilibrium constant increases. (**c**) The forward rate constant increases by a larger amount than the reverse rate constant. **15.33** (**a**) $k_f > k_r$ (**b**) The equilibrium constant is greater than one. **15.35** K is greater than one. **15.37** $A(g) + B(g) \rightleftharpoons AB(g)$ has the larger equilibrium constant. **15.38** From the smallest to the largest equilibrium constant, (**c**) < (**b**) < (**a**). **15.39** Statement (**b**) is true. **15.41** Two B atoms should be added to the diagram. **15.43** K_c decreases as T increases, so the reaction is exothermic. **15.46** (**a**) $K_c = [I^2]/[I_2]$; homogeneous (**b**) $K_c = [SO_3]^2/[SO_2]^2[O_2]$; homogeneous (**c**) $K_c = [CO]^2/[CO]$; heterogeneous (**d**) $K_c = [CO_2][H_2]/[H_2O][CO]$; homogeneous (**e**) $K_c = [HCO_3^-][H^+]/[CO_2]$; homogeneous (**f**) $K_c = [Zn^{2+}][Fe^{2+}]$; heterogeneous (**g**) $K_c = [Ca^{2+}][CO_3^{2-}]$; heterogeneous **15.47** (**a**) Mostly products (**b**) at low total pressure, mostly reactants **15.48** (**a**) True (**b**) false (**c**) false **15.49** $K_p = 1.6 \times 10^{-9}$ **15.50** (**a**) The equilibrium favors NO and Br_2 at this temperature. (**b**) $K_c = 77$ (**c**) $K_c = 8.8$ **15.51** (**a**) $K_p = 5.44$ (**b**) $K_p = 0.034$ (**c**) $K_c = 283$ **15.52** $K_c = 2.9 \times 10^{-3}$ **15.53** (**a**) $K_p = P_{O_2}$ (**b**) $K_c = [Hg(solv)]^4[O_2(solv)]$ **15.55** (**a**) $K_p = 0.61$ (**b**) $K_c = 2.8 \times 10^3$ **15.58** (**a**) $P_{H_2O} = 326$ kPa, $P_{H_2} = 203$ kPa, $P_{CO_2} = 405$ kPa (**b**) $P_{H_2O} = 347$ kPa, $P_{H_2O} = 182$ kPa, $P_{CO_2} = 384$ kPa, $P_{CO} = 21$ kPa (**c**) $K_p = 0.10$ (**d**) $K_c = 0.10$ **15.60** $K_c = 2.0 \times 10^4$ **15.61** (**a**) The value of Q_c is zero. (**b**) As the reaction proceeds, the value of Q_c will increase. (**c**) The reaction must be at equilibrium. **15.62** (**a**) $Q = 7.2 \times 10^{-6}$, the reaction will proceed to the left. (**b**) $Q = 3.0 \times 10^{-11}$, the reaction will proceed to the right. (**c**) $Q = 5.18 \times 10^{-9}$, the reaction will proceed to the left. **15.63** $P_{Cl_2} = 395$ kPa
15.65 $[Br_2] = 0.00939\,M$, $[Br] = 0.00312\,M$, 0.250 g Br(g)
15.67 $[I] = 4.73 \times 10^{-5}M$, $[I_2] = 7.2 \times 10^{-5}M$, 0.092 g I_2
15.68 $[NO] = 0.003\,M$, $[N_2] = [O_2] = 0.12\,M$
15.69 The equilibrium pressure of $Br_2(g)$ is 205 kPa.
15.71 (**a**) $[Ca^{2+}] = [SO_4^{2-}] = 4.9 \times 10^{-3}\,M$ (**b**) A bit more than 1.0 g $CaSO_4$ is needed in order to have some undissolved $CaSO_4$ (s) in equilibrium with 1.4 L of saturated solution.
15.72 $[IBr] = 0.180\,M$, $[I_2] = [Br_2] = 0.0102\,M$
15.74 (**a**) $P_{CH_3I} = P_{HI} = 130$ Pa, $P_{CH_4} = 13.2$ kPa, $P_{I_2} = 6.5$ kPa
15.76 (**a**) No effect (**b**) shift equilibrium to the left (**c**) shift equilibrium to the right (**d**) shift equilibrium to the left (**e**) shift equilibrium to the left (**f**) no effect **15.77** (**a**) No effect (**b**) no effect (**c**) increase K_P (**d**) no effect (**e**) decrease K_P **15.78** (**a**) $\Delta H° = -155.7$ kJ (**b**) The reaction is exothermic, so the equilibrium constant will decrease with increasing temperature. (**c**) Δn does not equal zero, so a change in volume at constant temperature will affect the fraction of products in the equilibrium mixture. **15.79** An increase in pressure favors formation of ozone. **15.83** $K_p = 2.5 \times 10^5$; $K_c = 3.67 \times 10^{-3}$ **15.86** (**a**) $P_{Br_2} = 16.3$ kPa $P_{NO} = 63.6$ kPa, $P_{NOBr} = 18.1$ kPa; $K_c = 0.0643$ (**b**) $P_t = 98.1$ kPa, (**c**) 10.49 g NOBr

15.90 $[CO_2] = [H_2] = 0.264\,M$, $[CO] = [H_2O] = 0.236\,M$ **15.98** $Q = 8 \times 10^{-6}$. $Q > K_p$, so the system is not at equilibrium; it will shift left to attain equilibrium. A catalyst that speeds up the reaction and thereby promotes the attainment of equilibrium would decrease the CO concentration in the exhaust. **15.100** At equilibrium, $[H_4IO_6^-] = 0.0015\,M$

Chapter 16

16.37 (**a**) $C_6H_5OH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$
(**b**) $K_b = 7.7 \times 10^{-5}$ (**c**) Phenol is a stronger acid than water.
16.47 $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. Ammonia, NH_3, acts as an Arrhenius base because it increases the concentration of hydroxide ion, OH^-, in aqueous solution. It acts like a Brønsted-Lowry base because it is a proton, H^+, acceptor. It acts like a Lewis base because it is an electron pair donor. **16.50** (**a**) HCl, the H^+ donor, is the Brønsted–Lowry acid. NH_3, the H^+ acceptor, is the Brønsted–Lowry base. (**b**) HCl, the electron pair acceptor, is the Lewis acid. NH_3, the electron pair donor, is the Lewis base. **16.54** (**a**) HY is a strong acid. There are no neutral HY molecules in solution, only H^+ cations and Y^- anions. (**b**) HX has the smallest K_a value. It has most neutral acid molecules and fewest ions. (**c**) HX has fewest H^+ and highest pH. **16.60** (**a**) Molecule (**b**) is more acidic because its conjugate base is resonance-stabilized and the ionization equilibrium favors the more stable products. (**b**) Increasing the electronegativity of X increases the strength of both acids. As X becomes more electronegative and attracts more electron density, the O—H bond becomes weaker, more polar, and more likely to be ionized. An electronegative X group also stabilizes the anionic conjugate bases by delocalizing the negative charge. The equilibria favor products and the values of K_a increase. **16.62** HCl is the Brønsted–Lowry acid; NH_3 is the Brønsted–Lowry base. **16.63** (**a**) (i) HPO_4^{2-} (ii) Br^- (**b**) (i) HCN (ii) H_2SO_4

16.64

Acid +	Base ⇌	Conjugate Acid +	Conjugate Base
(**a**) $NH_4^+(aq)$	$CN^-(aq)$	HCN(aq)	$NH_3(aq)$
(**b**) $H_2O(l)$	$(CH_3)_3N(aq)$	$(CH_3)_3NH^+(aq)$	$OH^-(aq)$
(**c**) HCOOH(aq)	$PO_4^{3-}(aq)$	$HPO_4^{2-}(aq)$	$HCOO^-(aq)$

16.65 (**a**) Acid: $HCO_3^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CO_3^{2-}(aq)$, Base: $HCO_3^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + H_2CO_3(aq)$ (**b**) H_2CO_3 is the conjugate acid of HCO_3^-. CO_3^{2-} is the conjugate base of HCO_3^-. **16.66** (**a**) F^-, weak base; HF, weak acid (**b**) HBr, strong acid; Br^-, negligible base (**c**) HS^-, strong base; H_2S, weak acid (**d**) ClO_4^-, negligible base; $HClO_4$, strong acid (**e**) $HCOO^-$, weak base; HCOOH, weak acid **16.67** (**a**) HBr (**b**) F^- **16.68** (**a**) $OH^-(aq) + OH^-(aq)$, the equilibrium lies to the right. (**b**) $H_2S(aq) + CH_3COO^-(aq)$, the equilibrium lies to the right. (**c**) $HNO_3(aq) + OH^-(aq)$, the equilibrium lies to the left. **16.69** Statement (ii) is correct. **16.70** (**a**) $[H^+] = 1.4 \times 10^{-5}\,M$, acidic (**b**) $[H^+] = 6.7 \times 10^{-13}\,M$, basic (**c**) $[H^+] = 3.16 \times 10^{-7}\,M$, acidic **16.71** $[H^+] = [OH^-] = 7.5 \times 10^{-7}\,M$ **16.72** (**a**) $[H^+]$ changes by a factor of 1000. (**b**) $[H^+]$ changes by a factor of 2.

16.73

$[H^+]$	$[OH^-]$	pH	pOH	Acidic or Basic
$5.7 \times 10^{-3}M$	$1.8 \times 10^{-12}M$	2.24	11.76	acidic
$1.6 \times 10^{-5}M$	$6.3 \times 10^{-10}M$	4.80	9.20	acidic
$1.1 \times 10^{-10}M$	$8.9 \times 10^{-5}M$	9.95	4.05	basic
$1.6 \times 10^{-10}M$	$6.3 \times 10^{-5}M$	9.80	4.20	basic

16.74 $[H^+] = 4.0 \times 10^{-8}\,M$, $[OH^-] = 6.0 \times 10^{-7}\,M$, pOH = 6.22
16.75 (**a**) Acidic (**b**) The range of possible integer pH values for the solution is 4-6. (**c**) Methyl red would help determine the pH of the solution more precisely. **16.76** (**a**) True (**b**) true (**c**) false
16.77 (**a**) $[H^+] = 8.3 \times 10^{-4}\,M$; pH = 3.08
(**b**) $[H^+] = 0.0381\,M$, pH = 1.42
(**c**) $[H^+] = 0.0125\,M$, pH = 1.903
(**d**) $[H^+] = 0.150\,M$, pH = 0.823
16.78 (**a**) $[OH^-] = 3.0 \times 10^{-3}\,M$, pH = 11.48
(**b**) $[OH^-] = 0.3758\,M$, pH = 13.5750
(**c**) $[OH^-] = 8.75 \times 10^{-5}\,M$, pH = 9.942
(**d**) $[OH^-] = 0.17\,M$, pH = 13.23 **16.79** 0.050 *M* NaOH
16.80 (**a**) $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$,
$K_a = [H^+][NO_2^-]/[HNO_2]$;
$HNO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$,
$K_a = [H_3O^+][NO_2^-]/HNO_2$
(**b**) $ClH_2CCOOH(aq) \rightleftharpoons H^+(aq) + ClH_2CCOOH^-(aq)$,
$K_a = [H^+][ClH_2CCOO^-]/[ClH_2CCOOH]$;
$ClH_2CCOOH(aq) + H_2O \rightleftharpoons H_3O^+(aq) + ClH_2CCOO^-(aq)$,
$K_a = [H_3O^+][ClH_2CCOO^-]/[ClH_2CCOOH]$
16.81 $K_a = 1.4 \times 10^{-4}$ **16.82** $[H^+] = [CNO^-] = 5.9 \times 10^{-3}\,M$, $[HCNO] = 9.4 \times 10^{-2}\,M$, $K_a = 3.7 \times 10^{-4}$ **16.83** 2.2 *M* CH_3COOH **16.85** $[H^+] = [C_6H_5COO^-] = 2.5 \times 10^{-3}\,M$, $[C_6H_5COOH] = 0.098\,M$ **16.86** $[H^+] = 3.2 \times 10^{-2}\,M$, pH = 1.49
16.87 (**a**) $[H^+] = 2.8 \times 10^{-3}\,M$, 0.69% ionization
(**b**) $[H^+] = 1.4 \times 10^{-3}\,M$, 1.4% ionization
(**c**) $[H^+] = 8.7 \times 10^{-4}\,M$, 2.2% ionization
16.88 (**a**) $[H^+] = 5.1 \times 10^{-3}\,M$, pH = 2.30. (**b**) Yes. We started the calculation by assuming that only the first step made a significant contribution to $[H^+]$ and pH. Calculation proved this assumption to be true. Next we assumed $[H^+]$ from the first ionization was small relative to 0.040 *M* citric acid; this assumption was not valid. Finally we assumed that additional ionization of $[H_2C_6H_5O_7^{2-}]$ was small, which was true. (**c**) $[C_6H_5O_7^{3-}]$ is much less than $[H^+]$. **16.89** (**a**) $HONH_3^+$ (**b**) When hydroxylamine acts as a base, the nitrogen atom accepts a proton. (**c**) In hydroxylamine, O and N are the atoms with nonbonding electron pairs; in the neutral molecule both have zero formal charges. Nitrogen is less electronegative than oxygen and more likely to share a lone pair of electrons with an incoming (and electron-deficient) H^+. The resulting cation with the +1 formal charge on N is more stable than the one with the +1 formal charge on O.
16.90 (**a**) $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$;
$K_b = [(CH_3)_3NH^+][OH^-]/[(CH_3)_3N]$
(**b**) $SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + OH^-(aq)$;
$K_b = [HSO_3^-][OH^-]/[SO_3^{2-}]$
(**c**) $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$;
$K_b = [HCN][OH^-]/[CN^-]$
16.91 From the quadratic formula, $[OH^-] = 5.4 \times 10^{-3}\,M$, pH = 11.73 **16.92** (**a**) $[C_{10}H_{15}ON] = 0.033\,M$, $[C_{10}H_{15}ONH^+] = [OH^+] = 2.1 \times 10^{-3}\,M$ (**b**) $K_b = 1.4 \times 10^{-4}$
16.94 (**a**) Hydrofluoric acid is stronger. (**b**) Cyanate ion is the stronger base. (**c**) For NCO^-, $K_b = 2.9 \times 10^{-11}$; for F^-, $K_b = 1.5 \times 10^{-11}$
16.95 (**a**) $[OH^-] = 5.7 \times 10^{-4}\,M$, pH = 10.75
(**b**) $[OH^-] = 1.3 \times 10^{-4}\,M$, pH = 10.10
(**c**) $[OH^-] = 3.5 \times 10^{-6}\,M$, pH = 8.54 **16.97** 0.11 *M* KCH_3COO
16.99 (**a**) Acidic (**b**) acidic (**c**) basic (**d**) neutral (**e**) acidic **16.100** K_b for the anion of the unknown salt is 1.4×10^{-11}; K_b for F^- is 1.5×10^{-11}; The unknown salt is NaF. **16.101** (**a**) HNO_3 is a stronger acid than HNO_2 (**b**) H_2S is a stronger acid than H_2O. (**c**) H_2SO_4 is a stronger acid than H_2SeO_4. (**d**) CCl_3COOH is stronger than CH_3COOH **16.102** (**a**) BrO^- (**b**) BrO^- (**c**) HPO_4^{2-} **16.103** (**a**) True (**b**) False. In a series of acids that have the same central atom, acid strength increases with the number of nonprotonated oxygen atoms bonded to the central atom. (**c**) False. H_2Te is a stronger acid than H_2S because the H—Te bond is longer, weaker, and more easily ionized than the H—S bond. **16.105** (**a**) Acid, $Fe(ClO_4)_3$ or Fe^{3+}, base, H_2O (**b**) Acid, H_2O; base, CN^- (**c**) Acid, BF_3; base, $(CH_3)_3N$ (**d**) Acid, HIO; base, NH_2^- **16.106** (**a**) Cu^{2+}, higher cation charge (**b**) Fe^{3+}, higher cation charge (**c**) Al^{3+}, smaller cation radius, same charge **16.107** (**a**) $[H^+] = 1.3 \times 10^{-3}\,M$, pH = 2.85
(**b**) $[H^+] = 2.7 \times 10^{-4}\,M$, pH = 3.56
(**c**) $[OH^-] = 3.6 \times 10^{-5}\,M$, pH = 9.55 **16.111** $K = 3.3 \times 10^7$
16.116 pH = 7.03 (not 6.1, from the typical calculation, which does not make sense). Usually we assume that $[H^+]$ and $[OH^-]$ from the autoprotolysis of water do not contribute to the overall $[H^+]$ and $[OH^-]$. However, for acid or base solute concentrations less than $1.0 \times 10^{-6}\,M$, the autoprotolysis of water produces significant $[H^+]$ and $[OH^-]$ and we must consider it when calculating pH. **16.119** (**a**) $pK_a = 4.84$ (**b**) pH = 2.98 (**c**) pH = 8.86 **16.123** Nicotine, protonated; caffeine, neutral base; strychnine, protonated; quinine, protonated **16.126** 6.0×10^{13} H^+ ions **16.129** (**a**) To the precision of the reported data, the pH of rainwater 40 years ago was 5.4, no different from the pH today. With extra significant figures, $[H^+] = 3.61 \times 10^{-6}\,M$, pH = 5.443 (**b**) A 20.0-L bucket of today's rainwater contains 0.02 L (with extra significant figures, 0.0200 L) of dissolved CO_2. **16.133** Rx 1, $\Delta H = 104$ kJ; Rx 2, $\Delta H = -32$ kJ. Reaction 2 is exothermic while reaction 1 is endothermic. For binary acids with heavy atoms (X) in the same family, the longer and weaker the H—X bond, the stronger the acid (and the more exothermic the ionization reaction). **16.136** (**a**) K(i) = 5.6×10^3, K(ii) = 10 (**b**) Both (**i**) and (ii) have $K > 1$, so both could be written with a single arrow.

Chapter 17

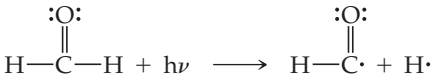
17.17 (**a**) Curve B (**b**) pH at the approximate equivalence point of curve A = 8.0, pH at the approximate equivalence point of curve B = 7.0 (**c**) For equal volumes of A and B, the concentration of acid B is greater, since it requires a larger volume of base to reach the equivalence point. (**d**) The pK_a value of the weak acid is approximately 4.5 **17.35** More soluble in acid: (**b**) CuS (**c**) $Cd(OH)_2$ (**d**) PbF_2 **17.45** (**a**) Base is required to increase $[PO_4^{3-}]$ so that the solubility product of the metal phosphates of interest is exceeded and the phosphate salts precipitate. (**b**) K_{sp} for the cations in group 3 is much larger; to exceed K_{sp}, a higher $[S^{2-}]$ is required. (**c**) They should all redissolve in strongly acidic solution.
17.46 The middle box has the highest pH. For equal amounts of acid HX, the greater the amount of conjugate base X^-, the smaller the amount of H^+ and the higher the pH. **17.52** (**a**) The red curve corresponds to the more concentrated acid solution. (**b**) On the titration curve of a weak acid, pH = pK_a at the volume halfway to the equivalence point. Reading the pK_a values from the two curves, the red curve has the smaller pK_a and the larger K_a. **17.54** (**a**) The right-most diagram represents the solubility of $BaCO_3$ as HNO_3 is added. (**b**) The left-most diagram represents the solubility of $BaCO_3$ as Na_2CO_3 is added. (**c**) The center diagram represents the solubility of $BaCO_3$ as $NaNO_3$ is added. **17.58** Statement (**a**) is most correct. **17.59** (**a**) $[H^+] = 1.58 \times 10^{-5}\,M$, pH = 4.80 (**b**) $[OH^-] = 5.44 \times 10^{-5}\,M$, pH = 9.74 (**c**) $[H^+] = 1.44 \times 10^{-5}\,M$, pH = 4.84 **17.60** (**a**) 4.2% ionization (**b**) 0.020 % ionization **17.61** Only solution (**b**) is a buffer
17.62 (**a**) pH = 3.76 (**b**) pH = 3.28 **17.63** (**a**) pH = 5.31
(**b**) $Na^+(aq) + CH_3COO^-(aq) + H^+(aq) + NO_3^-(aq) \longrightarrow CH_3COOH(aq) + Na^+(aq) + NO_3^-(aq)$
(**c**) $CH_3COOH(aq) + K^+(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + K^+(aq) + H_2O(l)$ **17.64** (**a**) pH = 1.65 (**b**) 10 g NaF
17.65 (**a**) pH = 4.84 (**b**) pH = 5.05 (**c**) pH = 4.65

17.66 (**a**) $[HCO_3^-]/[H_2CO_3] = 11$ (**b**) $[HCO_3^-]/[H_2CO_3] = 5.4$
17.67 1.41 L of 0.2 *M* KH_2PO_4, 0.59 L of 0.2 *M* H_3PO_4
17.69 (**a**) False (**b**) true (**c**) true **17.70** (**a**) Above pH 7 (**b**) below pH 7 (**c**) at pH 7 **17.71** The second color change of thymol blue is in the correct pH range to show the equivalence point of the titration of a weak acid with a strong base. **17.72** (**a**) 36.0 mL KOH soln (**b**) 45.0 mL KOH soln (**c**) 24.7 mL KOH soln **17.73** (**a**) pH = 1.54 (**b**) pH = 3.30 (**c**) pH = 7.00 (**d**) pH = 10.69 (**e**) pH = 12.74
17.74 (**a**) pH = 2.67 (**b**) pH = 4.74 (**c**) pH = 6.43 (**d**) pH = 8.80 (**e**) pH = 11.15 (**f**) pH = 12.10 **17.75** (**a**) pH = 7.00 (**b**) $[HONH_3^+] = 0.100\,M$, pH = 3.52 (**c**) $[C_6H_5NH_3^+] = 0.100\,M$, pH = 2.82 **17.76** (**a**) True (**b**) false (**c**) false (**d**) true
17.77 $K_{sp} = [Ba^{2+}][CrO_4^{2-}]$; $K_{sp} = [Cu^{2+}][S^{2-}]$; $K_{sp} = [Pb^{2+}][Cl^-]^2$; $K_{sp} = [La^{3+}][F^-]^3$ **17.78** (**a**) $K_{sp} = 7.63 \times 10^{-9}$ (**b**) $K_{sp} = 2.7 \times 10^{-9}$ (**c**) 5.3×10^{-4} mol $Ba(IO_3)_2$/L
17.79 $K_{sp} = 2.3 \times 10^{-10}$ **17.80** (**a**) 9.1×10^{-9} mol AgI/L (**b**) 5.5×10^{-16} mol AgI/L (**c**) 1.7×10^{-15} mol AgI/L **17.81** (**a**) The amount of $CaF_2(s)$ on the bottom of the beaker increases. (**b**) The $[Ca^{2+}]$ in solution increases. (**c**) The $[F^-]$ in solution decreases.
17.82 (**a**) 1.4×10^3 g $Mn(OH)_2$/L (**b**) 0.014 g/L (**c**) 3.6×10^{-7} g/L
17.84 $[Cu^{2+}] = 7 \times 10^{-11}\,M$, $[Cu(NH_3)_4^{2+}] = 3.72 \times 10^{-2}\,M$
17.85 (**a**) 9.1×10^{-9} mol AgI per L pure water (**b**) $K = K_{sp} \times K_f = 8 \times 10^4$ (**c**) 0.0500 mol AgI per L 0.100 *M* NaCN
17.86 (**a**) $Q < K_{sp}$; no $Ca(OH)_2$ precipitates (**b**) $Q < K_{sp}$; no Ag_2SO_4 precipitates **17.87** pH = 11.5 **17.88** LaF_3 will precipitate first, at $[F^-] = 1 \times 10^{-5}\,M$. **17.89** AgCl will precipitate first. **17.90** Ag^+ (Group 1) and Mg^{2+} (Group 4) are definitely absent. Al^{3+} (Group 3) is definitely present and Na^+ (Group 5) is possibly present. **17.91** (**a**) Make the solution acidic with 0.2 *M* HCl; saturate with H_2S. CdS will precipitate; ZnS will not. (**b**) Add excess base; $Fe(OH_3)(s)$ precipitates, but Cr^{3+} forms the soluble complex $Cr(OH)_4^-$. (**c**) Add $(NH_4)_2HPO_4$; Mg^{2+} precipitates as $MgNH_4PO_4$; K^+ remains soluble. (**d**) Add 6 *M* HCl; precipitate Ag^+ as $AgCl(s)$; Mn^{2+} remains soluble.
17.93 $pOH = pK_b + \log\{[BH^-]/[B]\}$ **17.99** (**a**) 6.5 mL glacial acetic acid, 5.25 g CH_3COONa **17.101** (**a**) The molar mass of the acid is 121 g/mol. (**b**) $K_a = 6.3 \times 10^{-5}$ **17.107** (**a**) $[Pb^{2+}] = 2.7 \times 10^{-7}\,M$ (**b**) 56 ppb Pb^{2+} (**c**) The solubility of $PbCO_3$ increases as pH is lowered. (**d**) A saturated solution of lead carbonate, with a lead concentration of 56 ppb, exceeds the EPA acceptable lead level of 15 ppb. **17.112** The solubility of $Fe(OH)_2$ in 0.50 *M* NH_4Cl is 5.34×10^{-3} mol/L
17.118 $[OH^-] \geq 1.0 \times 10^{-2}\,M$ or pH ≥ 12.02 **17.121** (**a**) The molar mass of the acid is 94.5 g/mol. (**b**) $K_a = 1.3 \times 10^{-5}$ (**c**) From Appendix D, butanoic acid is the closest match for K_a and molar mass, but the agreement is not exact. **17.123** (**a**) At the conditions given for the stomach, 99.7% of the aspirin is present as neutral molecules.
17.127 (**a**) $[Ag^+]$ from AgCl is 1.4×10^3 ppb or 1.4 ppm. (**b**) $[Ag^+]$ from AgBr is 76 ppb. (**c**) $[Ag^+]$ from AgI is 0.98 ppb. AgBr would maintain $[Ag^+]$ in the correct range.

Chapter 18

18.5 (**a**) The partial pressure of O_3 is 8.5×10^{-3} Pa. (**b**) 2.0×10^{15} O_3 molecules/1.0 L air **18.13** (**a**) A chlorofluorocarbon is a compound that contains chlorine, fluorine, and carbon, while a hydrofluorocarbon is a compound that contains hydrogen, fluorine, and carbon. An HFC contains hydrogen in place of the chlorine present in a CFC. (**b**) HFCs are potentially less harmful to the ozone layer than CFCs because their photodissociation does not produce Cl atoms, which catalyze the destruction of ozone. **18.33** (**a**) A volume greater than 22.4 L (**b**) No. The relative volumes of one mole of an ideal gas at 50 km and 85 km depend on the temperature and pressure at the two altitudes. From Figure 18.1, the gas will occupy a much larger volume at 85 km than at 50 km. (**c**) We expect gases to behave most ideally in the thermosphere, around the stratopause and in the troposphere at low altitude. **18.35** (**a**) A = troposphere, 0–10 km; B = stratosphere, 12–50 km; C = mesosphere, 50–85 km (**b**) Ozone is a pollutant in the troposphere and filters UV radiation in the stratosphere. (**c**) The troposphere (**d**) Only region C in the diagram is involved in an aurora borealis, assuming a narrow "boundary" between the stratosphere and mesosphere at 50 km. (**e**) The concentration of water vapor is greatest near Earth's surface in region A and decreases with altitude. Water's single bonds are susceptible to photodissociation in regions B and C, so its concentration is likely to be very low in these regions. The relative concentration of CO_2, with strong double bonds, increases in regions B and C, because it is less susceptible to photodissociation.
18.37 The Sun **18.39** $CO_2(g)$ dissolves in seawater to form $H_2CO_3(aq)$. The basic pH of the ocean encourages ionization of $H_2CO_3(aq)$ to form $HCO_3^-(aq)$ and $CO_3^{2-}(aq)$. Under the correct conditions, carbon is removed from the ocean as $CaCO_3(s)$ (sea shells, coral, chalk cliffs). As carbon is removed, more $CO_2(g)$ dissolves to maintain the balance of complex and interacting acid-base and precipitation equilibria. **18.41** Above ground, evaporation of petroleum gases and hydrogen sulfide at the well head, evaporation of volatile petroleum products and organic compounds from waste ponds, as well as leakage and overflow from the ponds are potential sources of contamination. Below ground, petroleum gases and fracking liquid can migrate into groundwater, both deep and shallow aquifers. **18.43** (**a**) Its temperature profile (**b**) troposphere, 0 to 12 km; stratosphere, 12 to 50 km; mesosphere, 50 to 85 km; thermosphere, 85 to 110 km **18.45** 7.3×10^{16} CO molecules/1.0 L air **18.46** (**a**) 499 nm (**b**) visible electromagnetic radiation **18.47** (**a**) *Photodissociation* is cleavage of a bond such that two neutral species are produced. *Photoionization* is absorption of a photon with sufficient energy to eject an electron, producing an ion and the ejected electron. (**b**) Photoionization of O_2 requires 1205 kJ/mol. Photodissociation requires only 495 kJ/mol. At lower elevations, high-energy short-wavelength solar radiation has already been absorbed. Below 90 km, the increased concentration of O_2 and the availability of longer-wavelength radiation cause the photodissociation process to dominate. **18.48** (**a**) 127 nm (**b**) A wavelength of 127 nm is in the ultraviolet portion of the electromagnetic spectrum. The energy is not enough energy to photoionize N_2. **18.49** Ozone depletion reactions, which involve only O_3, O_2, or O (oxidation state = 0), do not involve a change in oxidation state for oxygen atoms. Reactions involving ClO and one of the oxygen species with a zero oxidation state do involve a change in the oxidation state of oxygen atoms. **18.51** (**a**) The maximum wavelength of a single photon that will break a C—C bond is 344 nm. The maximum wavelength of a single photon that will break a C—H bond is 291 nm. (**b**) The photodissociation of both C—C bonds and C—H bonds will be significant. **18.52** $2\,NO_2(g) + H_2O(l) \rightleftharpoons HNO_2 + HNO_3(aq)$; $2\,NO(g) + O_2 + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3$
18.53 (**a**) $H_2SO_4(aq) + Fe(s) \longrightarrow FeSO_4(aq) + H_2(g)$ (**b**) As copper is a much more noble metal than iron, acid alone cannot attack copper. But the combination of acid and oxygen is a very corrosive medium, that can dissolve copper: $H_2SO_4(aq) + \frac{1}{2}O_2(g) + Cu(s) \longrightarrow CuSO_4(aq) + H_2O(l)$ **18.54** (**a**) Ultraviolet (**b**) 357 kJ/mol (**c**) The average C—H bond energy from Table 8.3 is 413 kJ/mol. The C—H bond energy in CH_2O, 357 kJ/mol, is less than the "average" C—H bond energy.

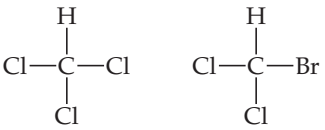
(**d**)



18.55 (**a**) 235 W/m^2. (**b**) Four sources, surface radiation, evapotranspiration, incoming solar radiation and convective heating, transfer energy to the atmosphere. Surface radiation makes the

largest contribution and convective heating the smallest. (**c**) Of the 519 W/m^2 absorbed by the atmosphere, 324 W/m^2 are radiated back to the surface. The percentage is 62.4%. **18.56** 0.445 *M* **18.57** (**a**) 3.22×10^3 gH_2O (**b**) The final temperature is 43.4 °C. **18.58** 961.4 kg CaO **18.59** (**a**) The total cation charge is 5.866 = 5.9 C; the total anion charge is 5.847 = 5.8 C. The two numbers vary in the third significant figure. This is not surprising, because the molarities of the various ions are given to two significant figures. **18.60** The minimum pressure required to initiate reverse osmosis is greater than 599 kPa. **18.61** (**a**) $CO_2(g)$, HCO_3^-, $H_2O(l)$, SO_4^{2-}, NO_3^-, HPO_4^{2-}, $H_2PO_4^-$ (**b**) $CH_4(g)$, $H_2S(g)$, $NH_3(g)$, $PH_3(g)$, **18.62** 8.1 g O_2 **18.63** $5\ Ca^{2+}(aq) + 4\ OH^-(aq) + 3\ HPO_4^{2-}(aq) \longrightarrow Ca_5(OH)(PO_4)_3(s) + 3\ H_2O(l)$ **18.64** (**a**) *Trihalomethanes* are the by-products of water chlorination; they contain one central carbon atom bound to one hydrogen and three halogen atoms.

(**b**)



18.65 The fewer steps in a process, the less waste is generated. Processes with fewer steps require less energy at the site of the process and for subsequent cleanup or disposal of waste. **18.66** (**a**) H_2O (**b**) It is better to prevent waste than to treat it. Atom economy. Less hazardous chemical synthesis and inherently safer for accident prevention. Catalysis and design for energy efficiency. Raw materials should be renewable. **18.67** (**a**) Vegetable oil as a raw material, by criteria 5, 7, and 12. (**b**) Water as a solvent, by criteria 5, 7, and 12. (**c**) Catalyzed reaction, by criteria 6, 9 and 12. **18.71** Multiply equations 18.7 and 18.9 by a factor of 2. Add these two equations to a third equation, $O(g) + O(g) \longrightarrow O_2(g)$. 2 $Cl(g)$ and 2 $ClO(g)$ cancel from each side of the resulting equation to produce equation 18.10. **18.74** (**a**) A CFC has C—Cl bonds and C—F bonds. In an HFC, the C—Cl bonds are replaced by C—H bonds. (**b**) Stratospheric lifetime is significant because, the longer a halogen-containing molecule exists in the stratosphere, the greater the likelihood that it will encounter light with energy sufficient to dissociate a carbon-halogen bond. Free halogen atoms are the bad actors in ozone destruction. (**c**) HFCs have replaced CFCs because it is infrequent that light with energy sufficient to dissociate a C—F bond will reach an HFC molecule. F atoms are much less likely than Cl atoms to be produced by photodissociation in the stratosphere. (**d**) The main disadvantage of HFCs as replacements for CFCs is that they are potent greenhouse gases. **18.76** (**a**) $C_3H_8(l) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(g)$ (**b**) $C_3H_8(l) + \frac{7}{2}\ O_2(g) \longrightarrow 3\ CO(g) + 4\ H_2O(g)$ (**c**) 66 L of dry air **18.80** 20 m^2 **18.82** (**a**) $CO_3^{2-}(aq) + H_2O(l) \longrightarrow HCO_3^-(aq) + OH^-(aq)$; $Mg^{2+}(aq) + 2\ OH^-(aq) \longrightarrow Mg(OH)_2(s)$ (**b**) At these ion concentrations, Q > K_{sp} and $Mg(OH)_2$ will precipitate.

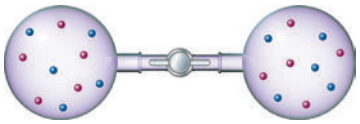
18.85 (**a**) 4.2×10^6 ton CO_2, 8.6×10^4 ton SO_2 (**b**) 8.0×10^4 ton $CaSO_3$

18.88 (**a**) H—Ö—H ⟶ H· + ·Ö—H (**b**) 258 nm (**c**) The overall reaction is $O_3(g) + O(g) \longrightarrow 2O_2(g)$. $OH(g)$ is the catalyst in the overall reaction because it is consumed and then reproduced. **18.90** The enthalpy change for the first step is −141 kJ, for the second step, −249 kJ, for the overall reaction, −390 kJ. **18.93** (**a**) Rate = $k[O_3][H]$ (**b**) $k_{avg} = 1.11 \times 10^{44} M^{-1}s^{-1}$ **18.97** (**a**) Process (**i**) is greener because it involves neither the toxic reactant phosgene nor the by-product HCl. (**b**) Reaction (**i**): C in CO_2 is linear with *sp* hybridization; C in R—N=C=O is linear with *sp* hybridization; C in the urethane monomer is trigonal planar with sp^2 hybridization. Reaction (ii): C in $COCl_2$ is trigonal planar with sp^2 hybridization; C in R—N=C=O is linear with *sp* hybridization; C in the urethane monomer is trigonal planar with sp^2 hybridization. (**c**) The greenest way to promote formation of the isocyanate is to remove by-product, either water or HCl, from the reaction mixture.

Chapter 19

19.24 (**a**) $C_4H_{10}(g)$ (**b**) $C_4H_{10}(g)$ **19.30** (**a**) Yes. $\Delta G = \Delta H - T\Delta S$ (**b**) No. If ΔG is positive, the process is nonspontaneous. (**c**) No. There is no relationship between ΔG and rate of reaction. **19.36** (**a**) The forward reaction is spontaneous at low temperatures but becomes nonspontaneous at higher temperatures. (**b**) The reaction is nonspontaneous in the forward direction at all temperatures. (**c**) The forward reaction is nonspontaneous at low temperatures but becomes spontaneous at higher temperatures.

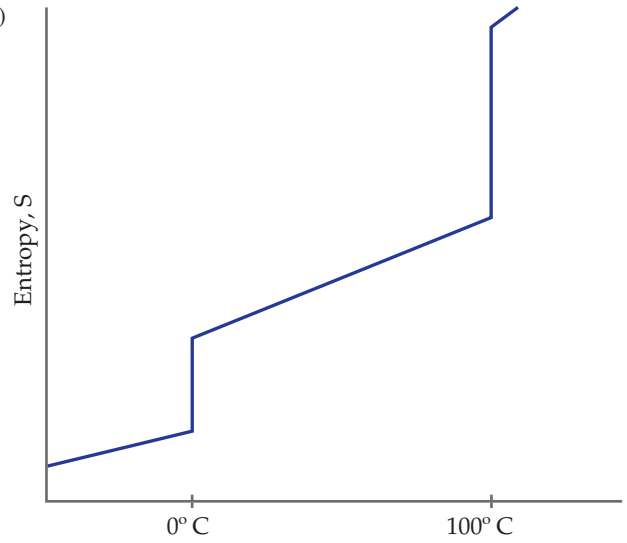
19.47 (**a**)



(**b**) $\Delta H = 0$ for mixing ideal gases. ΔS is positive because the disorder of the system increases. (**c**) The process is spontaneous and therefore irreversible. (**d**) Since $\Delta H = 0$, the process does not affect the entropy of the surroundings. **19.50** Both ΔH and ΔS are positive. The net change in the chemical reaction is the breaking of five blue-blue bonds. Enthalpies for bond breaking are always positive. There are twice as many molecules of gas in the products, so ΔS is positive for this reaction. **19.53** (**a**) At 300 K, $\Delta G = 0$, and the system is at equilibrium. (**b**) The reaction is spontaneous at temperatures above 300 K. **19.56** (**a**) True (**b**) false (**c**) false (**d**) false (**e**) true **19.57** Spontaneous: a, d; nonspontaneous: b, c, e **19.58** (**a**) True, assuming that the forward and reverse processes occur at the same conditions. (**b**) false (**c**) false (**d**) true (**e**) false **19.59** (**a**) Endothermic (**b**) above 0 °C (**c**) below 0 °C (**d**) at 0 °C **19.60** (**a**) No. An isothermal process occurs at constant temperature. (**b**) No. Temperature is a state function, so a change in temperature does not depend on pathway. (**c**) No. ΔE is a state function. **19.62** (**a**) An ice cube can melt reversibly at the conditions of temperature and pressure where the solid and liquid are in equilibrium. (**b**) No. We know that ΔH is a state function, and that melting is endothermic. Whether the ice cube melts reversibly or irreversibly, ΔH for the process is not zero. **19.63** (**a**) False (**b**) true (**c**) true (**d**) false **19.64** (**a**) Entropy increases (**b**) 188 J/K **19.65** (**a**) True (**b**) false (**c**) false **19.66** (**a**) Positive ΔS (**b**) $\Delta S = 1.02$ J/K (**c**) Temperature need not be specified to calculate ΔS, as long as the expansion is isothermal. **19.67** (**a**) $T_b = 57$ °C (**b**) From the *Handbook of Chemistry and Physics*, 74th Edition, $T_b = 58.8$ °C. The values are remarkably close; the small difference is primarily due to the fact that we used thermodynamic data at 25 °C for our calculation. **19.68** (**a**) Yes, the expansion is spontaneous. (**b**) As the ideal gas expands into the vacuum, there is nothing for it to "push back," so no work is done. Mathematically, $w = -P_{ext}\Delta V$. Since the gas expands into a vacuum, $P_{ext} = 0$ and $w = 0$. (**c**) The "driving force" for the expansion of the gas is the increase in entropy. **19.69** (**a**) An increase in temperature produces more available microstates for a system. (**b**) A decrease in volume produces fewer available microstates for a system. (**c**) Going from liquid to gas, the number of available microstates increases. **19.70** (**a**) ΔS is negative. (**b**) S of the system increases in 19.11 (a), (b) and (c). **19.71** S increases in (**a**) and (**c**); S decreases in (**b**). **19.72** (**a**) False (**b**) true (**c**) false (**d**) true **19. 73** (**a**) $I_2(g)$ (**b**) $O_2(g)$ at 50.7 kPa pressure (**c**) 1 mol of N_2 in 44.8 L (**d**) $CH_3OH(l)$ **19.74** (**a**) $\Delta S < 0$ (**b**) $\Delta S < 0$ (**c**) $\Delta S > 0$ (**d**) $\Delta S < 0$

19.75

(**a**)



(**b**) Boiling water, at 100 °C, has a much larger entropy change than melting ice at 0 °C. **19.77** (**a**) $HNO_3(g)$ will have the higher standard entropy at 25 °C. $HNO_3(g)$, 266.4 J/mol K; $HNO_3(aq)$, 146 J/mol K (**b**) $PCl_3(g)$ will have the higher standard entropy at 25 °C. $PCl_3(l)$, 217 J/mol K; $PCl_3(g)$, 311.7 J/mol K (**c**) $Fe_3O_4(s)$ will have the higher standard entropy at 25 °C. $Fe_2O_3(s)$, 89.96 J/mol K; $Fe_3O_4(s)$, 146.4 J/mol K. (**d**) Li(*g*) will have the higher standard entropy at 25 °C. Li(*s*), 29.09 J/mol K; Li(*g*), 138.8 J/mol K. **19.78** For elements with similar structures, the heavier the atoms, the lower the vibrational frequencies at a given temperature. This means that more vibrations can be accessed at a particular temperature, resulting in greater absolute entropy for the heavier elements. **19.79** (**a**) $\Delta S° = +75.3$ J/K. $\Delta S°$ is positive because the product contains more total particles with more motional freedom. (**b**) $\Delta S° = +221.46$ J/K. $\Delta S°$ is positive because there are more moles of gas in the products. (**c**) $\Delta S° = 5.04$ J/K. $\Delta S°$ is almost zero, as there are equal moles of gas in the products and in the reactants. (**d**) $\Delta S° = 242.88$ J/K. $\Delta S°$ is negative because there are fewer moles of gas in the products. **19.81** (**a**) $\Delta S°$ is negative; the reaction leads to a decrease in disorder of the system. (**b**) $\Delta H°$ is negative; the reaction leads to an increase in disorder of the surroundings. (**c**) $\Delta G° = +4.7$kJ (**d**) If all reactants and products are present in their standard states, the reaction is nonspontaneous in the forward direction at this temperature.

19.82 (**a**) $\Delta H° = -804.2$ kJ, $\Delta S° = -254.8$ J/K, $\Delta G° = -728.1$ kJ, $\Delta G° = \Delta H° - T\Delta G° = -728.3$ kJ
(**b**) $\Delta H° = -56.1$ kJ, $\Delta S° = 79.1$ J/K, $\Delta G° = -79.7$ kJ, $\Delta G° = \Delta H° - T\Delta G° = -79.7$ kJ
(**c**) $\Delta H° = -394.5$ kJ, $\Delta S° = 176.3$ J/K, $\Delta G° = -447.7$ kJ, $\Delta G° = \Delta H° - T\Delta G° = -447.1$ kJ (**d**) $\Delta H° = -27.6$ kJ, $\Delta S° = 269.5$ J/K, $\Delta G° = -107.6$ kJ, $\Delta G° = \Delta H° - T\Delta G° = -107.9$ kJ. The discrepancy in $\Delta G°$ values is due to experimental uncertainties in the tabulated thermodynamic data. **19.83** (**a**) $\Delta G° = -636.4$ kJ, spontaneous (**b**) $\Delta G° = 856.3$ kJ, nonspontaneous (**c**) $\Delta G° = 44.2$ kJ, nonspontaneous (**d**) $\Delta G° = 159.2$ kJ, nonspontaneous

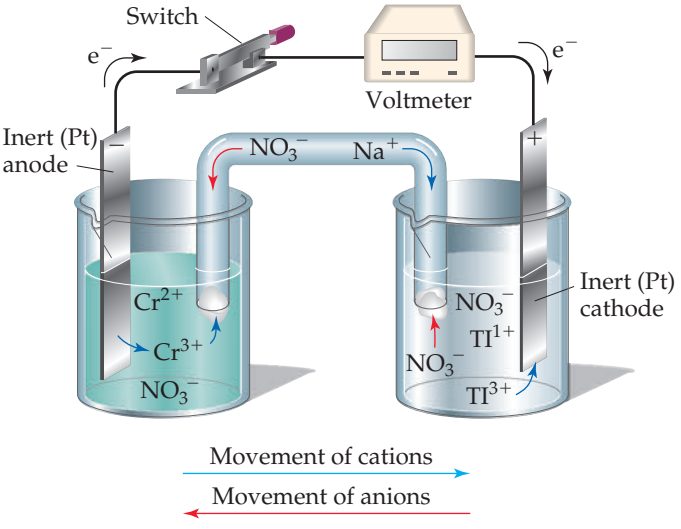
19.84 (**a**) $C_{31}H_{64}(s) + 47\ O_2(g) \rightarrow 31\ CO_2(g) + 32\ H_2O(g)$ (**b**) Because $\Delta S°$ is positive, $\Delta G°$ is more negative than $\Delta H°$. **19.86** $\Delta S > 47.5$ J/K **19.87** (**a**) $T = 333$ K (**b**) spontaneous **19.88** (**a**) $\Delta H° = 155.7$ kJ, $\Delta S° = 171.4$ kJ. Since $\Delta S°$ is positive, $\Delta G°$ becomes more negative with increasing temperature. (**b**) $\Delta G° = 19$ kJ. The reaction is not spontaneous under standard conditions at 800 K (**c**) $\Delta G° = -15.7$ kJ. The reaction is spontaneous under standard conditions at 1000 K.

19.90 (**a**) $C_2H_2(g) + \frac{5}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l)$
(**b**) −1299.5 kJ of heat produced / mol C_2H_2 burned
(**c**) $w_{max} = -1235.1$ kJ / mol C_2H_2 **19.91** (**a**) ΔG increases; it becomes more positive. (**b**) ΔG decreases; it becomes more negative. (**c**) ΔG increases; it becomes more positive. **19.92** (**a**) $\Delta G° = -69.74$ kJ (**b**) $\Delta G = -67$ kJ **19.93** (**a**) $\Delta G° = -16.77$ kJ, $K = 870$
(**b**) $\Delta G° = 8.0$ kJ, $K = 0.039$ (**c**) $\Delta G° = -497.9$ kJ, $K = 2 \times 10^{87}$
19.94 $\Delta H° = 269.3$ kJ, $\Delta S° = 0.1719$ kJ / K (**a**) $P_{CO_2} = 6.1 \times 10^{-37}$ kPa (**b**) $P_{CO_2} = 1.6 \times 10^{-2}$ kPa
19.95 (**a**) $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$ (**b**) $\Delta G° = 19.1$ kJ
(**c**) $\Delta G = 0$ at equilibrium (**d**) $\Delta G = -2.7$ kJ **19.96** (**a**) The thermodynamic quantities *P*, *H* and *G* are state functions (**b**) $w_{rev} < w_{irrev}$ (**c**) $q_{rev} > q_{irrev}$ (**d**) $\Delta H = q_{rev} + w_{rev} + p\Delta V$, $\Delta G = w_{rev} + p\Delta V$
19.105 (**a**) $C(s) + 2\ H_2(g) \rightarrow CH_4(g)$; $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$
(**b**) In both reactions, ΔG_f^0 will be more positive (less negative) than ΔH_f^0. (**c**) Condition (iii), when ΔS_f^0 is negative. **19.110** (**a**) For the oxidation of glucose in the body, $\Delta G° = -2878.8$ kJ, $K = 5 \times 10^{504}$; for the anaerobic decomposition of glucose, $\Delta G° = -228.0$ kJ, $K = 9 \times 10^{39}$
(**b**) A greater maximum amount of work at standard conditions can be obtained from the oxidation of glucose in the body, because ΔG° is much more negative. **19.114** (**a**) Acetone, $\Delta S°_{vap} = 88.4$ J/mol K; dimethyl ether, $\Delta S°_{vap} = 86.6$ J/mol K; ethanol, $\Delta S°_{vap} = 110$ J/mol K; octane, $\Delta S°_{vap} = 86.3$ J/mol K; pyridine, $\Delta S°_{vap} = 90.4$ J/mol K. Ethanol does not obey Trouton's rule. (**b**) Hydrogen bonding (in ethanol and other liquids) leads to more ordering in the liquid state and a greater than usual increase in entropy upon vaporization. Liquids that experience hydrogen bonding are probably exceptions to Trouton's rule. (**c**) Owing to strong hydrogen bonding interactions, water probably does not obey Trouton's rule. $\Delta S°_{vap} = 109.0$ J/mol K. (**d**) ΔH_{vap} for $C_6H_5Cl \approx 36$ kJ/mol **19.121** (**a**) 682 K or 409 °C (**b**) 782 K or 509 °C

Chapter 20

20.42 (**a**) anode: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2\ e^-$; cathode: $O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O(l)$ (**b**) $2\ Fe^{2+}(aq) + 3\ H_2O(l) + 3\ H_2O(l) \longrightarrow Fe_2O_3 \cdot 3\ H_2O(s) + 6\ H^+(aq) + 2\ e^-$; $O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O(l)$ **20.50** In this analogy, the electron is analogous to the proton (H^+). Redox reactions can be viewed as electron-transfer reactions, just as acid-base reactions can be viewed as proton-transfer reactions. Oxidizing agents are themselves reduced; they gain electrons. A strong oxidizing agent would be analogous to a strong base. **20.52** (**a**) The process represents oxidation. (**b**) The electrode is the anode. (**c**) When a neutral atom loses a valence electron, the radius of the resulting cation is smaller than the radius of the neutral atom. **20.56** (**a**) The sign of $\Delta G°$ is positive. (**b**) The equilibrium constant is less than one. (**c**) No. An electrochemical cell based on this reaction cannot accomplish work on its surroundings. **20.59** (**a**) Zinc is the anode. (**b**) The energy density of the silver oxide battery is most similar to the nickel-cadmium battery. The molar masses of the electrode materials and the cell potentials for these two batteries are most similar. **20.62** (**a**) *Oxidation* is the loss of electrons. (**b**) Electrons appear on the products' side (right side). (**c**) The *oxidant* is the reactant that is reduced. (**d**) An *oxidizing agent* is the substance that promotes oxidation; it is the oxidant. **20.63** (**a**) True (**b**) false (**c**) true
20.64 (**a**) (i) Reactants: H, +1; Mn, +2; Na, +1; Bi, +5; O, −2. Products: H, +1; O, −2; Mn, +7; Bi, +3, Na, +1 (ii) The total number of electrons transferred is 10. (**b**) Reactants: K, +1; Mn, +7; O, −2; Na, +1; S, +4; O, −2; H, +1. Products: Mn, +4; O, −2; Na, +1; S, +6, K, +1; H, +1 (ii) The total number of electrons transferred is 6. (**c**) (i) Reactants: Cu, 0; Ag, +1; N, +5; O, −2. Products: Ag, 0; Cu, +2; N, +5; O, −2. (ii) The total number of electrons transferred is 2.

20.65 (**a**) Nitrogen is oxidized from +4 to +5; oxygen is reduced from −1 to −2. (**b**) no oxidation-reduction (**c**) Iron is oxidized from 0 to +2; nitrogen is reduced from +5 to +4. **20.66** (**a**) $SiCl_4(g) + 2\,H_2(g) \rightarrow Si(s) + 4\,HCl(g)$ (**b**) $H_2(g)$ is oxidized; $SiCl_4(g)$ is reduced. (**c**) $H_2(g)$ is the reductant; $SiCl_4(g)$ is the oxidant. **20.67** (**a**) $14\,H^+(aq) + Cr_2O_7^{2-}(aq) + 6\,e^- \rightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$, reduction (**b**) $4\,H_2O(l) + Mn^{2+}(aq) \rightarrow MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^-$, oxidation (**c**) $I_2(s) + 6\,H_2O(l) \rightarrow 2\,IO_3^-(aq) + 12\,H^+(aq) + 10\,e^-$, oxidation (**d**) $S(s) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2S(g)$, reduction (**e**) $H_2O(l) + 2\,e^- + NO_3^-(aq) \rightarrow NO_2^-(aq) + 2\,OH^-(aq)$ reduction (**f**) $H_2O_2(aq) + 2\,e^- \rightarrow 2\,OH^-(aq)$, reduction **20.68** (**a**) $Cr_2O_7^{2-}(aq) + I^-(aq) + 8\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + IO_3^-(aq) + 4\,H_2O(l)$; oxidizing agent, $Cr_2O_7^{2-}$; reducing agent, I^- (**b**) $4\,MnO_4^-(aq) + 5\,CH_3OH(aq) + 12\,H^+(aq) \longrightarrow 4\,Mn^{2+}(aq) + 5\,HCOOH(aq) + 12\,H_2O(aq)$; oxidizing agent, MnO_4^-; reducing agent, CH_3OH (**c**) $I_2(s) + 5\,OCl^-(aq) + H_2O(l) \longrightarrow 2\,IO_3^-(aq) + 5\,Cl^-(aq) + 2\,H^+(aq)$; oxidizing agent, OCl^-; reducing agent, I_2 (**d**) $As_2O_3(s) + 2\,NO_3^-(aq) + 2\,H_2O(l) + 2\,H^+(aq) \longrightarrow 2\,H_3AsO_4(aq) + N_2O_3(aq)$; oxidizing agent, NO_3^-; reducing agent, As_2O_3 (**e**) $2\,MnO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2\,OH^-(aq)$; oxidizing agent, MnO_4^-; reducing agent, Br^- (**f**) $Pb(OH)_4^{2-}(aq) + ClO^-(aq) \longrightarrow PbO_2(s) + Cl^-(aq) + 2\,OH^-(aq) + H_2O(l)$; oxidizing agent, $ClO^-(aq)$; reducing agent, $Pb(OH)_4^{2-}$ **20.69** (**a**) False (**b**) true (**c**) true **20.70** (**a**) Mg is oxidized, Ni^{2+} is reduced. (**b**) $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-$; $Ni^{2+}(aq) + 2\,e^- \rightarrow Ni(s)$ (**c**) Mg is the anode, Ni is the cathode. (**d**) Mg(*s*) is negative; Ni(*s*) is positive. (**e**) Electrons flow from the Mg electrode (–) toward the Ni electrode (+). (**f**) Anions migrate toward the Mg(*s*) anode; cations migrate towards the Ni(*s*) cathode. **20.71** (**a**) One *volt* is the potential energy difference required to impart 1 J of energy to a charge of 1 coulomb. (**b**) Yes. All voltaic cells involve spontaneous redox reactions that produce positive cell potentials or emfs. **20.72** (**a**) $O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$ (**b**) $2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ (**c**) A *standard* oxygen electrode is an oxygen electrode where the components are at standard conditions, 1 *M* $H^+(aq)$ and $O_2(g)$ at 101.3 kPa, such that $E° = 1.23$ V. **20.74** (**a**) $Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + e^-$; $Tl^{3+}(aq) + 2\,e^- \longrightarrow Tl^+(aq)$ (**b**) $E°_{red} = 0.78\ V$ (**c**)



20.75 (**a**) $E° = 0.82$ V (**b**) $E° = 1.89$ V (**c**) $E° = 1.21$ V (**d**) $E° = 0.62$ V **20.76** (**a**) $Fe(s) + 2\,Ag^+(aq) \rightarrow 2\,Ag(s) + 2\,Fe^{2+}(aq)$, $E^0_{cell} = 1.239$ V (**b**) $Fe(s) + Cd^{2+}(aq) \rightarrow Cd(s) + 2\,Fe^{2+}(aq)$, $E^0_{cell} = 0.037$ V

20.77 (**a**) Anode, Cu(*s*); cathode, Ag(*s*). (**b**) The silver electrode gains mass as Ag is plated out, and the Cu electrode loses mass as Cu is oxidized. (**c**) $Cu(s) + 2\,Ag^+(aq) \rightarrow 2\,Ag(s) + 2\,Cu^{2+}(aq)$ (**d**) $E^0_{cell} = 0.462$ V **20.78** (**a**) Mg(*s*) (**b**) Fe(*s*) (**c**) Sn(*s*) (**d**) $I^-(aq)$ **20.79** (**a**) $H_2(g)$, basic, reductant (**b**) $Cr_2O_7^{2-}(aq)$, acidic, oxidant (**c**) $F_2(g)$, oxidant (**d**) Li(*s*), reductant **20.80** (**a**) $HSO_4^-(aq) < O_2(g) < MnO_4^-(aq) < HClO(aq) < O_3(g)$ (**b**) $Cr(OH)_3(s) < Fe(s) < H_2(g) < Mn(s) < Ca(s)$ **20.82** Al and $H_2C_2O_4$ **20.83** (**a**) $2\,Fe^{2+}(aq) + S_2O_6^{2-}(aq) + 4\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + 2\,H_2SO_3(aq)$; $2\,Fe^{2+}(aq) + N_2O(aq) + 2\,H^+(aq) \longrightarrow 2\,Fe^{3+}(aq) + N_2(g) + H_2O(l)$; $Fe^{2+}(aq) + VO_2^+(aq) + 2\,H^+(aq) \longrightarrow Fe^{3+}(aq) + VO^{2+}(aq) + H_2O(l)$ (**b**) $E° = -0.17$ V, $\Delta G° = 33$ kJ; $E° = -2.54$ V, $\Delta G° = 4.90 \times 10^2$ kJ; $E° = 0.23$ V, $\Delta G° = -22$ kJ (**c**) $K = 1.8 \times 10^{-6} = 10^{-6}$; $K = 1.2 \times 10^{-86} = 10^{-86}$; $K = 7.8 \times 10^3 = 8 \times 10^3$ **20.84** $\Delta G° = 27$ kJ, $E^0_{cell} = -0.28$ V **20.85** (**a**) $E° = 0.16$ V, $K = 2.54 \times 10^5 = 3 \times 10^5$ (**b**) $E° = 0.28$ V, $K = 2.93 \times 10^9 = 3 \times 10^9$ (**c**) $E° = 0.44$ V, $K = 2.40 \times 10^{74} = 10^{74}$ **20.86** (**a**) $K = 2.2 \times 10^4$ (**b**) $K = 4.9 \times 10^8$ (**c**) $K = 1.1 \times 10^{13}$ **20.87** $w_{max} = 1.3 \times 10^2$ kJ/mol Sn; 8.3×10^4 J/75.0 g Sn **20.88** (**a**) In the Nernst equation, $Q = 1$ if all reactants and products are at standard conditions. (**b**) Yes. The Nernst equation is applicable to cell emf at nonstandard conditions, so it must be applicable at temperatures other than 298 K. Values of $E°$ at temperatures other than 298 K are required. And, there is a variable for T in the second term. If the short-hand form of the equation, Equation 20.18, is used, a coefficient other than 0.0592 is required. **20.89** (**a**) *E* decreases (**b**) *E* increases (**c**) no effect (**d**) *E* decreases **20.90** (**a**) $E° = 0.48$ V (**b**) $E = 0.52$ V (**c**) $E = 0.46$ V **20.91** (**a**) $E° = 0.46$ V (**b**) $E = 0.37$ V **20.92** (**a**) The compartment with $[Cu^{2+}] = 0.100\,M$ is the cathode. (**b**) $E° = 0$ (**c**) $E = 0.0888$ V (**d**) In the anode compartment $[Cu^{2+}]$ increases; in the cathode compartment $[Cu^{2+}]$ decreases. **20.93** $E° = 0.76$ V, pH = 2.2 **20.94** (**a**) 260 g Pb (**b**) 2.42×10^5 C **20.95** (**a**) The anode (**b**) $E° = 3.50$ V (**c**) The emf of the battery, 3.5 V, is exactly the standard cell potential calculated in part (**b**). (**d**) At ambient conditions, $E \approx E°$, so $\log Q \approx 1$. Assuming that the value of $E°$ is relatively constant with temperature, the value of the second term in the Nernst equation is approximately zero at 37 °C, and $E \approx 3.5$ V. **20.96** (**a**) The cell emf will have a smaller value. (**b**) NiMH batteries use an alloy such as $ZrNi_2$ as the anode material. This eliminates the use and disposal problems associated with Cd, a toxic heavy metal. **20.97** (**a**) When the battery is fully charged, the mole ratio of the elements in the cathode is: 0.5 mol Li^+ to 0.5 mol Co^{3+} to 0.5 mol Co^{4+} to 2 mol O^{2-}. The material is $LiCo_2O_4$ (**b**) 4.9×10^3 C of electricity delivered on full discharge of a fully charged battery **20.98** (**a**) The spontaneous reaction in the hydrogen fuel cell is hydrogen gas plus oxygen gas makes water. (**b**) $E° = 1.23$ V **20.100** (**a**) Al is called a "sacrificial anode" because it has a more negative E^0_{red} than the pipeline metal and is preferentially oxidized when the two are coupled. It is sacrificed to preserve the pipeline. (**b**) E^0_{red} for Al^{3+} is −1.66 V, more negative than most metals present in pipelines, including Fe and Zn. **20.101** (**a**) +3 (**b**) +8/3 or +2.67 (**c**) 2 Fe(III) and 1 Fe(II) **20.102** (**a**) *Electrolysis* is an electrochemical process driven by an outside energy source. (**b**) By definition, electrolysis reactions are nonspontaneous. (**c**) $2\,Cl^-(l) \longrightarrow Cl_2(g) + 2\,e^-$ (**d**) When an aqueous solution of NaCl undergoes electrolysis, sodium metal is not formed because H_2O is preferentially reduced to form $H_2(g)$ **20.103** (**a**) 236 g Cr(*s*) (**b**) 2.51 A **20.104** (**a**) 4.0×10^5 g Li (**b**) The minimum voltage required to drive the electrolysis is +4.41 V. **20.105** Gold is less active than copper and thus more difficult to oxidize. When a mixture of copper and gold is refined by electrolysis, Cu is oxidized from the anode, but any metallic gold present in the mixture is not oxidized, so it accumulates near the anode, available for collection.

20.106 (**a**) $3\ Fe^{2+}(aq) \rightarrow Fe(s) + 2\ Fe^{3+}(aq)$
(**b**) $3\ Br_2(l) + 3\ H_2O(l) \rightarrow 6\ H^+(aq) + 5\ Br^-(aq) + BrO_3^-(aq)$
(**c**) $4\ Cr^{3+}(aq) + 7\ H_2O(l) \rightarrow 14\ H^+(aq) + Cr_2O_7^{2-}(aq) + 2\ Cr(s)$
(**d**) $5\ NO_2^-(aq) + 2\ H^+(aq) \rightarrow H_2O(l) + N_2(g) + 3\ NO_3^-(aq)$
20.108 (**a**) $E° = 0.226$ V, spontaneous (**b**) $E° = -0.44$ V, nonspontaneous (**c**) $E° = -0.144$ V, nonspontaneous (**d**) $E° = -0.434$ V, nonspontaneous **20.112** $K = 1.22 \times 10^{-41}$ **20.115** (**a**) By analogy to O in hydroxide (OH^-) and in alcohol (R−OH), the oxidation state of S in a thiol (R−SH) is −2. (**b**) By analogy to O in peroxide (−O−O−), the oxidation state of S in a disulfide (−S−S−) is −1. (**c**) The oxidation number of S becomes more positive and the thiols are oxidized. (**d**) Converting a disulfide to two thiols is the reverse of the process described in part (**c**). In order to reduce the disulfide, a reducing agent must be added to the solution. (**e**) When two thiols (R−SH) react to form a disulfide (R−S−S−R), the H atoms are probably removed by base before the oxidizing agent does its work. **20.118** 1.5×10^4 kWh required **20.123** (**a**) $E° = 0.728$ V, (**b**) cathode: $Br_2(l) + 2\ e^- \rightarrow 2\ Br^-(aq)$; anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2\ e^-$
(**c**) $\Delta S° = -123.78$ J. Because $\Delta S°$ is negative, $\Delta G°$ will become more positive and $E°$ will become more negative as temperature is increased. **20.126** K_{sp} for AgCl is 1.8×10^{-10}.

Chapter 21

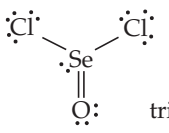
21.24 (**a**) NaI is a good source of iodine because iodine is a large percentage of its mass; it is completely dissociated into ions in aqueous solution, and iodine in the form of $I^-(aq)$ is mobile and immediately available for biouptake. (**b**) A Geiger counter placed near the thyroid immediately after ingestion will register background, then gradually increase in signal until the concentration of iodine in the thyroid reaches a maximum. Over time, iodine-131 decays, and the signal decreases. (**c**) The radioactive iodine will decay to 0.01% of the original amount in approximately 107 days. **21.29** (**a**) 1.71×10^5 kg/d (**b**) 2.1×10^8 g ^{235}U **21.30** ^{55}Mn is likely to have the largest mass defect per nucleon. **21.36** Hydrogen abstraction: $RCOOH + {\bullet}OH^- \longrightarrow RCOO{\bullet} + H_2O$; deprotonation: $RCOOH + OH^- \longrightarrow RCOO^- + H_2O$. Hydroxyl radical is more toxic to living systems because it produces other radicals when it reacts with molecules in the organism. Hydroxide ion, OH^-, on the other hand, will be readily neutralized in the buffered cell environment. The acid–base reactions of OH^- are usually much less disruptive to the organism than the chain of redox reactions initiated by OH radical. **21.38** (**a**) ^{24}Ne; outside; reduce neutron-to-proton ratio via β decay (**b**) ^{32}Cl; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (**c**) ^{108}Sn; outside; increase neutron-to-proton ratio via positron emission or orbital electron capture (**d**) ^{216}Po; outside; nuclei with $Z \geq 84$ usually decay via α emission. **21.43** (**a**) 7 min (**b**) 0.1 min^{-1} (**c**) 30% (3/10) of the sample remains after 12 min. (**d**) $^{88}_{41}Nb$ **21.44** (**a**) $^{10}_{5}B$, $^{11}_{5}B$; $^{12}_{6}C$, $^{13}_{6}C$; $^{14}_{7}N$, $^{15}_{7}N$; $^{16}_{8}O$, $^{17}_{8}O$, $^{18}_{8}O$; $^{19}_{9}F$ (**b**) $^{14}_{6}C$ (**c**) $^{11}_{6}C$, $^{13}_{7}N$, $^{15}_{8}O$, $^{18}_{9}F$ (**d**) $^{11}_{6}C$ **21.46** (**a**) $^{239}_{94}Pu$, 94p, 145n (**b**) $^{142}_{56}Ba$: 56p, 86n (**c**) potassium-41: 19p, 22n **21.47** (**a**) Proton (**b**) electron or beta particle (**c**) positron
21.48 (**a**) $^{198}_{86}Rn \rightarrow {}^{4}_{2}He + {}^{194}_{84}Po$
(**b**) $^{234}_{90}Th \rightarrow {}^{0}_{-1}e + {}^{234}_{91}Pa$ (**c**) $^{61}_{29}Cu \rightarrow {}^{0}_{+1}e + {}^{61}_{28}Ni$
(**d**) $^{106}_{47}Ag + {}^{0}_{-1}e \rightarrow {}^{106}_{46}Pd$ **21.49** (**a**) $^{239}_{94}Pu \rightarrow {}^{4}_{2}He + {}^{235}_{92}U$
(**b**) $^{26}_{14}Si \rightarrow {}^{0}_{+1}e + {}^{26}_{13}Al$ (**c**) $^{6}_{3}Li \rightarrow {}^{4}_{2}He + {}^{2}_{1}He$
(**d**) $^{90}_{38}Sr \rightarrow {}^{0}_{-1}e + {}^{90}_{39}Y$ **21.50** 7 alpha emissions, 4 beta emissions **21.51** (**a**) Positron emission (for low atomic numbers, positron emission is more common than orbital electron capture) (**b**) positron emission (**c**) beta emission (**d**) beta emission **21.52** (**a**) $^{102}_{44}Ru$, stable, even proton, even neutron; $^{92}_{44}Ru$, radioactive, low neutron/proton ratio (**b**) $^{138}_{56}Ba$, stable, even proton, even neutron, 82 neutrons is a magic number; $^{139}_{56}Ba$; radioactive, even proton, odd neutron (**c**) $^{109}_{50}Sn$, radioactive, low neutron/proton ratio; $^{120}_{50}Sn$; stable, even proton, even neutron. **21.53** (**d**) $^{56}_{28}Ni$ **21.54** Statement (**a**) is the best explanation. **21.55** Statement (**b**) is the best explanation.
21.56 (**a**) $^{239}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{0}_{-1}e + {}^{240}_{95}Am$ (**b**) $^{238}_{92}U + {}^{4}_{2}He \rightarrow 3\ {}^{1}_{0}n + {}^{239}_{94}U$
(**c**) $^{218}_{85}At \rightarrow {}^{0}_{-1}e + {}^{218}_{86}Rn$
(**d**) $^{146}_{62}Sm \rightarrow {}^{142}_{60}Nd + {}^{4}_{2}He$ (**e**) $^{118}_{53}I + {}^{0}_{-1}e \rightarrow {}^{118}_{52}Te$
21.57 (**a**) $^{238}_{92}U + {}^{4}_{2}He \longrightarrow {}^{241}_{94}Pu + {}^{1}_{0}n$
(**b**) $^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$ (**c**) $^{56}_{26}Fe + {}^{4}_{2}He \longrightarrow {}^{60}_{29}Cu + {}^{0}_{-1}e$
21.58 (**a**) True (**b**) false (**c**) true **21.59** When the watch is 50 years old, only 6% of the tritium remains. The dial will be dimmed by 94%. **21.60** The source must be replaced after 2.18 yr or 26.2 months; this corresponds to August 2018. **21.61** (**a**) 1.1×10^{11} alpha particles emitted in 5.0 min (**b**) 9.9 mCi
21.62 $k = 1.213 \times 10^{-4}\ yr^{-1}$; $t = 8.99 \times 10^3$ yr **21.63** 0.817 mg **21.65** 9×10^6 kJ
21.67 $\Delta m = 0.2414960$ u, $\Delta E = 3.604129 \times 10^{-11}$ J/^{27}Al nucleus required, 8.044234×10^{13} J/100 g ^{27}Al **21.68** (**a**) Nuclear mass: ^2H, 2.013553 u; ^4He, 4.001505 u; ^6Li, 6.0134771 u
(**b**) nuclear binding energy: ^2H, 3.564×10^{-13} J; ^4He, 4.5336×10^{-12} J; ^6Li, 5.12602×10^{-12} J. (**c**) binding energy/nucleon: ^2H, 1.782×10^{-13} J/nucleon; ^4He, 1.1334×10^{-12} J/nucleon; ^6Li, 8.54337×10^{-13} J/nucleon. (**d**) Of the three isotopes, ^4He has the largest binding energy per nucleon; this anomaly is apparent in Figure 12.12. The trend in binding energy/nucleon agrees with the curve in the figure. **21.71** (**a**) Characteristics (ii) and (iv) are required for a fuel in a nuclear power plant. (**b**) ^{235}U **21.72** The *control rods* in a nuclear reactor regulate the flux of neutrons to keep the reaction chain self-sustaining and also to prevent the reactor core from overheating. They are composed of materials such as boron or cadmium that absorb neutrons. **21.73** (**a**) $^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{92}_{36}Kr + {}^{141}_{56}Zn + 3{}^{1}_{0}n$
(**b**) $^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$ **21.74** $\Delta m = 0.006627$ g/mol;
$\Delta E = 5.956 \times 10^{11}$ J $= 5.956 \times 10^8$ kJ/mol ^1H **21.76** (**a**) Boiling water reactor (**b**) fast breeder reactor (**c**) gas-cooled reactor
21.78 (**a**) 5.3×10^8 dis/s, 5.3×10^8 Bq
(**b**) 6.1×10^2 mrad, 6.1×10^{-3} Gy
(**c**) 5.8×10^3 mrem, 5.8×10^{-2} Sv **21.80** $^{205}_{81}Tl$ **21.82**
(**a**) $^{36}_{17}Cl \longrightarrow {}^{36}_{18}Ar + {}^{0}_{-1}e$ (**b**) ^{35}Cl and ^{37}Cl both have an odd number of protons but an even number of neutrons. ^{36}Cl has an odd number of protons and neutrons, so it is less stable than the other two isotopes. **21.84** (**a**) $^{12}_{6}C + {}^{12}_{6}C \rightarrow {}^{20}_{10}Ne + {}^{4}_{2}He$
(**b**) $^{6}_{3}Li + {}^{63}_{28}Ni \rightarrow {}^{69}_{31}Ga$
(**c**) $^{252}_{98}Cf + {}^{10}_{5}B \rightarrow {}^{262}_{103}Lr$
(**d**) $^{238}_{92}U + {}^{12}_{6}C \rightarrow {}^{246}_{98}Cf + 4\ {}^{1}_{0}n$
21.90 ^7Be, 8.612×10^{-13} J/nucleon; ^9Be, 1.035×10^{-12} J/nucleon; ^{10}Be: 1.042×10^{-12} J/nucleon. The binding energies/ nucleon for ^9Be and ^{10}Be are very similar; that for ^{10}Be is slightly higher. **21.96** 1.688×10^4 kg CH_4

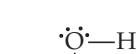
Chapter 22

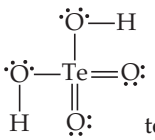
22.7 (**a**) ^1H, protium; ^2H, deuterium; ^3H, tritium (**b**) in order of decreasing natural abundance: protium > deuterium > tritium
(**c**) Tritium, ^3H, is radioactive. (**d**) $^{3}_{1}H \longrightarrow {}^{3}_{2}He + {}^{0}_{-1}e$
22.46 Statement (**c**) is correct. **22.48** Molecules (**b**) and (**d**) will have the seesaw structure shown in the figure. **22.51** The graph shows the trend in (**c**) density for the group 16 elements. Going down the family, atomic mass increases faster than atomic volume (radius), and density increases. **22.54** The compound on the left, with the strained three-membered ring, will be the most generally reactive. The larger the deviation from ideal bond angles, the more strain in the molecule and the more generally reactive it is. **22.56** Metals: (**b**) Ba (**d**) Cs, (**e**) Y; nonmetals: (**c**) Ar, (**f**) At; metalloids: (**a**) B **22.57** (**a**) F (**b**) Te (**c**) Rb (**d**) N (**e**) Ir (**f**) Si **22.58** Statements (**b**) and (**d**) are true.
22.59 (**a**) $NaOCH_3(s) + H_2O(l) \longrightarrow NaOH(aq) + CH_3OH(aq)$
(**b**) $CuO(s) + 2\ HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l)$
(**c**) $WO_3(s) + 3\ H_2(g) \xrightarrow{\Delta} W(s) + 3H_2O(g)$

(**d**) $4\ NH_2OH(l) + O_2(g) \longrightarrow 6\ H_2O(l) + 2\ N_2(g)$
(**e**) $Al_4C_3(s) + 12\ H_2O(l) \longrightarrow 4\ Al(OH)_3(s) + 3\ CH_4(g)$
22.61 Like other elements in group 1, hydrogen has only one valence electron and its most common oxidation number is +1.
22.62 (**a**) $NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$
(**b**) $Fe(s) + H_2SO_4(aq) \longrightarrow Fe^{2+}(aq) + H_2(g) + SO_4^{2-}(aq)$
(**c**) $H_2(g) + Br_2(g) \longrightarrow 2\ HBr(g)$
(**d**) $2\ Na(l) + H_2(g) \longrightarrow 2\ NaH(s)$
(**e**) $PbO(s) + H_2(g) \xrightarrow{\Delta} Pb(s) + H_2O(g)$ **22.63** (**a**) Molecular (nonmetal hydride) **(b)** ionic (metal hydride) **(c)** metallic (nonstoichiometric transition metal hydride) **22.64** Vehicle fuels produce energy via combustion reactions. The combustion of hydrogen is very exothermic and its only product, H_2O, is a non-pollutant. **22.65** Xenon has a lower ionization energy than argon; because the valence electrons are not as strongly attracted to the nucleus, they are more readily promoted to a state in which the atom can form bonds with fluorine. Also, Xe is larger and can more easily accommodate an expanded octet of electrons. **22.66** (**a**) XeO_3F_2, Xe, +8 (**b**) ClO_2 Cl, +4 (**c**) MoF_6, F, −1 (**d**) HlO_3, l, +5 (**e**) NaOBr, Br, +1 (**f**) $Mg(lO_2)_2$, l, +3 **22.67** (**a**) Cobalt(III) Iodate, I, +5 (**b**) calcium periodate, I, +7 (**c**) phosphorus hexafluoride F, −1 (**d**) iodine trichloride I, +5 Cl, −1 (**e**) hypobromous acid, Br: +1 (**f**) hydrogen astatide, At, −1 **22.68** (**a**) van der Waals intermolecular attractive forces increase with increasing number of electrons in the atoms. (**b**) F_2 reacts with water: $F_2(g) + H_2O(l) \longrightarrow 2\ HF(g) + O_2(g)$. That is, fluorine is too strong an oxidizing agent to exist in water. (**c**) HF has extensive hydrogen bonding. (**d**) Oxidizing power is related to electronegativity. Electronegativity and oxidizing power decrease in the order given.
22.69 (**a**) $2\ HgO(s) \xrightarrow{\Delta} 2\ Hg(l) + O_2(g)$
(**b**) $2\ Cu(NO_3)_2(s) \xrightarrow{\Delta} 2\ CuO(s) + 4\ NO_2(g) + O_2(g)$
(**c**) $PbS(s) + 4\ O_3(g) \longrightarrow PbSO_4(s) + 4\ O_2(g)$
(**d**) $2\ ZnS(s) + 3\ O_2(g) \longrightarrow 2\ ZnO(s) + 2\ SO_2(g)$
(**e**) $2\ K_2O_2(s) + 2\ CO_2(g) \longrightarrow 2\ K_2CO_3(s) + O_2(g)$
(**f**) $3\ O_2(g) \xrightarrow{h\nu} 2\ O_3(g)$ **22.70** (**a**) Acidic (**b**) basic (**c**) amphoteric (**d**) amphoteric **22.71** (**a**) K_2O_2, O, −1 (**b**) $K_2S_2O_3$, O, −2; S, +2 (**c**) $SeOCl_2$, O, −2; Se, +4 (**d**) Na_2Te, Te, −2 (**e**) $MgSO_3$, O, −2; S, +4 (**f**) SeF_6, Se, +6
22.72 (**a**) $2\ Fe^{3+}(aq) + H_2S(aq) \longrightarrow 2\ Fe^{2+}(aq) + S(s) + 2\ H^+(aq)$
(**b**) $Br_2(l) + H_2S(aq) \longrightarrow 2\ Br^-(aq) + S(s) + 2\ H^+(aq)$
(**c**) $2\ MnO_4^-(aq) + 6\ H^+(aq) + 5\ H_2S(aq) \longrightarrow 2\ Mn^{2+}(aq) + 5\ S(s) + 8\ H_2O(l)$
(**d**) $2\ NO_3^-(aq) + H_2S(aq) + 2\ H^+(aq) \longrightarrow 2\ NO_2(aq) + S(s) + 2\ H_2O(l)$

22.73

(**a**)  trigonal pyramidal

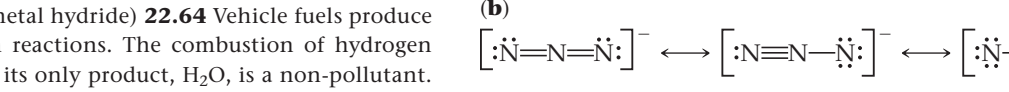
(**b**)  linear

(**c**)  tetrahedral

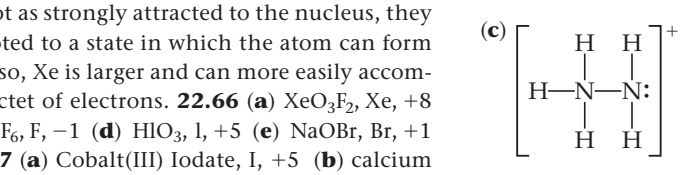
22.74
(**a**) $SO_2(s) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$
(**b**) $ZnS(s) + 2\ HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$
(**c**) $8\ SO_3^{2-}(aq) + S_8(s) \longrightarrow 8\ S_2O_3^{2-}(aq)$
(**d**) $SO_3(aq) + H_2SO_4(l) \longrightarrow H_2S_2O_7(l)$ **22.75** (**a**) NaN_3, −1/3 (**b**) NH_4^+, −3 (**c**) HNO_2, +3 (**d**) Mg_3N_2, −3 (**e**) N_2H_2, −1 (**f**) $NaNO_3$, +5 (**g**) NF_3, +3 (**h**) HNO_3, +5

22.76 (**a**) 

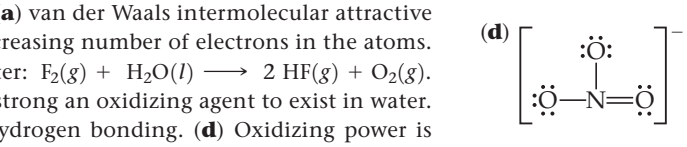
The molecule is bent around the central oxygen and nitrogen atoms; the four atoms need not be coplanar. The right-most form does not minimize formal charges and is less important in the actual bonding model. The oxidation state of N is + 3.
(**b**)



The molecule is linear. The oxidation state of N is −1/3.

(**c**) 

The geometry is tetrahedral around the left nitrogen, trigonal pyramidal around the right. The oxidation state of N is −2.

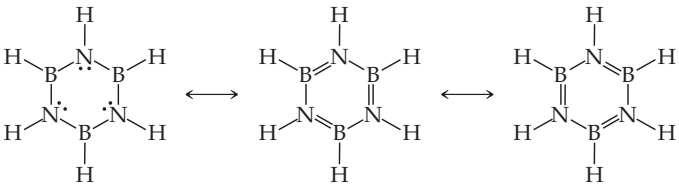
(**d**) 

The ion is trigonal planar; it has three equivalent resonance forms. The oxidation state of N is +5.

22.77 (**a**) $Mg_3N_2(s) + 6\ H_2O(l) \longrightarrow 3\ Mg(OH)_2(s) + 2\ NH_3(aq)$
(**b**) $2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$, redox reaction
(**c**) $N_2O_5(g) + H_2O(l) \longrightarrow 2\ H^+(aq) + 2\ NO_3^-(aq)$
(**d**) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$
(**e**) $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\ H_2O(g)$, redox reaction
22.78 (**a**) $HNO_2(aq) + H_2O(l) \longrightarrow NO_3^-(aq) + 2\ e^-$
(**b**) $N_2(g) + H_2O(l) \longrightarrow N_2O(aq) + 2\ H^+(aq) + 2\ e^-$
22.79 (**a**) SbF_6^-, +5 (**b**) $Ca_3(PO_4)_2$, +5 (**c**) KH_2PO_4, +5 (**d**) As_2O_3, +3 (**e**) P_4O_6, +3 (**f**) AsF_3, +3 **22.80** (**a**) Phosphorus is a larger atom than nitrogen, and P has energetically available 3*d* orbitals, which participate in the bonding, but nitrogen does not. (**b**) Only one of the three hydrogens in H_3PO_2 is bonded to oxygen. The other two are bonded directly to phosphorus and are not easily ionized. (**c**) PH_3 is a weaker base than H_2O so any attempt to add H^+ to PH_3 in the presence of H_2O causes protonation of H_2O. (**d**) The P_4 molecules in white phosphorus have more severely strained bond angles than the chains in red phosphorus, causing white phosphorus to be more reactive.
22.81
(**a**) $2\ Ca_3PO_4(s) + 6\ SiO_2(s) + 10\ C(s) \longrightarrow P_4(g) + 6\ CaSiO_3(l) + 10\ CO(g)$ (**b**) $PBr_3(l) + 3\ H_2O(l) \longrightarrow H_3PO_3(aq) + 3\ HBr(aq)$
(**c**) $4\ PBr_3(g) + 6\ H_2(g) \longrightarrow P_4(g) + 12\ HBr(g)$
22.82 (**a**) $CuCO_3$ (**b**) CO (**c**) $Mg(HCO_3)_2$ (**d**) Li_2C_2 (**e**) CF_4
22.83 (**a**) $ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$
(**b**) $BaC_2(s) + 2\ H_2O(l) \longrightarrow Ba^{2+}(aq) + 2\ OH^-(aq) + C_2H_2(g)$
(**c**) $2\ C_2H_2(g) + 5\ O_2(g) \longrightarrow 4\ CO_2 + (g) + 2\ H_2O(g)$
(**d**) $CS_2(g) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)$
(**e**) $Ca(CN)_2(s) + 2\ HBr(aq) \longrightarrow CaBr_2(aq) + 2\ HCN(aq)$
22.84 (**a**) $2\ CH_4(g) + 2\ NH_3(g) + 3\ O_2(g) \xrightarrow{800°C} 2\ HCN(g) + 6\ H_2O(g)$
(**b**) $NaHCO_3(s) + H^+(aq) \longrightarrow CO_2(g) + H_2O(l) + Na^+(aq)$
(**c**) $2\ BaCO_3(s) + O_2(g) + 2\ SO_2(g) \longrightarrow 2\ BaSO_4(s) + 2\ CO_2(g)$
22.85 (**a**) Carbon (**b**) silicon (**c**) lead **22.86** (**a**) Tetrahedral (**b**) Metasilicic acid will probably adopt the single-strand silicate chain structure

shown in Figure 22.32 (**b**). The Si to O ratio is correct and there are two terminal O atoms per Si that can accommodate the two H atoms associated with each Si atom of the acid. **22.87** (**a**) Two Ca^{2+} (**b**) two OH^- **22.88** (**a**) SiH_4, −4 (**b**) $GeCl_2$, +2 (**c**) SnS, +2 (**d**) $NaBH_4$, B: +3 (**e**) $Pb(NO_3)_4$, Pb: +4 (**f**) SnO_2, +4 **22.89** (**a**) Diborane has bridging H atoms linking the two B atoms. The structure of ethane has the C atoms bound directly, with no bridging atoms. (**b**) B_2H_6 is an electron-deficient molecule. The 6 valence electron pairs are all involved in B—H sigma bonding, so the only way to satisfy the octet rule at B is to have the bridging H atoms shown in Figure 22.35. (**c**) The term *hydridic* indicates that the H atoms in B_2H_6 have more than the usual amount of electron density for a covalently bound H atom. **22.90** (**a**) False (**b**) true (**c**) false (**d**) true (**e**) true (**f**) true (**g**) false **22.93** (**a**) SO_3 (**b**) Cl_2O_5 (**c**) N_2O_3 (**d**) CO_2 (**e**) P_2O_5 **22.96** (**a**) PO_6^-, $^+5$; NF_3, +3 (**b**) According to the Octet rule, because N is a period 2 element which has 5 valance electrons, it can only form 4 covalent bonds at the most. Therefore, it cannot form an NF_6^- anion. In contrast, P is a period 3 element which can use the d orbitals in hybridization to form covalent bonds with 6 fluorine atoms. Therefore, a stable PF_6^- anion can be formed. **22.102** (**a**) 1.94×10^3 g H_2 (**b**) 2.16×10^4 L H_2 (**c**) 2.76×10^5 kJ **22.104** (**a**) −285.83 kJ/mol H_2; −890.4 kJ/mol CH_4 (**b**) −141.79 kJ/g H_2; −55.50 kJ/g CH_4 (**c**) 1.276×10^4 kJ/m^3 H_2; 3.975×10^4 kJ/m^3 CH_4 **22.105** (**a**) $[HClO] = 0.036\ M$ (**b**) pH = 1.4 **22.109** (**a**) $CaCO_3(s) + SO_2(g) \longrightarrow CaSO_3(s) + CO_2(g)$ (**b**) 249.7 kg (**c**) 55.9 m^3 **22.111** The average bond enthalpies are H—O, 463 kJ; H—S, 367 kJ; H—Se, 317 kJ; H—Te, 267 kJ. The H—X bond enthalpy decreases steadily in the series. The origin of this effect is probably the increasing size of the orbital from X with which the hydrogen 1*s* orbital must overlap. **22.114** Dimethylhydrazine produces 0.0369 mol gas per gram of reactants, while methylhydrazine produces 0.0388 mol gas per gram of reactants. Methylhydrazine has marginally greater thrust. **22.115** (**a**) $3\ B_2H_6(g) + 6\ NH_3(g) \longrightarrow 2\ (BH)_3(NH)_3(l) + 12\ H_2(g)$; $3\ LiBH_4(s) + 3\ NH_4Cl(s) \longrightarrow 2\ (BH)_3(NH)_3(l) + 9\ H_2(g) + 3\ LiCl(s)$

(**b**)

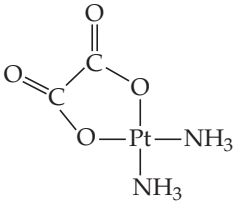


(**c**) 2.40 g $(BH)_3(NH)_3$

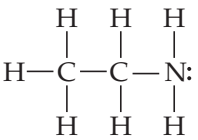
Chapter 23

23.3 (**a**) Cu^{2+}, $[Ar]3d^9$ (**b**) Cu^+, $[Ar]3d^{10}$ (**c**) V^{5+}, [Ar] (**d**) Mn^{2+}, $[Ar]3d^5$

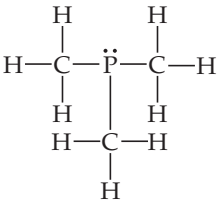
23.35



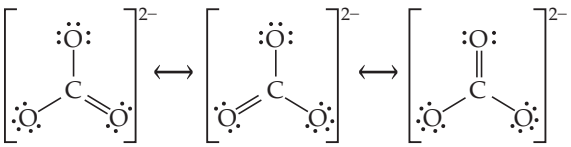
(**a**) Coordination number is 4 (**b**) coordination geometry is square planar (**c**) oxidation state is +2 (**d**) no unpaired electrons **23.39** Molecules (1), (3), and (4) are chiral because their mirror images are not superimposible on the original molecules. **23.41** (**a**) Diagram (4) (**b**) diagram (1) (**c**) diagram (3) (**d**) diagram (2) **23.44** The lanthanide contraction explains trend (**c**). The lanthanide contraction is the name given to the decrease in atomic size due to the build-up in effective nuclear charge as we move through the lanthanides and beyond them. This effect offsets the expected increase in atomic size going from period 5 to period 6 transition elements. **23.46** (**a**) Sc^{2+}, $[Ar]3d^1$ (**b**) Mo^{2+}, $[Kr]4d^4$ (**c**) Rh^{3+}, $[Kr]4d^6$ (**d**) Fe^{3+}, $[Ar]3d^5$ **23.47** (**a**) The unpaired electrons in a paramagnetic material cause it to be weakly attracted into a magnetic field. **23.48** The diagram shows a material with misaligned spins that become aligned in the direction of an applied magnetic field. This is a paramagnetic material. **23.50** (**a**) *Primary valence* is roughly the same as oxidation number. Oxidation number is a broader term than ionic charge, but Werner's complexes contain metal ions where cation charge and oxidation number are equal. (**b**) Coordination number is the modern term for secondary valence. (**c**) NH_3 can serve as a ligand because it has an unshared electron pair, while BH_3 does not. Ligands are the Lewis base in metal–ligand interactions. As such, they must possess at least one unshared electron pair. **23.51** (**a**) +2 (**b**) 6 (**c**) 2 mol AgBr(s) will precipitate per mole of complex. **23.52** (**a**) Coordination number = 6, oxidation number = +2 (**b**) 4, +7 (**c**) 4, +2 (**d**) 6, +3 (**e**) 4, +1 (**f**) 4, +2 **23.53** (**a**) Monodentate ligand



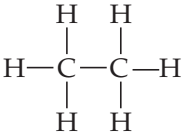
(**b**) monodentate ligand



(**c**) either monodentate or bidentate ligand



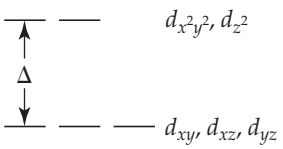
(**d**) unlikely to act as a ligand



23.54 (**a**) Ethylenediaminetetraacetate, EDTA is hexadentate (**b**) oxalate, $C_2O_4^{2-}$, is bidentate (**c**) ethylenediamine, en, is bidentate (**d**) ortho-Phenanthroline, o-phen, is bidentate. **23.55** (**a**) CO_3^{2-} (**b**) H_2O (**c**) PH_3 **23.56** True. The ligand shown in the figure can act as a bidentate ligand for a single metal center. The CH_2 groups between the two oxygen atoms are sp^3 hybridized and allow some bending in the molecule so that the two oxygen atoms can approach one single metal center simultaneously for chelation. **23.57** (**a**) $[Cr(NH_3)_3(H_2O)_3](NO_3)_3$ (**b**) $[Pt(en)Cl_2]$ (**c**) $[Fe(CO)_5]$ (**d**) $(NH_4)_2[CO(C_2O_4)_2(H_2O)_2]$

(**e**) $[Co(bipy)_3]_2(SO_4)_3$ **23.58** (**a**) diamminesilver(I) nitrate (**b**) mercury(II) tetrathiocyanatocobaltate(II) (**c**) trichlorotris (triphenylphosphine)ruthenium(III) (**d**) pentaamminecarbonatocobalt(III) sulphate **23.59** (**a**) Complexes 1, 2, and 3 can have geometric isomers; they each have *cis-trans* isomers. (**b**) Complex 2 can have linkage isomers, owing to the presence of the nitrite ligand. (**c**) The *cis* geometric isomer of complex 3 can have optical isomers (**d**) Complex 1 can have coordination sphere isomers. It is the only complex with a counter ion that can also be a ligand. **23.60** Yes. No structural or stereoisomers are possible for a tetrahedral complex of the form MA_2B_2. The complex must be square planar with *cis* and *trans* geometric isomers. **23.61** (**a**) Unique structure, no other isomers (**b**) two geometric isomers, *trans* and *cis* isomers with 180° and 90° Cl—Ir—Cl angles, respectively (**c**) three geometric isomers; *trans* and *cis* isomers with 180° and 90° Cl—Fe—Cl angles, respectively; the *cis* isomer has enantiomers **23.62** (**a**) Not chiral (**b**) not chiral (**c**) chiral, has optical isomers **23.63** (**a**) Blue (**b**) $E = 3.26 \times 10^{-19}$ J/photon (**c**) $E = 196$ kJ/mol **23.64** (**a**) Co^{3+}, $[Ar]3d^6$. No unpaired electrons. (**b**) W^{3+}, $[Xe]4f^{14}d^3$. Paramagnetic. (**c**) V^{3+}, $[Ar]3d^2$. Paramagnetic. (**d**) Rh^{3+}, $[Kr]4d^6$ Diamagnetic. **23.65** An electron in a *d* orbital with lobes that point directly at the ligands will have higher energy than an electron in a *d* orbital with lobes that do not point directly at the ligands.

23.66 (**a**)



(**b**) The magnitude of Δ and the energy of the *d-d* transition for a d^1 complex are equal. (**c**) $\Delta = 220$ kJ/mol **23.67** (**a**) Both minerals contain Cu^{2+}, $[Ar]3d^9$. (**b**) Azurite will probably have the larger Δ. It absorbs orange visible light, which has shorter wavelengths than the red light absorbed by malachite. **23.68** (**a**) Pt^{3+}, d^8 (**b**) Cu^{2+}, d^9 (**c**) Os^{3+}, d^5 (**d**) Cr^{2+}, d^4 (**e**) Cd^{2+}, d^{10} **23.69** Yes. A weak-field ligand leads to a small Δ value and a small *d*-orbital splitting energy. If the splitting energy of a complex is smaller than the energy required to pair electrons in an orbital, the complex is high spin. **23.70** (**a**) Mn, $[Ar]4s^23d^5$; Mn^{2+}, $[Ar]3d^5$; 1 unpaired electron



(**b**) Ru, $[Kr]5s^14d^7$; Ru^{2+}, $[Kr]4d^6$; 0 unpaired electrons

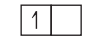


(**c**) Rh, $[Kr]5s^14d^8$; Rh^{2+}, $[Kr]4d^7$; 1 unpaired electron



23.71 All complexes in this exercise are six-coordinate octahedral.

(**a**)



d^4, high spin

(**b**)



d^5, high spin

(**c**)



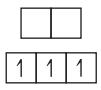
d^6, low spin

(**d**)



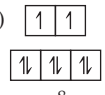
d^5, low spin

(**e**)



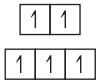
d^3

(**f**)



d^8

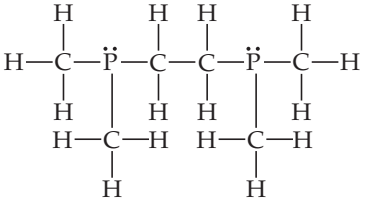
23.72



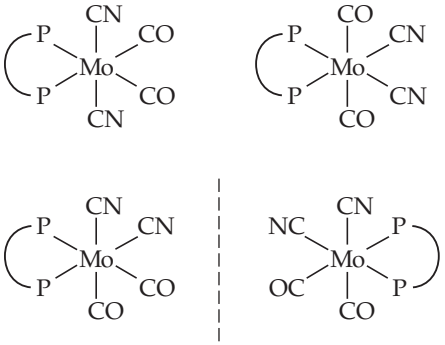
high spin

23.75 $[Pt(NH_3)_6]Cl_4$; $[Pt(NH_3)_4Cl_2]Cl_2$; $[Pt(NH_3)_3Cl_3]Cl$; $[Pt(NH_3)_2Cl_4]$; $K[Pt(NH_3)Cl_5]$

23.79



Both dmpe and en are bidentate ligands, binding through P and N, respectively. Because phosphorus is less electronegative than N, dmpe is a stronger electron pair donor and Lewis base than en. Dmpe creates a stronger ligand field and is higher on the spectrochemical series. Structurally, dmpe occupies a larger volume than en. M–P bonds are longer than M—N bonds and the two $-CH_3$ groups on each P atom in dmpe create more steric hindrance than the H atoms on N in en. (**b**) The oxidation state of Mo is zero. (**c**) The symbol $\widehat{PP}$ represents the bidentate dmpe ligand.

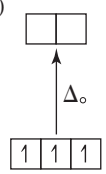


optical isomers

23.82 (**a**) Iron (**b**) magnesium (**c**) iron (**d**) copper **23.84** (**a**) Pentacarbonyliron(0) (**b**) The oxidation state of iron must be zero. (**c**) Two. One isomer has CN in an axial position and the other has it in an equatorial position.

23.86

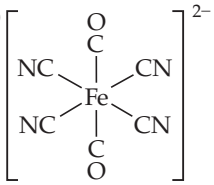
(**a**)



(**b**) These complexes are colored because the crystal-field splitting energy, Δ, is in the visible portion of the electromagnetic spectrum. Visible light with $\lambda = hc/\Delta$ is absorbed, promoting one of the

d-electrons into a higher energy *d*-orbital. The remaining wavelengths of visible light are reflected or transmitted; the combination of these wavelengths is the color we see. (**c**) $[Cr(NH_3)_6]^{3+}$ will absorb light with higher energy. NH_3 is in the middle of the spectrochemical series, and causes a larger Δ than Br^-, a weak-field ligand. Because Δ and λ are inversely related, larger Δ corresponds to higher energy and shorter λ. **23.88** $[Co(NH_3)_6]^{3+}$, yellow; $[Co(H_2O)_6]^{2+}$, pink; $[CoCl_4]^{2-}$, blue

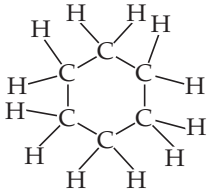
23.89 (**a**)



(**b**) sodium dicarbonyltetracyanoferrate(II) (**c**) +2, 6 *d*-electrons (**d**) We expect the complex to be low spin. Cyanide (and carbonyl) are high on the spectrochemical series, which means the complex will have a large Δ splitting, characteristic of low-spin complexes. **23.99** (**a**) Yes, the oxidation state of Co is +3 in both complexes. (**b**) Compound A has SO_4^{2-} outside the coordination sphere and coordinated Br^-, so it forms a precipitate with $BaCl_2(aq)$ but not $AgNO_3(aq)$. Compound B has Br^- outside the coordination sphere and coordinated SO_4^{2-} so it forms a precipitate with $AgNO_3(aq)$ but not $BaCl_2(aq)$. (**c**) Compounds A and B are coordination sphere isomers. (**d**) Both compounds are strong electrolytes. **23.102** The chemical formula is $[Pt(NH_3)_2Cl_2]$. This should be a neutral square-planar complex of Pt(II), a nonelectrolyte. Because it has a net dipole moment, we can infer that it must be the cis isomer. **23.104** 47.3 mg Mg^{2+}/L, 53.4 mg Ca^{2+}/L **23.106** $\Delta E = 3.30 \times 10^{-19}$ J/photon, $\lambda = 602$ nm. The complex will absorb in the visible around 600 nm and appear blue.

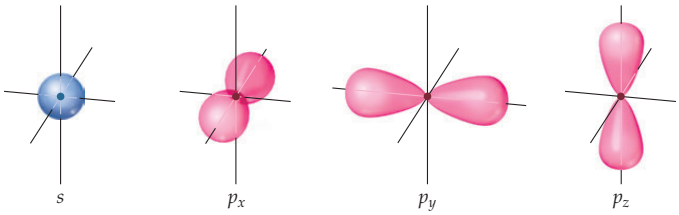
Chapter 24

24.3 The bond enthalpies in kJ mol^{-1} are: C—H, 413; C—C, 348; C—O, 358; C—CI, 328. The bond enthalpies indicate that C—H bonds are most difficult to break and C—CI bonds least difficult. However, they do not explain the reactivity of C—O bonds, or stability of C—C bonds. The reactivity of molecules containing C—O and C—CI bonds is a result of their unequal charge distribution, which attracts reactants that are either electron deficient (electrophilic) or electron rich (nucleophilic). **24.6** An empirical formula shows the simplest mole ratio of elements in a compound. For example, an empirical formula of CH_2 implies that the molecule contains only carbon and hydrogen and that they are present in a 1:2 ratio. A molecular formula shows the exact number and kinds of atoms in a molecule. For example, C_6H_{12} ($(CH_2)_6$) tells us the number of carbons and hydrogens actually found within a molecule of the compound. A structural formula shows the bonding of atoms within a molecule. In this instance, it shows that the hydrocarbon is cyclic.



24.7 (**a**) A compound that contains only hydrogen and carbon atoms. (**b**) Yes. (**c**) $CH_3CH_2CH_3$ (**d**) butane: $CH_3CH_2CH_2CH_3$, molecular formula = C_4H_{10}, empirical formula = C_2H_5. **24.9** Ethanol < hexane < palmitic acid

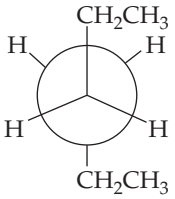
24.12



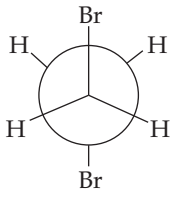
The drawings represent the probability of an electron occupying a given space. The blending (hybridisation) of all these orbitals leads to one sp^3 hybrid orbital. **24.13** Five: $CH_3CH_2CH_2CH_2CH_2CH_3$; $CH_3CH(CH_3)CH_2CH_2CH_3$; $CH_3CH_2CH(CH_3)CH_2CH_3$; $CH_3CH(CH_3)CH(CH_3)CH_3$; $CH_3C(CH_3)_2CH_2CH_3$. **24.14** Constitutional isomers have the same molecular formula but a different connectivity for the atoms. Constitutional isomers are not interconvertable without the breaking or formation of a C—C bond. For example, butane and 2-methylpropane are constitutional isomers. Conformational isomers are isomers that differ only in their three-dimensional arrangement in space by rotation about a single C—C bond; for example, the eclipsed and staggered forms of butane.

24.16

(**a**)

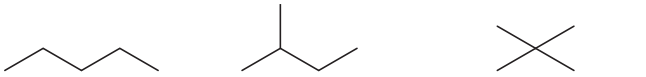


(**b**)



24.18 $CH_3CH_2CH_2$.

24.19



pentane 2-methylbutane 2,2-dimethypropane

24.25 (**a**)



cyclopentane cyclobutane

(**b**) Cyclobutane, because the sp^3 centred carbon atoms are furthest removed from a bond angle of 109.5°. **24.27** The *trans* compound (shown right) would be lowest in energy because the two methyl groups are furthest apart. The name of this structure is: *trans*-1,2-dimethylcyclopentane. **24.29** (**a**) C_8H_{16}, ethylcyclohexane (**b**) C_4H_{10}, methylpropane (**c**) C_6H_{12}, 1,2,3-trimethylcyclopropane (**d**) C_6H_{14}, 3-methylpentane

Constitutional isomers:

(**a**) (**b**)

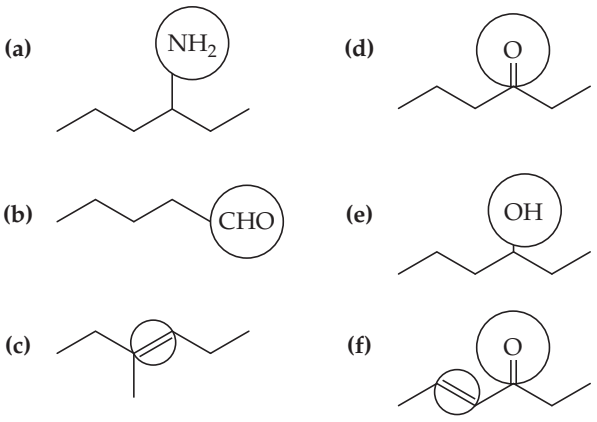


(**c**) (**d**)

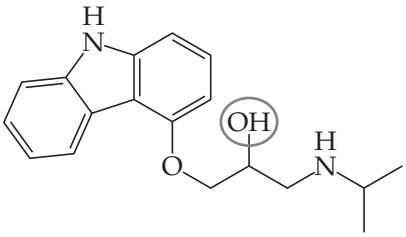


For structures (**a**), (**c**), and (**d**), other constitutional isomers are possible.

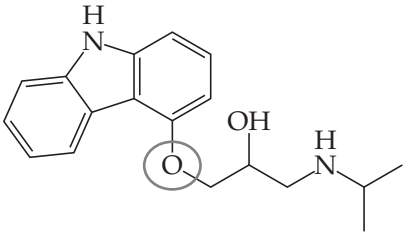
24.31



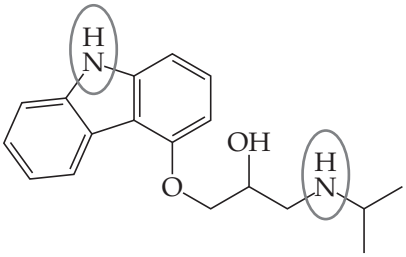
24.33 (**a**) Alcohols: 1



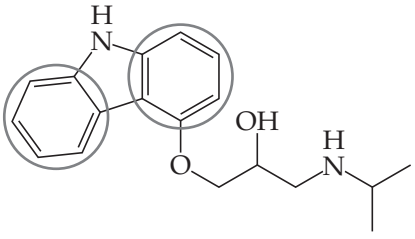
(**b**) Ethers: 1



(**c**) Amines: 2

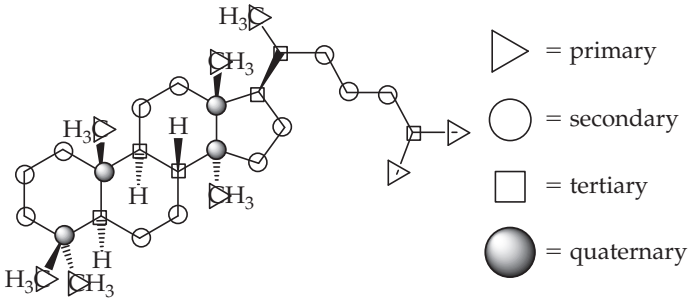


(**d**) Aromatic hydrocarbons: 2



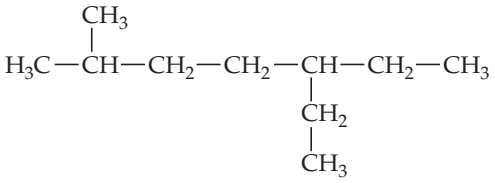
24.36 (**a**) $C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$ (**b**) $\Delta H = \Sigma$ bonds broken $- \Sigma$ bonds formed $\Delta H = (2 \times D(\text{C–C}) + 8 \times D(\text{C–H}) + 5 \times D(\text{O=O})) - (6 \times D(\text{C=O}) + 8 \times D(\text{O–H}))$ $\Delta H = 6475 - 8498$ kJ mol^{-1} $\Delta H = -2023$ kJ mol^{-1}

24.39



24.41 (**a**) Greater than 2:1 (cyclohexane:chlorine)
(**b**) The carbons (and hydrogens) in cyclohexane are all chemically equivalent (and secondary) and lead to the same product. Hexane has two types of secondary carbons which lead to two regioisomers formed. Some reaction at primary carbons also complicates matters.
24.42 (**c**) and (**d**) are the same **24.44** The end-on overlap of the atomic orbitals would form a σ-bond.

24.46



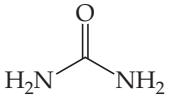
24.48



$CH_3—CHBr—CH_2—CH_2—CH_3$

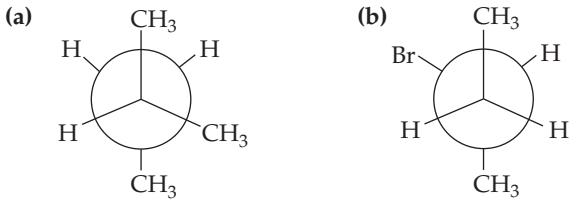
24.50 (**a**) Ether (O single bonded to two C) and two alkene groups (double bonded carbons). (**b**) Ester and five alcohols (OH groups). (**c**) Alcohol, alkene (double bonded carbons) and ketone (O double bonded to a C). (**d**) Ether, two alcohols, alkene and a tertiary amine (N bonded to three C). (Note that the ring of six carbons with three double bonds, although not covered in this chapter, is an aromatic ring, and is sometimes considered a functional group.) (**e**) Ester, two alcohols and chloroalkane.

24.52



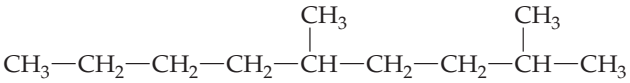
Urea would be considered an organic molecule because it is a carbon attached to two nitrogen atoms and double bonded to an oxygen atom. Thus it is a molecule containing carbon that created four bonds.

24.58

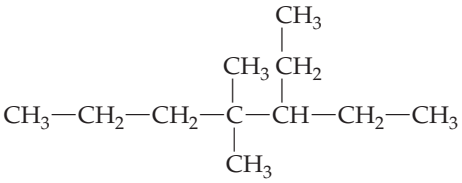


24.61 The polymer shown here is an alkane. Since molecules are more soluble in 'like' solvents, we would expect polyethylene to be more soluble in organic solvents such as hexane. **24.62** (**a**) 3,3,5-trimethylheptane (**b**) 3,4,4-trimethylheptane

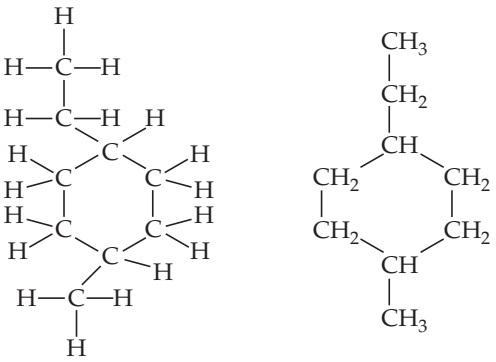
(**c**)



(**d**)

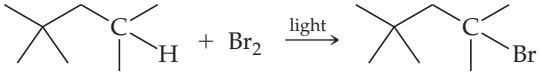


(**e**)



24.63 (**a**) 2,4-dimethylpentane (**b**) 3,5-dimethylheptane (**c**) 4-ethyl-2,4-dimethylhexane (**d**) 3-ethyl-2-methylpentane **24.64** 2,3,3-trimethylpentane **24.65** Butane and 2-methylpropane are constitutional isomers. Butane molecules are able to maximise their London dispersive forces when compared with 2-methylpropane which is more globular. The energy associated with this stabilising interaction needs to be overcome for butane to boil. The higher boiling point of butane equates to this extra energy. **24.66** ΔH_{comb}/mol CH_2 for cyclopropane = −2089/3 = 696.3 kJ, for cyclopentane = −3317/5 663.4 kJ. $\Delta H_{comb}/CH_2$ group for cyclopropane is greater because C_3H_6 contains a significantly more strained ring than C_5H_{10}. When combustion occurs, the strain is relieved and the stored energy is released. **24.68** (**a**) OH axial, Cl equatorial (**b**) all equatorial (**c**) OH and CH_3 axial (**d**) clockwise from OH - axial OH, equatorial Cl, axial CH_3, equatorial CH_3 **24.70** Cycloalkanes are able to have geometric isomerism due to the restricted (in fact, impossible) rotation about any C–C bond within the cyclic framework. Alkanes are able to rotate freely about C–C bonds and so are able to interconvert freely. Such isomers are known as conformational isomers. **24.73** (**a**) A functional group is a site of reactivity in an organic molecule (**b**) Functional groups are important because they not only provide a description of the molecule but also controls how the molecule will behave or function given certain conditions **24.76** (**a**) In a substitution reaction one atom or group of atoms replaces another atom. An oxidation reaction typically occurs with the loss of electrons within a chemical reaction. In terms of alkanes, combustion is classed as an oxidation reaction.

(**b**) The reaction is:



This substitution reaction is classed as regiospecific because it occurs preferentially at one carbon, namely the tertiary carbon.

(**c**) The reaction is:

$$C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O$$

24.78 (**a**) Then reaction is $C_6H_{12} + 9\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$. Nine moles of oxygen are required for each mole of cyclohexane. Moles of cyclohexane = 70 g / 84 g mol^{-1} = 0.83 mol Moles of $O_2 = 9 \times 0.83 = 7.5$ mol g $O_2 = 32$ g $mol^{-1} \times 7.5$ mol = 240 g (**b**) Six moles of carbon dioxide are produced for each mole of cyclohexane. Moles of $CO_2 = 6 \times 0.83 = 5.0$ mol g $CO_2 = 44$ g $mol^{-1} \times 5.0$ mol = 220 g

24.79 (**a**) Propagation

$$^{\bullet}Cl + CH_4 \longrightarrow HCl + {}^{\bullet}CH_3$$

$$^{\bullet}CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$$

$$CH_3Cl + Cl^{\bullet} \longrightarrow HCl + {}^{\bullet}CH_2Cl$$

$$^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

(**b**) Termination (for example)

$$^{\bullet}CH_3 + {}^{\bullet}CH_2Cl \longrightarrow CH_3CH_2Cl$$

$$^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$$

24.81 (**d**) >> (**c**),(**a**) > (**b**) (**d**) would be formed from a tertiary carbon, (**c**) and (**a**) from a secondary carbon, and (**b**) from a primary carbon. **24.84** *Analyse/Plan:* We are asked the number of structural isomers for two specified carbon chain lengths and a certain number of double bonds. Structural isomers have different connectivity. Since the chain length is specified, we can ignore structural isomers created by branching. We are not asked about geometrical isomers, so we can ignore those as well. The resulting question is: How many ways are there to place the specified number of double bonds along the specified C chain?

5 C chain with one double bond: 2 structural isomers

C═C—C—C—C C—C═C—C—C

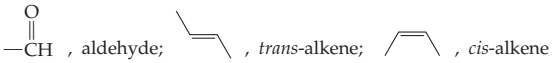
6 C chain with two double bonds: 6 structural isomers

C═C—C═C—C—C C═C—C—C═C—C C═C—C—C—C═C

C—C═C—C═C—C C═C═C—C—C—C C—C═C═C—C—C

24.86 The suffix –ene signifies an alkene, –one a ketone. The molecule has alkene and ketone functional groups.

24.88

(a)  , aldehyde; , *trans*-alkene; , *cis*-alkene

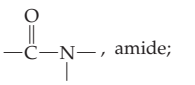
(b) —O— , ether; —OH , alcohol; C═C , alkene;

 , amine (two of these, one aliphatic and one aromatic);

 , aromatic (phenyl) ring

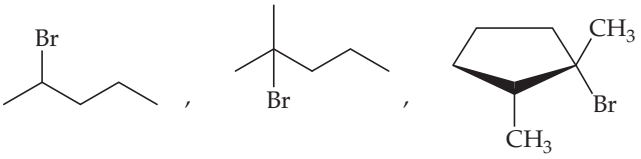
(c)  , ketone (2 of these);  , amine (2 of these)

 , aromatic (phenyl) ring (2 of these)

(d)  , amide; , aromatic (phenyl) ring;

—OH , alcohol (aromatic alcohol, phenol)

24.90 (**a**) Pentane and 2-methylbutane are constitutional isomers. More specifically they are non-superimposable mirror images of each other, which makes them enantiomers. (**b**) The two molecules shown are mirror images of each other. (**c**) 1,2-dimethylcyclopentane (**d**) The most likely point(s) for bromination will be the places where the most stable radicals are found. Thus we would expect bromination to occur most readily at a tertiary carbon if available, then secondary, and then primary. This leads to then following most likely products from bromination of pentane, 2-methylbutane, and 1,2-dimethylcyclopentane:



24.92 Determine the empirical formula, molar mass, and thus molecular formula of the compound. Confirm with physical data:

$$85.7\ \text{g C} \times \frac{1\ \text{mol}}{12.01\ \text{g}} = 7.136\ \text{mol C};\ 7.136/7.136 = 1$$

$$14.2\ \text{g H} \times \frac{1\ \text{mol}}{1.008\ \text{g}} = 14.19\ \text{mol H};\ 14.19/7.136 = 2$$

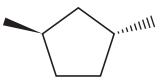
The empirical formula is CH_2. Use the relationship between molecular mass and the gas constant:

$$\frac{(2.21\ \text{g dm}^{-3})\ (0.08206\ \text{dm}^3\ \text{torr mol}^{-1}\ \text{K})\ (373\ \text{K})}{(735/760)\ \text{torr}} = 69.9\ \text{g mol}^{-1}$$

The molecular formula is this C_5H_{10}. The absence of reaction with bromine indicates the compound is not an alkene, so the compound is most likely a cycloalkane, likely cyclopentane. Physical properties such as the boiling point of cyclopentane (49° at 1 bar) can be used to confirm this deduction.

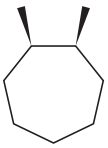
Chapter 25

25.4

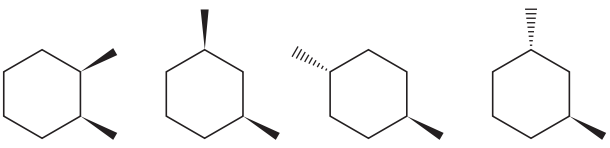


trans-1,3-dimethylcyclopentane

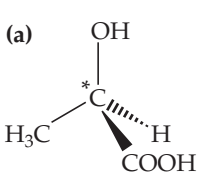
25.5



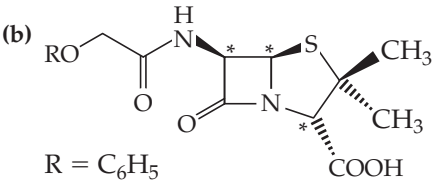
25.6
B and **D** are geometric isomers



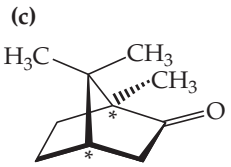
25.10 Chiral centres are marked with an asterisk.



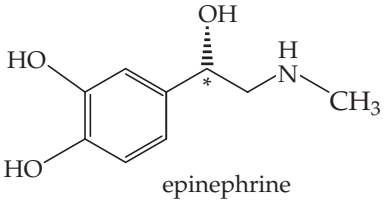
lactic acid



penicillin V

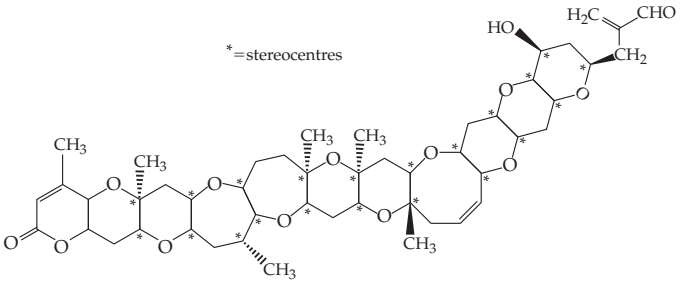


camphor



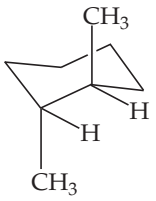
epinephrine

25.11



25.12 (**a**) and (**d**) **25.16** No. The optical rotation of a molecule can only be determined by experiment. **25.17** (**a**) *cis*-1,2-dimethylcyclopentane and *trans*-1,2-dimethylcyclopentane. All the chiral centres have absolute configuration of *S*. The *cis* isomer is achiral; it possesses a plane of symmetry.

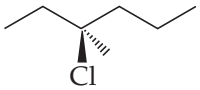
(**b**)



Both substituents are axial. This is the lowest energy conformation since the conformer with equatorial alkyl substituents would suffer from additional steric repulsion. (**c**) The structure drawn is (*1R,2R*)-*trans*-1,2-dimethylcyclohexane. ((*1S,2S*)-*trans*-1,2-dimethylcyclohexane is also possible.) **25.18** Yes, the molecule has optical isomers. The chiral carbon atom is attached to chloro, methyl, ethyl, and propyl groups. (If the root was a 5-Carbon chain, the molecule would not have optical isomers because two of the groups would be ethyl groups.)

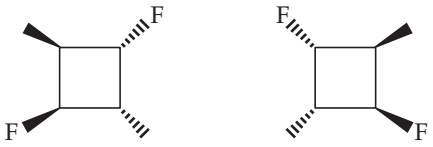


(3*R*)-3-chloro-3-methylhexane



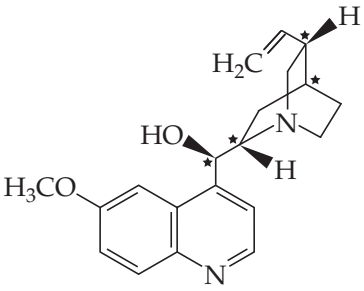
(3*S*)-3-chloro-3-methylhexane

25.20 No, it is not optical active. The structure has a centre of symmetry that can invert all atoms by mirroring into their symmetry equivalent atoms by mirroring. Therefore, the molecule is achiral and cannot be optical active.



(1*R*,2*R*,3*S*,4*S*)-1,3-difluoro-2,4-dimethylcyclobutane

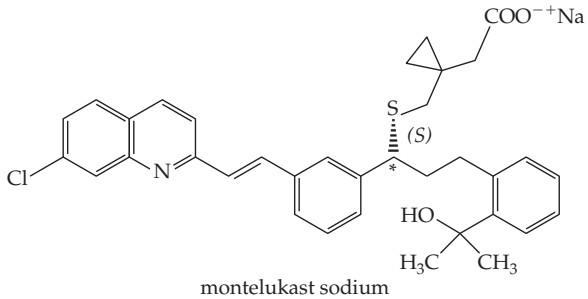
25.22 There are 4 chiral centres.



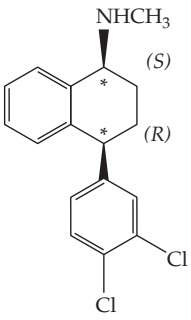
(quinine—an antimalarial drug)

Chiral centres are marked with an asterisk. **25.25** (**a**) A chiral molecule exhibiting a non-superimposable mirror image. (**b**) *R*,*S* relates to absolute stereochemistry while (*d*)–(+) and (*l*)–(–) relate to a physical measurement (optical rotation). There is no relationship between the two.

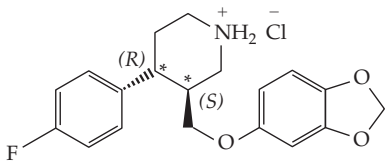
25.29



montelukast sodium
(singulair)

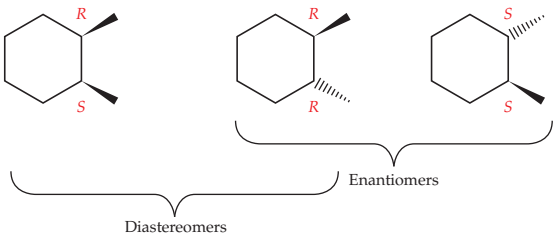


sertraline

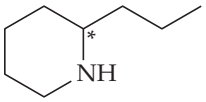


paroxetine hydrochloride

25.33

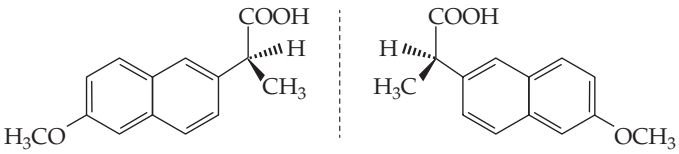


25.34 React the racemic acid with one enantiomer of a base to form two diastereomer salts. Separate the salts by, for example, crystallisation, and regenerate the acid by removal of the base. **25.36** DNA, hands, gloves, feet, socks, sea shells, and can openers, to name a few. **25.37** (**a**), (**c**), (**e**), (**f**)
25.38 (**a**) Stereocentre is marked with an asterisk.



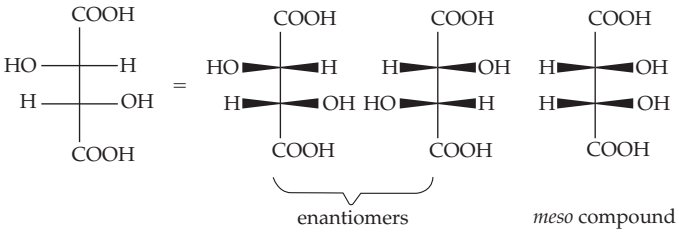
(**b**) Because nature is very specific in its use of chirality for a particular function, we would expect the enantiomer not to have the same effect, or a drastically lowered effect at best.

25.44



(S)-isomer mirror image

25.46



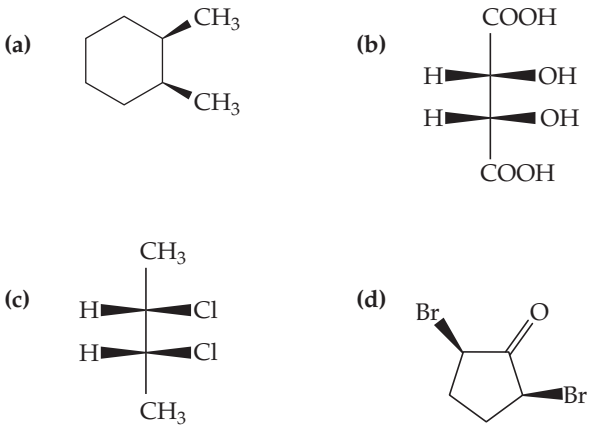
enantiomers *meso* compound

25.48 Yes, the molecule has optical isomers. The chiral carbon atom is attached to chloro, methyl, ethyl, and propyl groups. (If the root was a 5-Carbon chain, the molecule would not have optical isomers because two of the groups would be ethyl groups.)

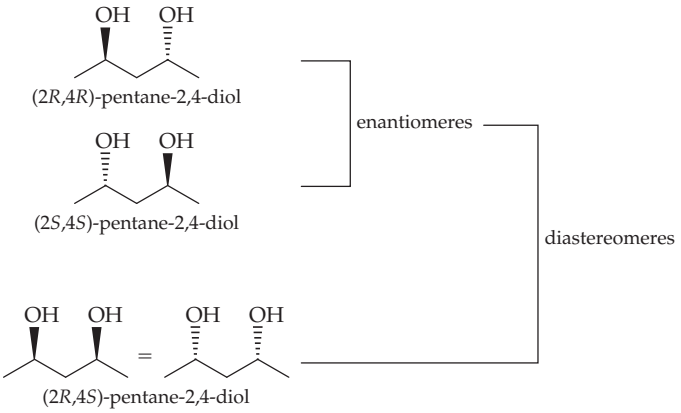


(3*R*)-3-chloro-3-methylhexane (3*S*)-3-chloro-3-methylhexane

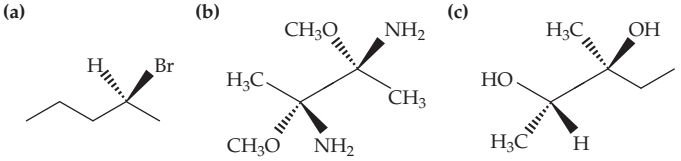
25.49



25.51



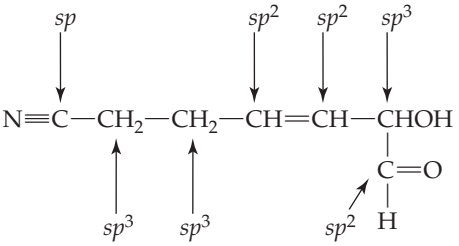
25.53



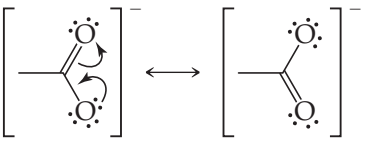
25.54 (**a**) diastereomers (**b**) enantiomers (**c**) diastereomers (**d**) identical (**e**) constitutional isomers

Chapter 26

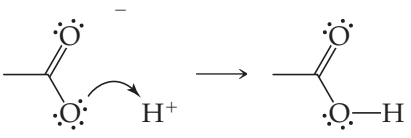
26.4 (**a**) C_5H_{12} *saturated* (**b**) C_5H_{10} *unsaturated* (**c**) C_5H_8 *unsaturated*
26.6 (**a**) 109.5° (**b**) 120° (**c**) 180°
26.7



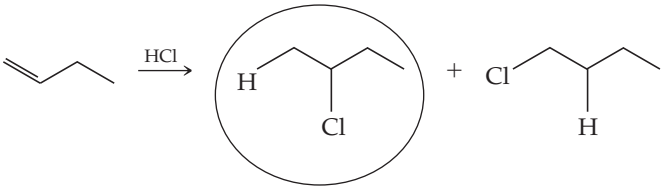
26.16



26.17

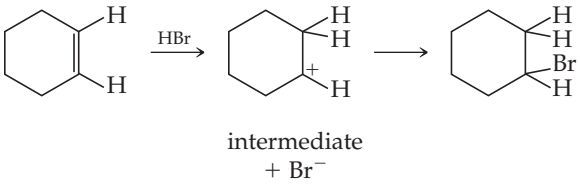


26.23 (**a**)



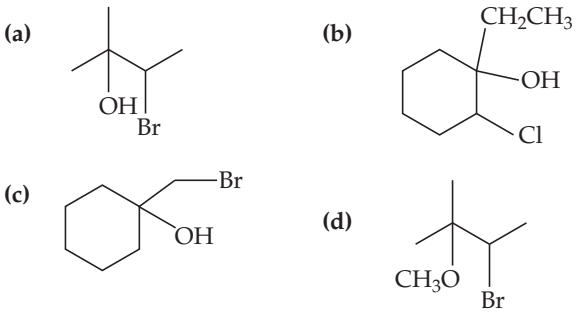
(**b**) The major product (circled) is formed from a 2° carbocation intermediate whereas the minor product would be formed from a less stable 1° carbocation intermediate.

26.24



intermediate
+ Br^-

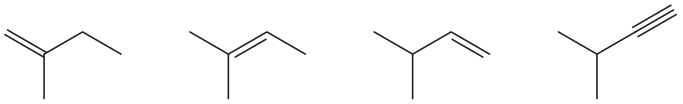
26.25 most stable (**a**) > (**c**) > (**b**) least stable
26.26



26.31



26.32 3 mol of hydrogen
26.33

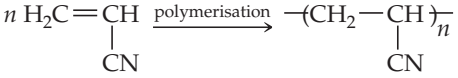


26.38 (**a**)

(a)



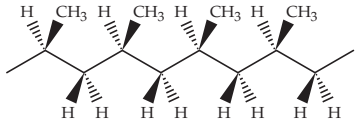
(b)



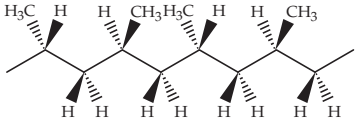
26.39 Most of a polymer backbone is composed of σ bonds. The geometry around individual atoms is tetrahedral with bond angles of 109°, so the polymer is not flat, and there is relatively free rotation around the σ-bonds. The flexibility of the molecular chains causes flexibility of the bulk material. Flexibility is enhanced by molecular features that inhibit order, such as branching, and diminished by features that encourage order, such as cross-linking or delocalised π-electron density. Cross-linking is the formation of chemical bonds between polymer chains. It reduces flexibility of the molecular chains and increases the hardness of the material. Cross-linked polymers are less chemically reactive because of the links. **26.40** (**a**) The orbitals at each carbon atom are sp^3 hybridised. The angles between the bonds are expected to be 109.5°.

(**b**)

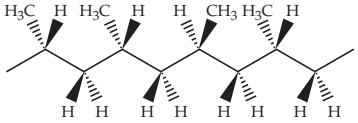
(i)



(ii)



(iii)

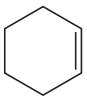


The isotactic polymer is the most crystalline and has the highest melting point (approx 175°C), as the regular arrangement of the methyl groups on the same side of the chain allows for closer packing of polymer chains. Because of the high degree of order, Van der Waals interactions also contribute to the high crystalline nature of the isotactic polymer. The syndiotactic polymer also exhibits crystallinity with a melting temperature of approximately 145°C. Due to the random arrangement of the methyl groups along the polymer chain the atactic polymer has the lowest melting point and is amorphous. (**c**) Cotton has many –OH groups along the molecular chain and as such can form hydrogen bonds with water. Polypropylene is a polymer containing only carbon and hydrogen. As such polypropylene is non-polar and does not interact with water. Hence, cotton materials absorb water while polypropylene materials repel water. **26.42** As the percentage of sulfur increases, the rubber becomes harder and less flexible. **26.43** (**c**) and (**d**) **26.45** Molecule (**c**)

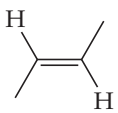
26.47



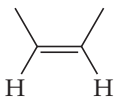
26.48 A cycloalkene is a cyclic hydrocarbon containing at least one double bond. For each double bond or ring the number of hydrogens required decreases by 2. Hence the general formula for a cycloalkene would be given by: C_nH_{2n-2}. This is the same general formula as an alkyne. Use an example to help understand what is happening:



The structure above has molecular formula: C_6H_{10}. This follows the general formula: C_nH_{2n-2} **26.50** (**a**) *trans*-hex-2-ene or (*E*)-hex-2-ene (**b**) *trans*-1-chloro-2-fluorocyclohexane (**c**) *cis*-pent-2-ene or (*Z*)-2-pentene **26.51** (**a**) Geometric (*cis/trans*) isomers: Same atoms involved in bonding, but different non-interchangeable orientations in space.

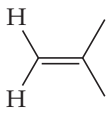


trans-but-2-ene

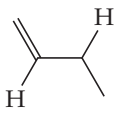


cis-2-butene

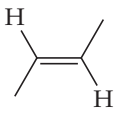
Structural (constitutional) isomers: Same molecular formula, but different bonding between atoms.



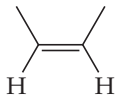
2-methylprop-1-ene



but-1-ene



(*E*)-but-2-ene

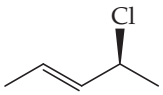


(*Z*)-but-2-ene



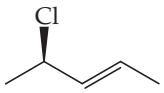
cyclobutane

(**b**) 4-chloropent-2-ene



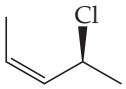
(*S,E*)-4-chloropent-2-ene

1



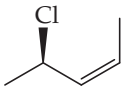
(*R,E*)-4-chloropent-2-ene

2



(*S,Z*)-4-chloropent-2-ene

3

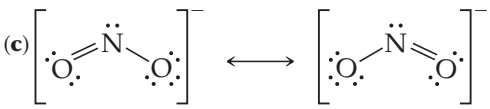


(*R,Z*)-4-chloropent-2-ene

4

The pairs 1 & 3 and 2 & 4 are geometric (*cis/trans*) isomers. The pairs 1 & 2 and 3 & 4 are enantiomers. The four isomers arise because the position of the double bond allows for *cis/trans* isomerism and the presence of a stereocentre at C4 gives R,S stereoisomerism. **26.54** (**a**) In a localised π bond, the electron density is concentrated strictly between the two atoms forming the bond. In a delocalised π bond, parallel *p* orbitals on more than two adjacent atoms overlap and the electron density is spread over all the atoms that contribute *p* orbitals to the network. There are still two regions of overlap, above and below the σ framework of the molecule. (b) The existence of more than one resonance form is a good indication that a molecule will have delocalised π bonding.

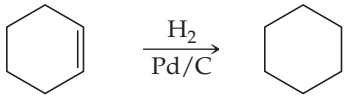
(**c**)



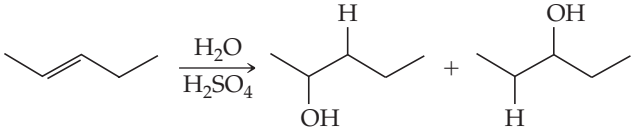
The existence of more than one resonance form for NO_2 indicates that the π bond is delocalised. From an orbital perspective, the electron-domain geometry around N is trigonal planar, so the hybridisation at N is sp^2. This leaves a *p* orbital on N and one on each O atom perpendicular to the trigonal plane of the molecule, in the correct orientation for delocalised π overlap. Physically, the two N–O bond lengths are equal, indicating that the two N–O bonds are equivalent, rather than one longer single bond and one shorter double bond.

26.55

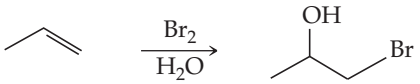
(a)



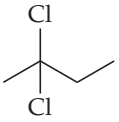
(b)



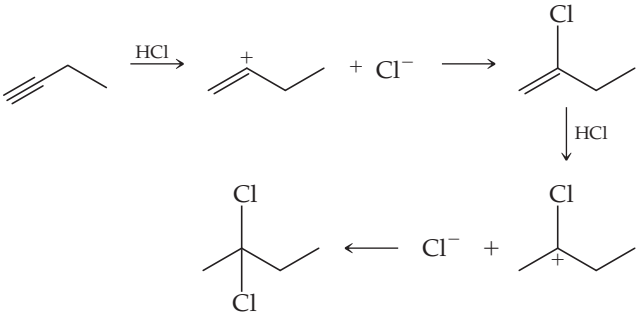
(c)



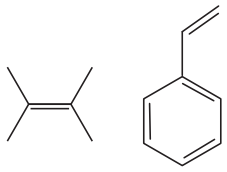
26.58 (**a**)



(**b**) One could imagine a sequence of steps as follows:



At each step, the introduction of the chlorine substituent is determined by addition of H^+ to form the most stable carbocation. **26.60** (**a**) H_2, Pd/C (**b**) Concentrated H_2SO_4/H_2O (**c**) H_2 (1 mol equivalent), Pd/C will allow formation of the alkene, but further reaction to the alkane is inevitable. A better method employs the use of a deactivated catalyst such as Lindlar's catalyst (Pd/C poisoned with $Pb(OAc)_2$ and quinoline) which allows for hydrogenation of the more reactive alkyne to the alkene, but does not allow further reduction of the alkene to the alkyne. (**d**) Excess Br_2 (**e**) Br_2 in methanol (CH_3OH) **26.63** Monomers are molecules of low molecular weight that are used as a repeating unit to construct a polymer. Some examples are:



$F_2C{=}CF_2$

Ethylene Styrene tetrafluoroethylene

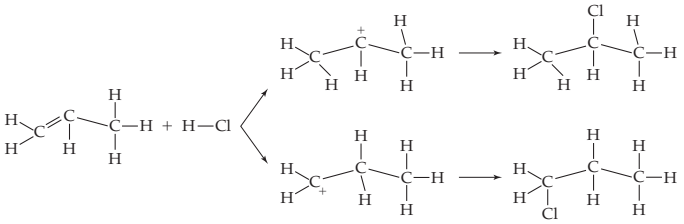
26.66 The function of the material (polymer) determines whether high molecular mass and high degree of crystallinity are desirable properties. If the material will be formed into containers or pipes, the rigidity and structural strength associated with high molecular mass are required. If the polymer will be used as a flexible wrapping or as a garment material, rigidity is an undesirable property. The viscosity of a polymer depends on its molecular weight, so it might be undesirable to have high molecular weight in a polymer adhesive solution that needs to be squeezed out of a tube, for example. **26.67** (**a**) sp^2 (**b**) The π-bond will be destroyed half way through the rotation because the two p orbitals that create it will no longer line up. (**c**) It can be assumed that the strength of the single π-bond would be the enthalpy of a carbon-carbon double bond (614 kJ mol^{-1}) minus the enthalpy of a carbon-carbon single bond (348 kJ mol^{-1}). 614 – 348 = 266 kJ mol^{-1} Since this is per mole, we would divide this value by Avogadro's number resulting in 4.419×10^{-22} kJ per bond.
(**d**)

$$\lambda = hc/E = 6.626 \times 10^{-34}\,\text{J s} \times 2.998 \times 10^{8}\,\text{m s}^{-1} \times \frac{1}{4.419 \times 10^{-19}\,\text{J}}$$

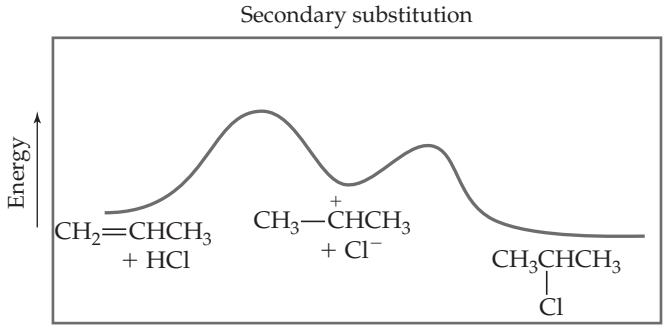
$$= 4.50 \times 10^{-7}\,\text{m} = 450\,\text{nm}$$

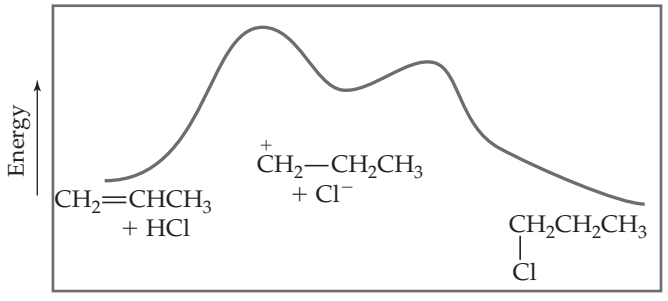
(**e**) 450 nm metres is in the visible spectrum. This is important as the visible spectrum is the portion of the electromagnetic spectrum that reacts with the rods and cones of the eye.

26.69 (**a**)



(**b**)



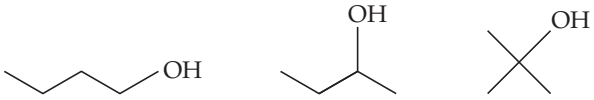


The carbocation in the secondary substitution is more stable. (**c**) If the temperature were increased, this would leave more stability to the primary carbocation, resulting in a higher proportion to the primary halogenated propane than at the previous temperature **26.71** (**a**) 3 $C_2H_2 \rightarrow C_6H_6$ (**b**) $\Delta H = \Sigma(\Delta H$ products) – $\Sigma(\Delta H$ reactants) However, since the heat of formation was given for acetylene, then sign of that value must be reversed. Thus we have the following equation: $\Delta H = 83 - 3(-227) = 764$ kJ mol^{-1}

Chapter 27

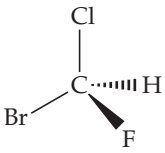
27.4 The solubility would be lower when the OH group is replaced by an OCH_3 group, because the solute can no longer act as a hydrogen-bonding donor to the water.

27.8

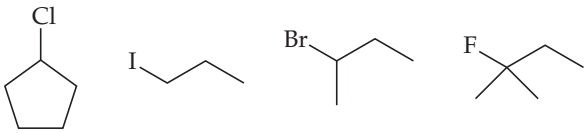


Primary Secondary Tertiary

27.10 (*R*)-bromochlorofluoromethane



27.11

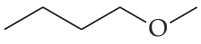


(a) **(b)** **(c)** **(d)**

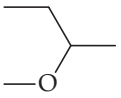
(**a**) chlorocyclopentane, secondary (**b**) 1-iodopropane, primary (**c**) 2-bromobutane, secondary (**d**) 2-fluoro-2-methylbutane, tertiary

27.14 Ethanol is able to form intermolecular hydrogen bonds, while dimethyl ether is unable to form hydrogen bonds and therefore has the lower boiling point. CH_2F_2 has an overall net dipole, which allows for intermolecular dipole-dipole interactions, while CF_4 has no net dipole because its bond dipoles cancel, so the only intermolecular interactions are weak dispersion forces, giving it a much lower boiling point than CH_2F_2.

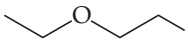
27.16



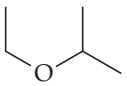
methyl butyl ether
1-ethoxypropane



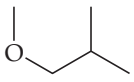
methyl (1-methylpropyl) ether or
2-methoxybutane



ethyl propyl ether or



2-ethoxypropane



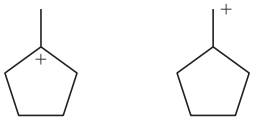
1-methoxy-2-methylpropane

27.17

- It is inert (does not react under the conditions of the experiment).
- It dissolves the solutes adequately.

27.18 The oxygen atoms can 'wrap around' the metal cations.

27.22

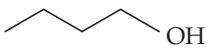


most stable least stable

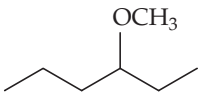
27.25 More water must be added to the reaction mixture. This would shift the equilibrium in favour of producing the alcohol.

27.28

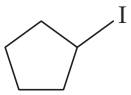
(a)



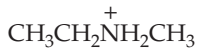
(b)



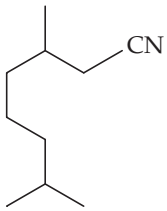
(c)



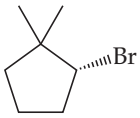
(d)



(e)

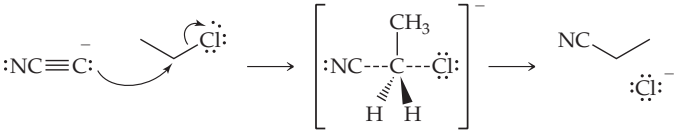


27.29



1-methoxy-2,2-dimethylcyclopentane

27.30



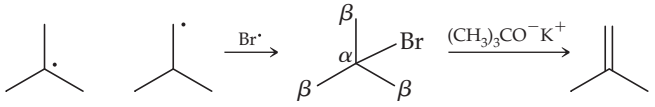
27.31 When OH^- acts as a base it is in a proton transfer reaction:
e.g. $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$
When OH^- acts as a nucleophile it is in, for example, a substitution reaction:
$CH_3I + OH^- \rightarrow CH_3OH + I$

27.32 $CH_3OH + HBr \rightarrow CH_3Br + H_2O$ and $CH_3OH + Na \rightarrow CH_3O^- + Na^+$ Combining the two products: $CH_3Br + CH_3O^- \rightarrow CH_3OCH_3 + Br^-$

27.34 2-Bromo-2-methylpentane **27.35** Either 2-chlorodecane or 3-chlorodecane could be used; however, 3-chlorodecane would form approximately equal amounts of dec-2-ene and dec-3-ene, while 2-chlorodecane would form predominately dec-2-ene. **27.36** This is a difficult one! The norbornane ring system is heavily strained as a result of the bridging CH_2 group. Having a double bond at the base of the bridge as shown below (Zaitsev product = most substituted double bond) would increase the strain even further. The geometry at the carbon found at the base of the bridge could not be trigonal planar.

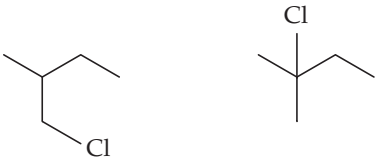


27.37 In the first step the free-radical bromination of 2-methyl propane will preferentially add the Br to the most substituted carbon (regioselective) as this comes from the most stable carbon radical (3° versus 1°).



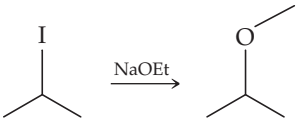
more stable radical only product

27.41

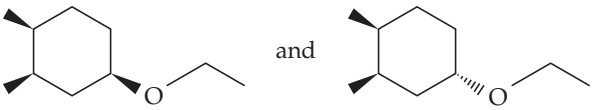


A **B**

Compound B gives the slowest S_N2 reaction. The tertiary carbon bearing the chloride is less accessible to the incoming nucleophile than the primary carbon in compound A. **27.42** (**a**) Methoxide is the stronger nucleophile because nucleophilicity is related to the rate of addition. In the gas phase, t-butoxide is a stronger base, but because it is highly sterically hindered it reacts more slowly and is not as good a nucleophile. (**b**)

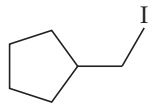


27.43 (**a**) The products will be a racemic mixture of

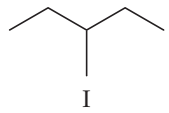


(**b**) The reaction most likely follows a S_N1 mechanism, because the reactants are a secondary haloalkane and a weak nucleophile. **27.45** The best substrate for the E2 reaction will be where the halogen is a good leaving group and where the adjacent carbon is easily accessible for deprotonation by the nucleophile. Iodide is a better leaving group than bromide which is a better leaving group than chloride, and the 2-haloalkanes provide the most accessibility at the adjacent carbons. Thus: (**a**) B is the most reactive in an E2 reaction. (**b**) D is the least reactive in an E2 reaction. **27.46** Iodine is shown in the results below, but Br or Cl would also give valid haloalkanes.

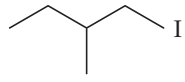
(i)



(ii)

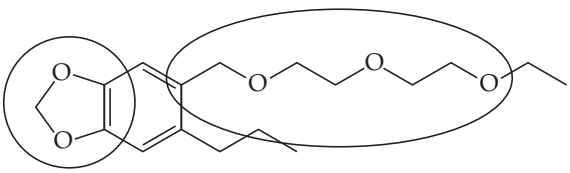


(iii)



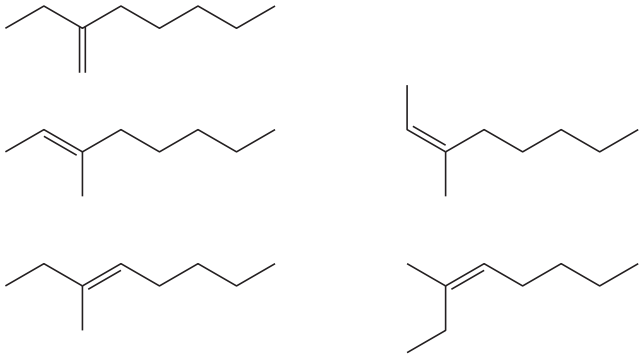
27.47 Less hindered hydrogen bonding interactions and maximisation of London dispersion forces in propan-1-ol lead to a higher boiling point.

27.49



cyclic ether acyclic polyether

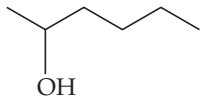
27.51 There are five possible alkene products.



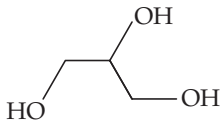
27.52 One oxygen-containing compound could be an alcohol that could participate in hydrogen bonding and so would have a higher boiling point than the corresponding ether, which is unable to participate in hydrogen bonding.

27.53

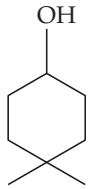
(a)



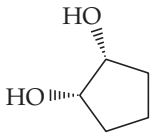
(b)



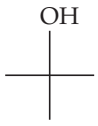
(c)



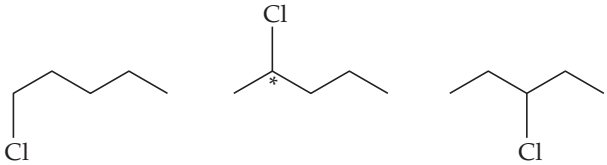
(d)



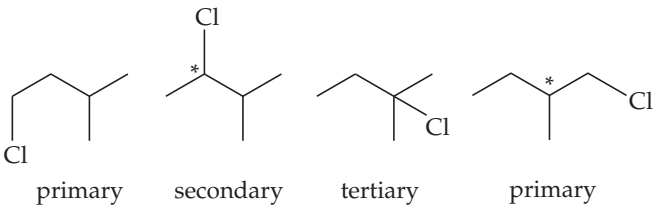
(e)

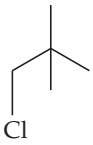


27.56



primary secondary secondary



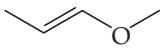


Only one isomer is a tertiary chloroalkane. (Chiral centres are marked with an asterisk.) **27.57** The carbon-chlorine bond of a haloalkane is polar because chlorine is more electronegative than carbon.

27.59 (**a**) C_4H_8O

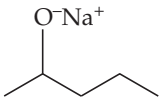


(**b**)

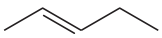


27.62

(a)

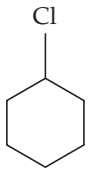


(b)

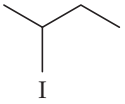


27.65

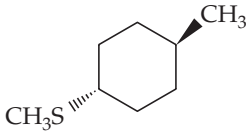
(a)



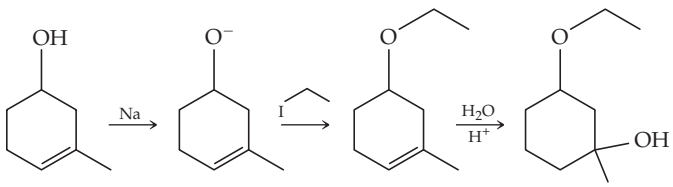
(b)



(c)

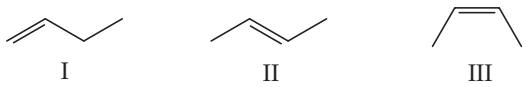


27.66



27.67

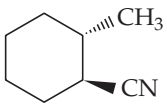
(a)



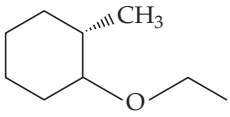
(**b**) The 2-butenes (II and III) are the major products because they arise from the more stable carbocation.

27.70

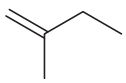
(a) S_N2



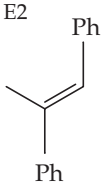
(b) S_N1



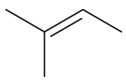
(c) E2



(d) E2



(e) E1



27.71

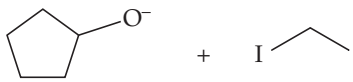
(a)



(b)

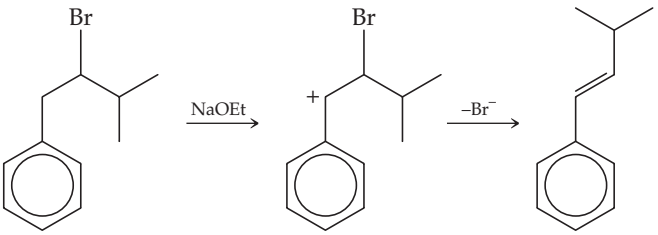


(c)



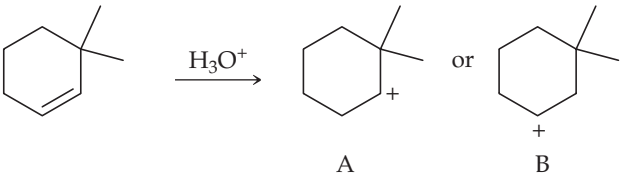
27.72 (**a**) CH_3CH_2OH (**b**) $CH_2{=}CH_2$

27.75



The intermediate benzylic carbocation shown above is stabilised by the adjacent benzene ring (conjugation), making it more stable than the tertiary carbocation that would otherwise be favoured. **27.77** The rate doubles when the concentration of bromoalkane doubles, but does not change when the amount of base doubles. Therefore the rate law is: rate = k[bromoalkane] The mechanism follows E1.

27.80 (**a**)



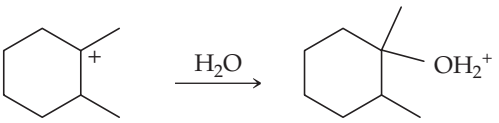
Cation A will be the more stable of the two possibilities because of the extra electron donation from the adjacent methyl groups.

(**b**)

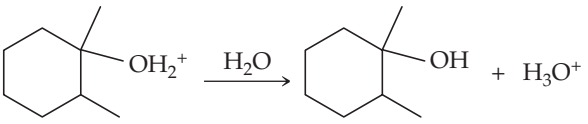


We have not discussed methyl migration in the text, but you should be able to see that this reaction might be favourable because it results in a very stable tertiary carbocation.

(**c**)

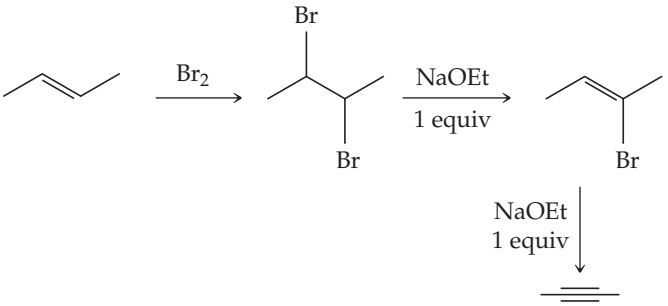


(**d**)

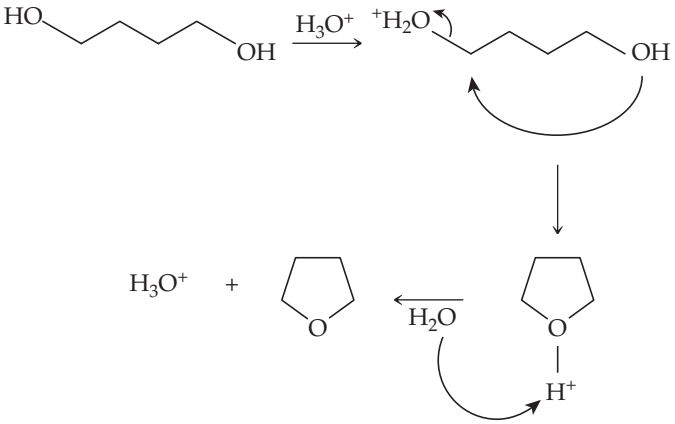


This shows that the acid acts as a catalyst.

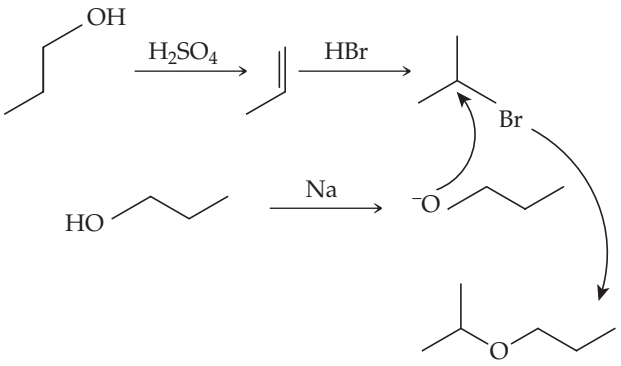
27.82



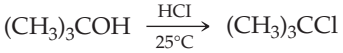
27.84



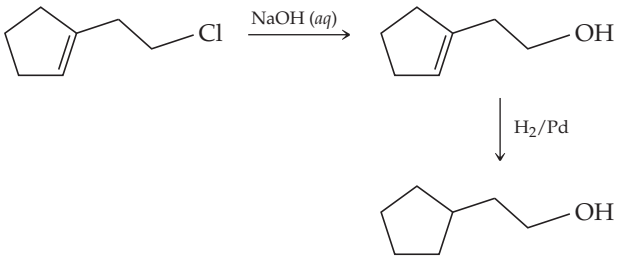
27.86



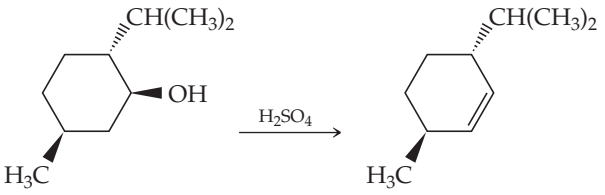
27.88 (**a**)



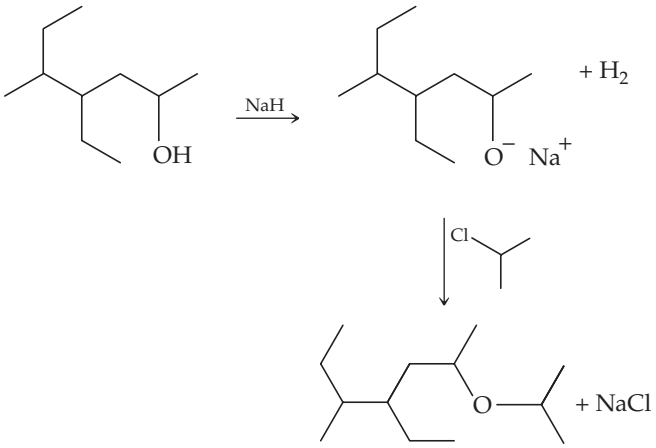
(**b**)



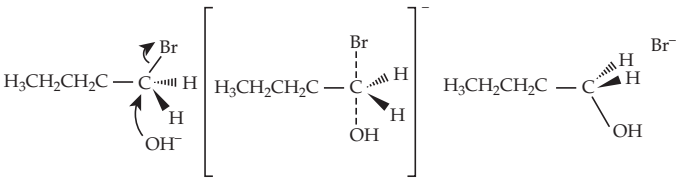
(**c**)

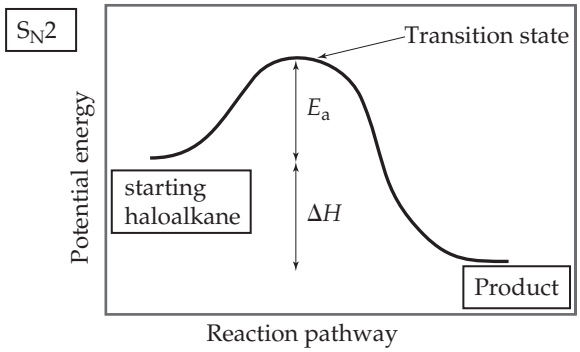


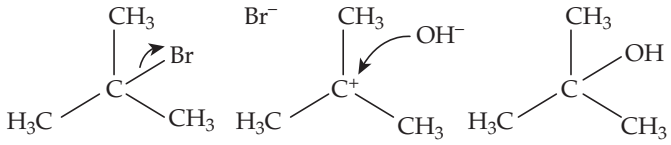
(d)

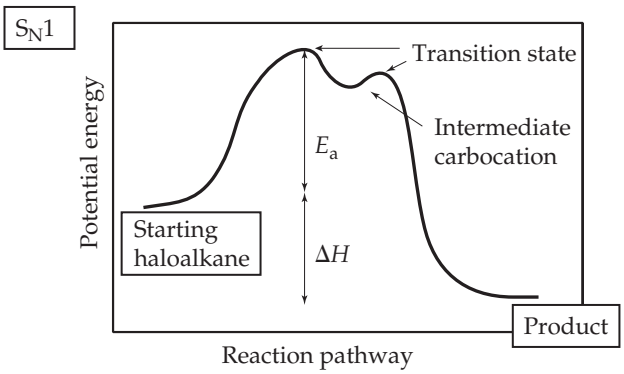


27.90 Energy profile of S_N2 and S_N1:







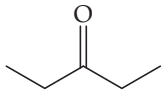


Chapter 28

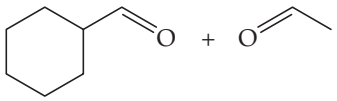
28.2 The 'one' ending indicates a ketone, which can only be positioned on the central carbon atom of propanone or one of the two equivalent inner carbon atoms of butanone. **28.3** (**a**) alkyne, aldehyde (**b**) alkene, carboxylic acid, aromatic, haloalkane (**c**) haloalkane, ketone (**d**) alkene, ester (**e**) amine, amide **28.5** (**a**) 2-pentanone (**b**) cyclopentanone (**c**) 4-bromo-2-methylcyclopentanone (**d**) propanal (**e**) 3-nitrobenzaldehyde (**f**) 4-methyl-2-pentanone

28.7

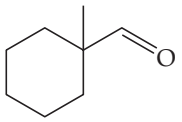
(a)



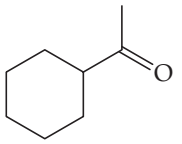
(b)



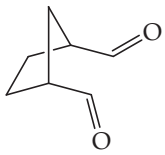
(c)



(d)

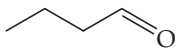


(e)



28.10

(a)



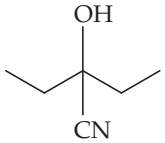
(b)



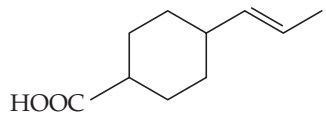
28.14 Use $LiAlH_4/H_2O$ or $NaBH_4/H_2O$ to carry out the reduction. **28.16** (**a**) cyclohexanone (**b**) $LiAlH_4$

28.19

(a)

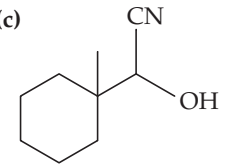


(b)

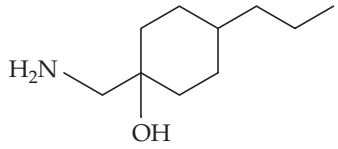


Depending on the reaction conditions (particularly the solvent) hydration of the alkene may also occur.

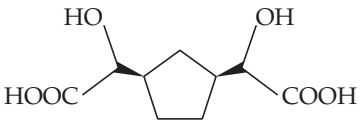
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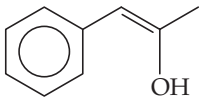
(d)



(e)



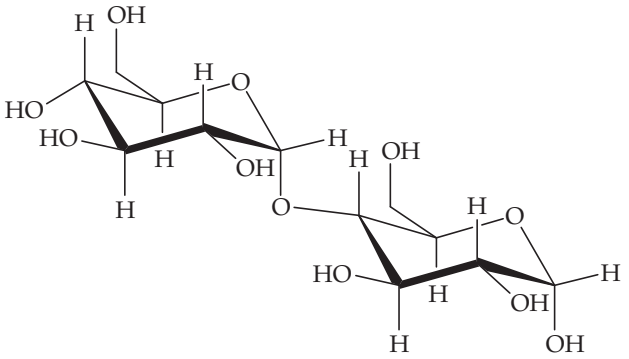
28.20



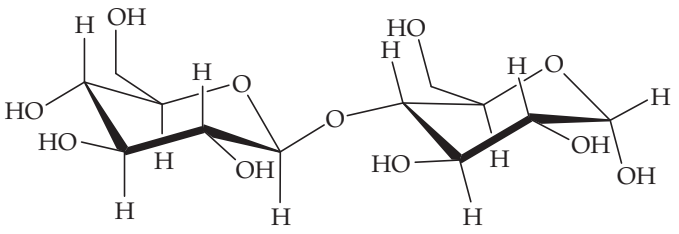
This is the most stable tautomer because the alkene double bond is conjugated with the benzene ring.

28.25 (**a**) The orientation of the hydroxyl group attached to the anomeric carbon differs between α and β-glucose.

(**b**)



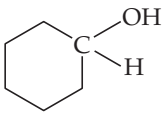
(**c**)



28.27 (**a**) $C_6H_{10}O_5$ (**b**) glucose (**c**) β-1,4-linkages.

28.33

(a)

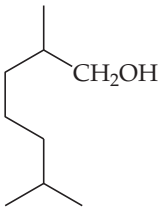


cyclohexanol
Conditions: $K_2Cr_2O_7/H_2SO_4$

(b)

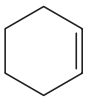
$CH_3CH_2CH_2CH_2CH_2CH_2OH$
1-hexanol
Conditions: PCC (pyridinium chlorochromate)

(c)



2,6-dimethylheptan-1-ol
Conditions: PCC

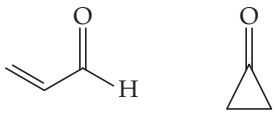
(d)



cyclohexene
Conditions: $O_3/(CH_3)_2S$

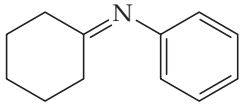
28.35 To act as a non-ionic detergent the molecule needs to contain both polar (e.g. OH) and non-polar (e.g. C_8H_{15}) groups. *n*-Octoglucoside has the properties of a surfactant; the long alkyl chain (non-polar) can bind hydrophobic portions of the protein whilst the glucoside group (polar) will facilitate water solubility of the protein-*n*-octoglucoside complex.

28.39

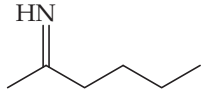


28.45

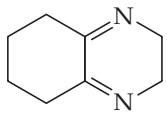
(a)



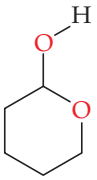
(b)



(c)

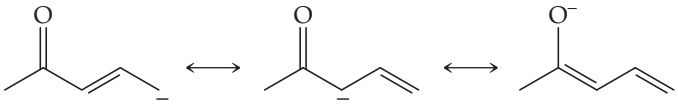


28.47 (**a**)



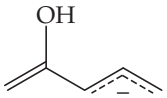
(**b**) hemi-acetal

28.48 (**a**)

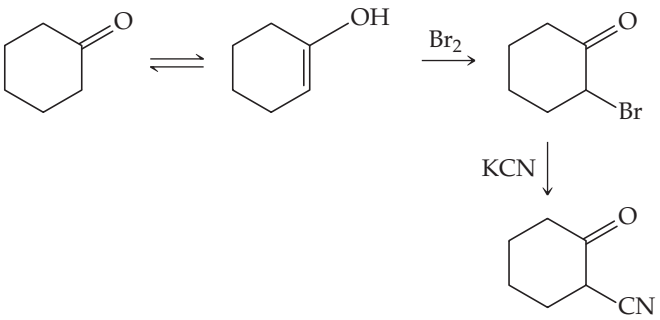


(**b**) keto keto enolate (**c**) These methyl protons are much more acidic than the ones in pentane because the conjugate base is much more stable (it is stabilised by resonance).

(**d**)

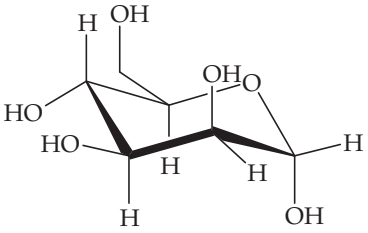


28.50



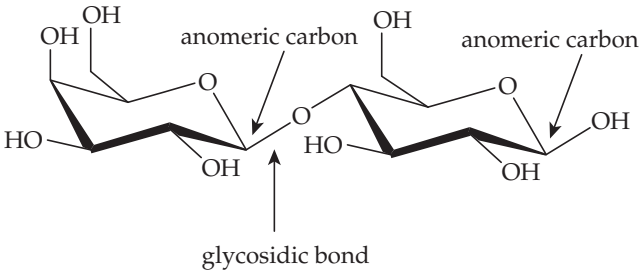
28.52 (**a**) four

(**b**)



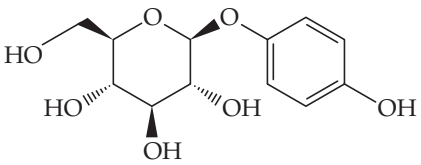
28.53 (**a**) Starch: glucose units are all in α-form, can exist in both branched and unbranched forms. Glycogen: similar to starch with greater branching. Cellulose: glucose units are in the β-form. (**b**) The α-1,4-glycosidic linkages in starch cause it to form a left handed helix. This formation is conducive to the formation of H-bonds with water, increasing its water solubility. The β-linkages found in cellulose promote the formation of intramolecular H-bonds. Cellulose polymers tend to form large aggregates which are insoluble in water. **28.54** (**a**) Disaccharide and a glycoside.

(**b**)



(**c**) 1,4-linkage

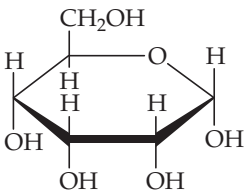
28.55



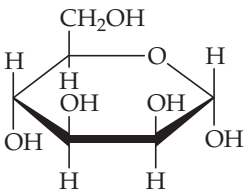
Arbutin

28.56

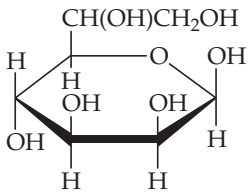
(**a**)



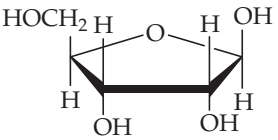
(**b**)



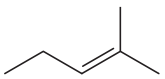
(**c**)



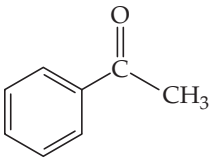
(**d**)

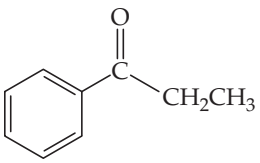


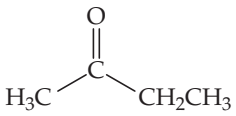
28.57



28.58

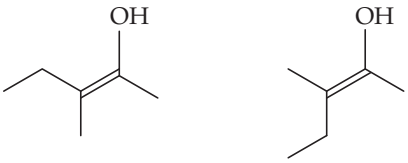






28.60 (**a**) There are two stereoisomers. Their configurations will be RR, SS, RS, and SR. Any confirmations that produce mirror images will be enantiomers and non-mirror images will be diastereoisomers. (**b**) $C_6H_{14}O + H_2Cr_2O_7 \rightarrow C_6H_{12}O_2$. The reaction converts the alcohol into a ketone. (**c**) The reaction destroys one of the stereocentres and thus the product only has two stereoisomers.

(**d**)



(**e**) The ketone products destroy one of the chiral centres. In addition the ketones are in equilibrium with their achiral enol forms. When the ketone reforms, a proton can be added to the chiral centre from either side leading to a more racemic mixture. Optical rotation will therefore eventually be reduced to zero. **28.62** To determine which molecule would release the most energy per gram, divide the energy released per mole by the molecular weight.

$-2803/180.16 = 15.56$ kJ g^{-1} glucose

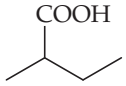
$-5640/342.30 = 16.48$ kJ g^{-1} sucrose

Chapter 29

29.3 (**a**) methanoic acid (**b**) butanoic acid (**c**) 3-methylpentanoic acid. **29.5** (**a**) The presence of both OH and C=O groups in pure acetic acid leads us to expect that it will be a strongly hydrogen-bonded substance. (**b**) That the melting and boiling points of pure acetic acid (m.p. 16, 6 °C; b.p. 117.9 °C) are both higher than those of water, a substance we know to be strongly hydrogen-bonded, supports this conclusion. **29.6** The carboxylic acid will react with the bicarbonate solution, resulting in the evolution of CO_2 (bubbles). The ester will not. **29.7** Acid A is most acidic. The trifluoromethane group is inductive, making the O–H bond weaker and compound A more acidic than compound B. Although the benzene ring has a stabilising effect on the conjugate base of Acid C, it is not as great as the inductive effect of the fluorines in Acid A.

29.9

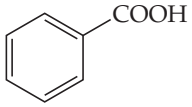
(**a**)



(**b**)



(**c**)

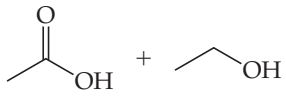


(**d**) $CH_3COOH + CH_3OH$

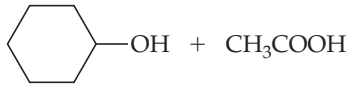
29.10 (**a**) i) Mg ii) CO_2 iii) H_3O^+ (**b**) $K_2Cr_2O_7$ and H_2SO_4 (**c**) $K_2Cr_2O_7$ and H_2SO_4 (**d**) i) NaOH(aq) ii) H_3O^+ **29.11** For oxidation to benzoic acid to occur. there needs to be a benzylic CH. This is present in toluene but absent in *tert*-butylbenzene. **29.13** (**a**) ketone (carbonyl group) (**b**) carboxylic acid (**c**) alcohol (hydroxyl group) (**d**) ester **29.15** (**a**) $(CH_3)_2CHCH_2COOH$ and CH_3OH (**b**) C_6H_5OH and CH_3CH_2COOH (**c**) $C_6H_5CH_2COOH$ and CH_3OH

29.16

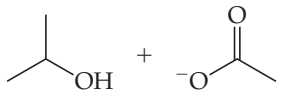
(**a**)



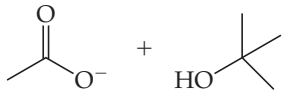
(**b**)



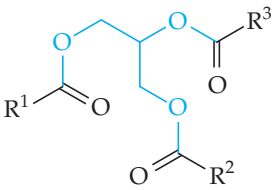
(**c**)



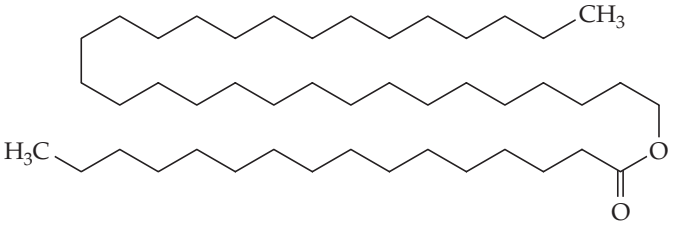
(**d**)



29.18 (**a**), (**b**) Fat, oil and lipid: triester of glycerol and fatty acids; generally soluble in organic compound; insoluble in water; solid or liquid at room temperature. The words 'oils', 'fats', and 'lipids' are all used to refer to fats. Oils usually refer to fats that are liquids at room temperature while fats are solid at room temperature. 'Lipids' is used to refer to both liquid and solid fats, along with other related substances, usually in a medical or biochemical context. The structure shows the triglyceride with three different fatty acids.



Wax: single ester from a fatty acid and a long chain alcohol; greasy solid or semi-solid at room temperature; insoluble in water but in organic, non-polar solvents. The example shows triacontanyl palmitate which is a major component of beeswax.



29.19

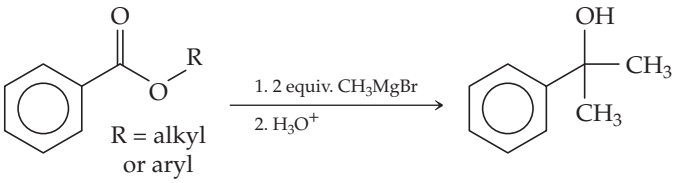
(**a**)

$$CH_3CH_2COOH + CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{H^+} CH_3CH_2COOCH_2CH_2CH_2CH_2CH_3 + H_2O$$

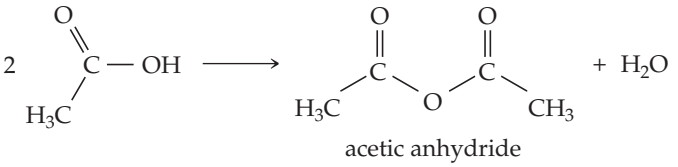
(**b**)

$$C_6H_5COOCH_3 + KOH \longrightarrow C_6H_5COOK + CH_3OH$$

29.23 The synthesis of 2-phenyl-2-propanol is shown:



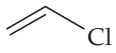
29.25



acetic anhydride

29.30

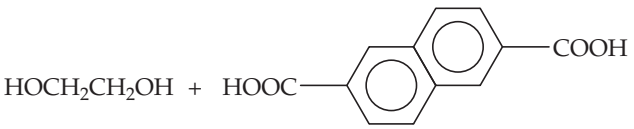
(a)



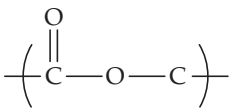
(b)

$H_2N(CH_2)_6NH_2$ + $HOOC(CH_2)_8COOH$

(c)

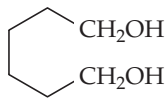


29.31 (**a**) (i) It is the only alkene shown. (**b**) (iii) It contains amine and carboxylic acid groups susceptible to condensation reaction. **29.34** Polystyrene is an essentially non-polar hydrocarbon, while poly(ethylene terephthalate) (PET) contains polar ester groups, as well as non-polar hydrocarbon portions. PET is more appropriate, because it provides polar ester groups



with hydrogen bonding capabilities where the cells can attach. Also, the ester linkages are susceptible to hydrolysis (the reverse of condensation); this renders the synthetic matrix biodegradable when employed in the body. **29.36** (**a**) nitro, phenyl, amide, chloroalkane, alcohol (**b**) phenyl, carboxylic acid, ester (**c**) phenol, amide (**d**) phenol, alcohol, ether, amine, alkene, ester

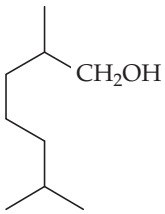
29.38 (**a**)



6-hydroxy-1-hexanol
Conditions: $K_2Cr_2O_7/H_2SO_4$

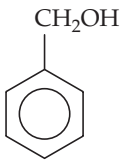
(**b**) $CH_3CH_2CH_2CH_2CH_2CH_2OH$ 1-hexanol Conditions: $K_2Cr_2O_7/H_2SO_4$

(**c**)



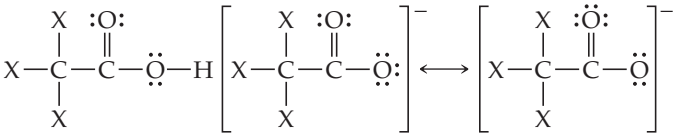
2,6-dimethylheptan-1-ol
Conditions: $K_2Cr_2O_7/H_2SO_4$

(**d**)



phenylmethanol
Conditions: $K_2Cr_2O_7/H_2SO_4$

29.40 Arachidic acid would form better micelles and hence be a better soap because molecules of arachidic acid can pack more tightly and interact more strongly due to their regular shape. **29.45** The general Lewis structures for these acids and their conjugate bases are shown below.



where X = H or Cl Replacement of H on the acid by the more electronegative chlorine atoms causes the central carbon to become more positively charged, thus withdrawing more electrons from the attached COOH group, in turn causing the O–H bond to be more polar, so that H^+ is more readily ionised. For the conjugate base (two resonance structures), the electronegative X atoms delocalise negative charge and stabilise these forms relative to the unsubstituted anions. This favours products in the ionisation equilibrium and increases the value of K_a. To calculate pH proceed as usual, except that the full quadratic formula

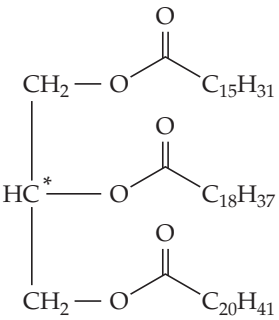
$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

must be used for all but acetic acid. ($[H^+]$ =, where a = 1, b = K_a and c = $-0.01 \times K_a$.)

Acid	pH
acetic	3.37
chloroacetic	2.51
dichloroacetic	2.09
trichloroacetic	2.0

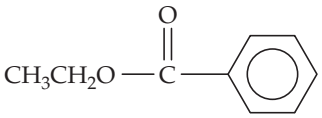
29.47 (**a**) Oxidation with chromic acid (CrO_3/H_2SO_4) (**b**) Oxidation with chromic acid (CrO_3/H_2SO_4) (**c**) Saponification with KOH followed by acidic workup (**d**) Addition of water

29.52 The chiral centre is marked with an asterisk.



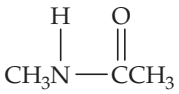
29.55

(a)



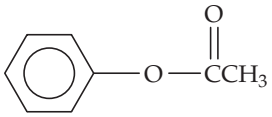
ethyl benzoate

(b)



N-methylethanamide or *N*-methylacetamide

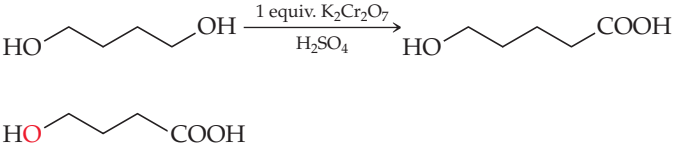
(c)



phenyl acetate

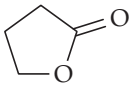
29.56 (**a**)

(a)

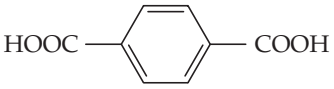


The compromise with this synthesis is that there will be some dicarboxylic butanoic acid formed as a by-product. This could be minimised by adding the oxidising agent slowly to a stirred solution of the 1,4-butanediol so as to keep the alcohol in excess.

(b)



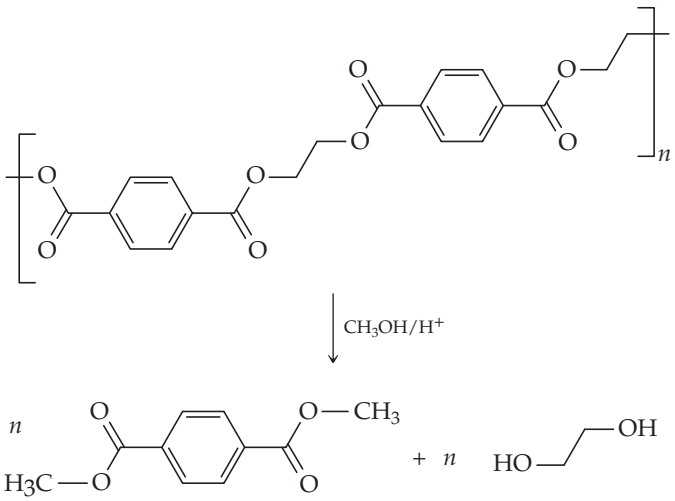
29.58



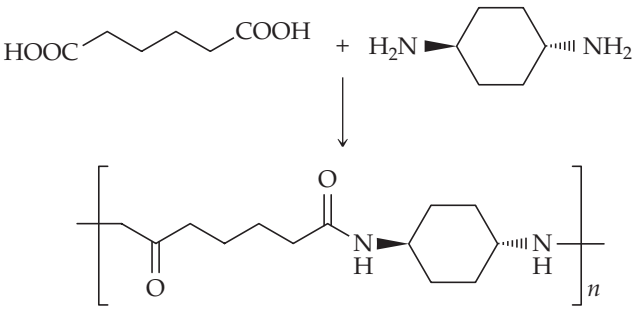


29.60 Failure to start with 1:1 stoichiometry of functional groups in condensation polymerisation so will lead to incomplete condensation between monomers and smaller polymeric (oligomeric) species.

29.62

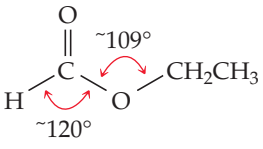


29.63 (**a**)



(**b**) The shape of the polymer would be quite different and it would have different mechanical and thermal properties. It might be expected that the cis-1,4-cyclohexanediamine would be more likely to introduce 'kinks' in the polymer, similar to cis double bonds in lipid side chains, to make a less rigid product. **29.64** Poly(phenylene ether) is more rigid, due to the phenyl rings. If used in a composite with nylon, it would confer rigidity and ensures that the nylon retained its shape.

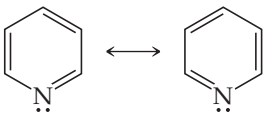
29.66 (**a**) Ethyl methanoate



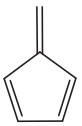
(**b**) Dispersion forces (**c**) Dispersion forces and dipole-dipole forces are present in esters. They are also present in carboxylic acids and alcohols from which esters are derived. In addition carboxylic acids and alcohols.

Chapter 30

30.2 (**a**) Yes
(**b**)



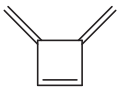
(**c**) The lone pair is in the plane of the ring and pointing away from the centre. It is not involved with the delocalised π-system.
30.4 The empirical formula of benzene is CH. Acetylene, C_2H_2, is the simplest compound with this empirical formula. Some compounds with the same molecular formula as benzene are:



methylenecyclopentadiene



Dewar benzene

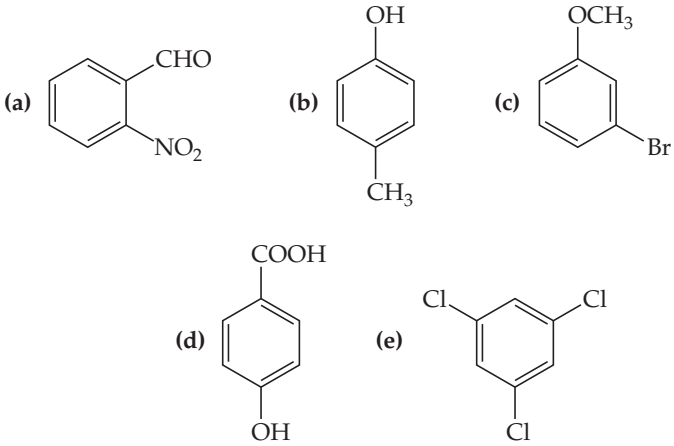


3,4-dimethylenecyclubutene



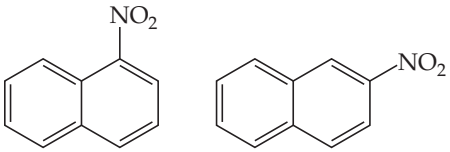
2,4-dimethylenebicyclo[1,1,0]butane

30.6

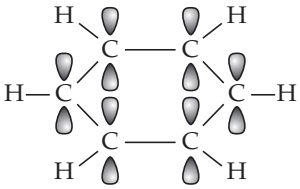


(**a**) 2-nitrobenzaldehyde (**b**) 4-methylphenol (common name: *para*-cresol) (**c**) 3-bromoanisole (**d**) 4-hydroxybenzoic acid (**e**) 1,3,5-trichlorobenzene

30.7

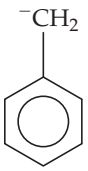


30.10 (**a**) The hydrogenation of benzene is much less energetically favourable than we would predict for a six-membered ring with three double bonds if we extrapolate from the enthalpy change associated with hydrogenation of cyclohexene and 1,4-cyclohexadiene – this suggests that benzene has some extra stability. Cyclohexene and 1,4 cyclodihexene also react readily by an addition mechanism- e.g., by bromination- while it is very difficult to carry out addition reactions on benzene; bromine reacts by substitution, not addition. This also suggests that the double bonds in benzene are unusually stable. (**b**) Aromatic systems have a delocalised p-bonding system in which each *p*-orbital connects to form a 'super π-way'. This is explained in the following diagram:

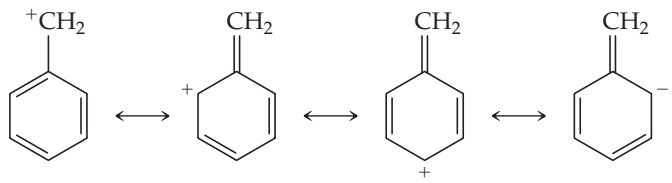


30.12

(a)

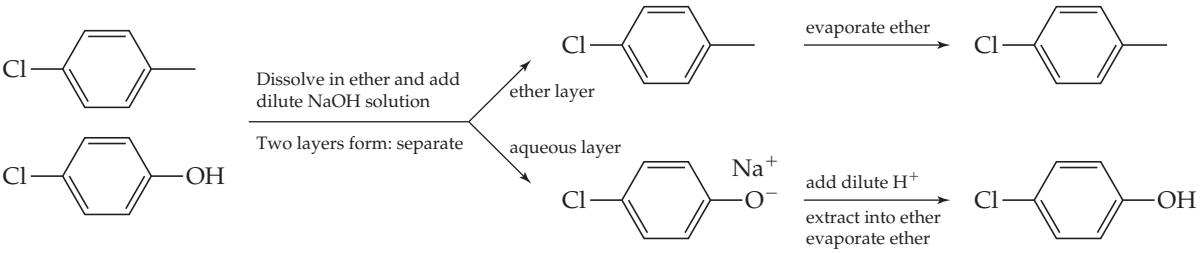


(b)

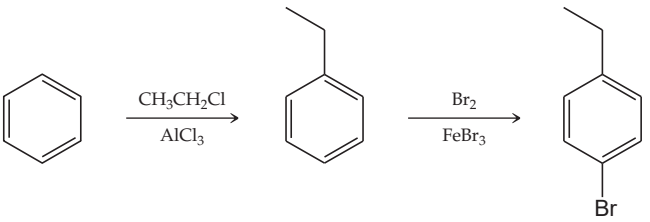


The benzylic cation is stabilized by resonance since the positive charge is delocalized over the benzene ring. This resonance stabilisation is unavailable to the methylcyclohexane primary carbocation. **30.14** (**a**) $4n+2$ (**b**) The compound has 8 π-electrons and would not be planar, so it does not fit the criteria stated in the solution to Problem 30.24. It is not aromatic. **30.16** An alkoxide will be a stronger base than a phenoxide as the anion of an alkoxide is not stabilized, unlike that of a phenoxide. **30.17** The chloro group acts as an electron withdrawing group, increasing the acidity of the phenol. This inductive effect is greatest if the interacting groups are close together and decreases as the number of bonds separating the groups increases.

30.18



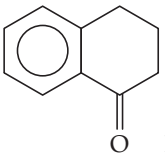
30.22



30.24 (**a**) $CH_3Cl/AlCl_3$ (**b**) $(CH_3)_2CHCl/AlCl_3$ (**c**) $Cl_2/FeCl_3$ (**d**) $CH_3COCl/AlCl_3$.

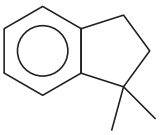
30.26

(a)



Friedel-Crafts acylation

(b)



Friedel-Crafts alkylation

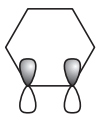
30.27 All of the functional groups activate the benzene ring towards electrophilic aromatic substitution. Therefore, benzene alone, (**e**), with no functional groups, will be the most deactivating. Of the rest, the ethyl group is the weakest activating group. The other three groups (methoxy, phenol and acetamide) all have the ability to stabilise the intermediate carbocation through resonance.

30.28

(a)



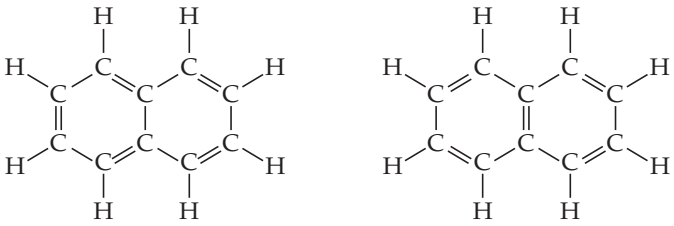
(b)



30.30 Compound (ii) is most likely to exhibit liquid crystalline behaviour as it has a long-chain alkane component greater than 5 carbons long linked to an aromatic ring. **30.32** (**a**) Not aromatic. Compound has 8 π-electrons therefore it does not satisfy the $[4n+2]$ rule and is not planar. (**b**) Aromatic. Compound is planar and satisfies the $[4n+2]$ rule ($n=3$). All atoms in ring have an unhybridised p orbital. (**c**) Not aromatic. Compound has 8π electrons therefore does not satisfy the $[4n+2]$ rule. Looks conjugated, but this compound is not planar. (**d**) Not aromatic. Compound satisfies the $[4n+2]$ rule but is not planar. One of the carbons in the ring does not have an unhybridised p orbital so therefore the molecule is not conjugated. **30.34** The change in visual appearance of the phase, from milky to clear, upon repeated heating and cooling. **30.36** The hydrogens of benzene are more acidic than those of cyclohexane because the resulting anion from benzene (the conjugate base) is stabilised by resonance.

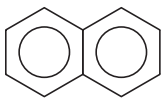
30.37

(a)

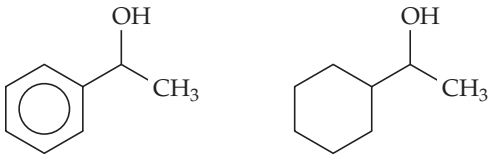


(**b**) This is because of the influence of the two canonical structures. Each C–C bond is neither a single nor a double bond, but is best represented as something in between; for example, as a '1.5' bond.

(c)

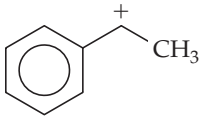


30.40



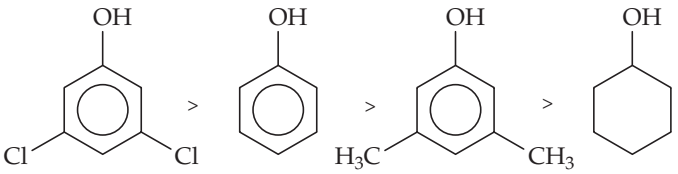
A **B**

Compound A undergoes dehydration more rapidly than compound B because the resulting intermediate carbocation, shown below, is stabilised by resonance.



30.42 Acidity depends on the stability of the conjugate base: i.e. HA $\rightleftharpoons A^- + H^+$ The more stable the conjugate base ($A^- = RO^-$ or ArO^- in this case) the more the equilibrium will be shifted to the right hand side and the greater will be the availability of the proton. So all we have to do is arrange the compounds in decreasing order of stability of RO^- or ArO^-. The compound on the left below (3,5-dichlorophenol) would form the most stable conjugate base because the chlorine atoms are electron withdrawing and would stabilise the anion. 3,5-Dimethylphenol

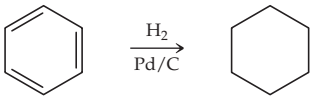
would form a less-stable conjugate base than phenol itself because the methyl groups are electron donating and would destabilise the anion. The compound on the right (cyclohexanol) would form the least stable conjugate base because it does not have an aromatic ring to help delocalise the negative charge.



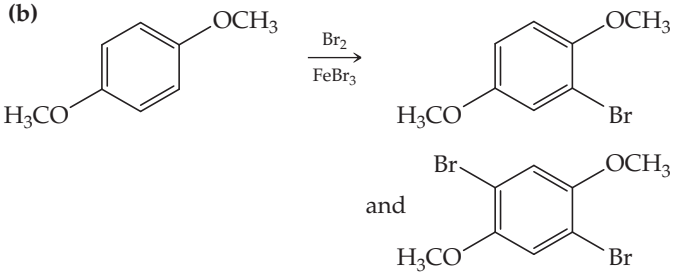
30.44 (**a**) The periphery of the BHT molecule is mostly non-polar groups, such as -CH_3. The one –OH group is rather buried inside and probably does little to enhance solubility in water. Thus, BHT is more likely to be soluble in the non-polar hydrocarbon hexane, C_6H_{14}, than in polar water. (**b**) BHT could be produced by reacting 4-methylphenol with $(CH_3)_3CCl/AlCl_3$.

30.45

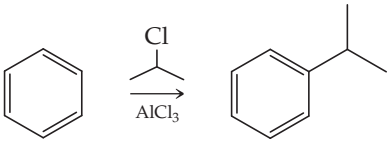
(a)



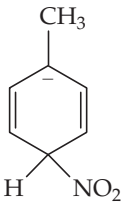
(b)



(c)

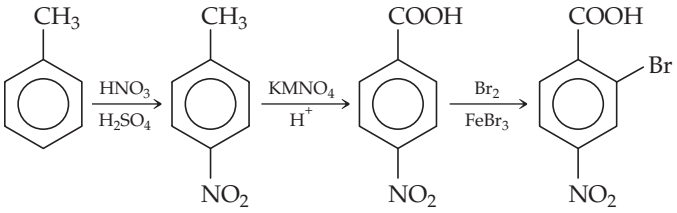


30.49



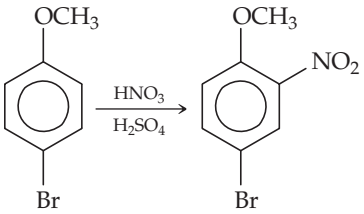
This is the only tertiary carbocation resonance structure, so should be most stable. **30.51** (**a**) A chloro substituent weakly deactivates the aromatic ring and directs the electrophile towards the *ortho* and *para* positions. (**b**) A nitro substituent strongly deactivates the aromatic ring and directs the electrophile towards the *meta* position. **30.53** The nitro group acts as a strong deactivator in nitrobenzene and makes it unreactive towards electrophilic aromatic substitution to such an extent that it can be used as a solvent for a Friedel-Crafts alkylation of a more reactive aromatic compound.

30.56



(In the last step, while both COOH and NO_2 are meta directing, the nitrogen group is a strong deactivator).

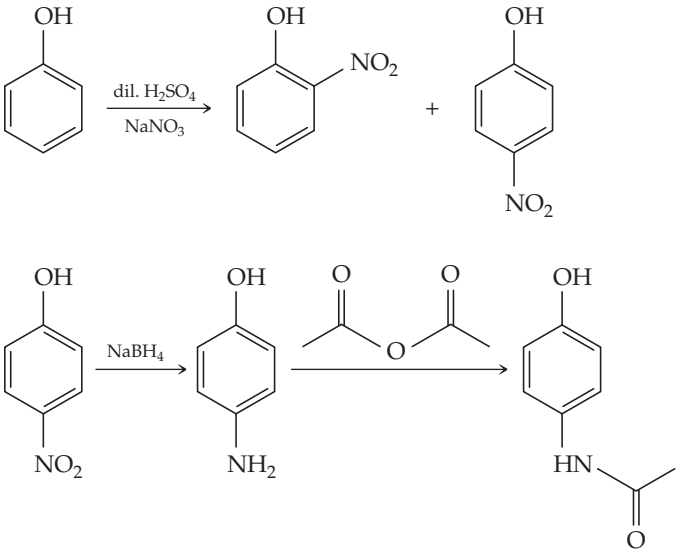
30.58



(The methoxy group is a much more strongly *ortho* directing than the bromo group).

30.60

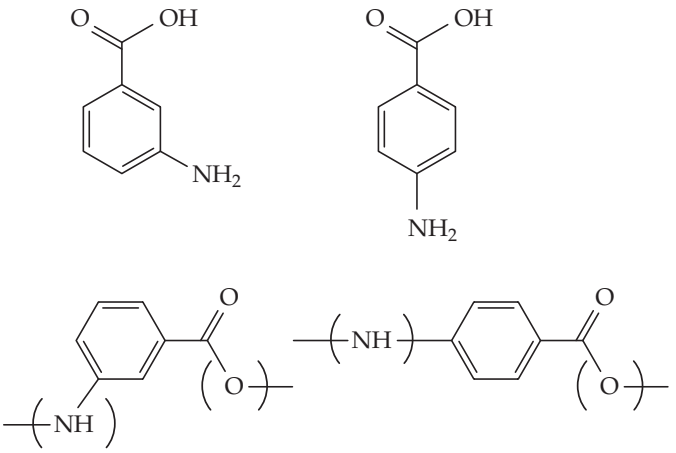
(a)



(**b**) The name 'paracetamol' suggests that the structure will be a benzene ring with two functional groups in the *para*-positions. **30.62** (1) Combustion of decahydronaphthalene: $C_{10}H_{18} + 14.5O_2 \rightarrow 10CO_2 + 9H_2O$, −6286 kJ mol^{-1} (2) Combustion of naphthalene: $C_{10}H_8 + 12\ O_2 \rightarrow 10CO_2 + 4H_2O$, -5157 kJ mol^{-1} (3) Formation of water: $H_2 + ½\ O_2 \rightarrow H_2O$ (l), −285.83 kJ mol^{-1} (4) Using Hess's Law, reaction (1) + (2): $C_{10}H_8 + 5H_2O \rightarrow C_{10}H_{18} + 2.5O_2$, +1129 kJ mol^{-1} (5) And again, reaction (3) × 5 + (4): $C_{10}H_8 + 5H_2 \rightarrow C_{10}H_{18\ 2}$, +1129 −1429.15 kJ mol^{-1} Heat of hydrogenation = −300 kJ mol^{-1} Yes, the value obtained for the heat of hydrogenation of naphthalene does provide evidence for aromatic character. The heat of hydrogenation of a double bond is roughly −116 kJ mol^{-1}. If naphthalene was treated as possessing 5 isolated double bonds, then we would expect it to have a heat of hydrogenation of approximately 5 × −116 kJ mol^{-1} = −580 kJ mol^{-1}. The difference between the 'expected' heat of hydrogenation (–580 kJ mol^{-1}) and the observed heat of hydrogenation (–300.15 kJ mol^{-1})

is due to stabilisation of the π-electrons through delocalisation. The difference of 280 kJ mol^{-1} is known as the 'resonance energy'. **30.64** The order for the synthesis of 4-aminobenzoic acid is as follows. The order for the synthesis of 3-aminobenzoic acid is as follows. 1. Oxidisation of the aromatic alkyl group with acidified potassium permanganate; 2.Nitration using concentrated nitric acid and concentrated sulfuric acid; 3. Reduction of a nitro group using hydrogen gas and palladium catalyst. (**a**) Structural isomers

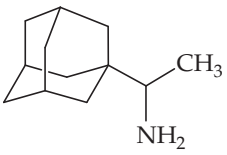
(b)



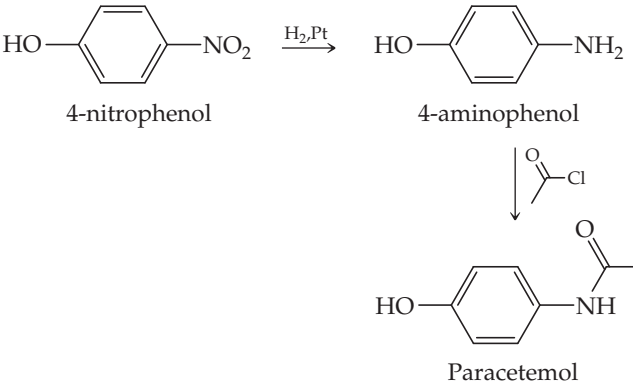
(**c**) 1. Nitration using concentrated nitric acid and concentrated sulfuric acid 2. Oxidisation of the aromatic alkyl group with acidified potassium permanganate 3. Reduction of a nitro group using hydrogen gas and palladium catalyst. **30.66** (**a**) Ketones, benzene ring, amines and alkene groups. (**b**) All carbon in indigo is sp^2 hybridised. (**c**) The reason indigo is planar is because it is only comprised of sp^2 hybridised orbital which have a trigonal planar shape. (**d**) 613 nm, which is orange light, corresponds to 3.24×10^{-19} J.

Chapter 31

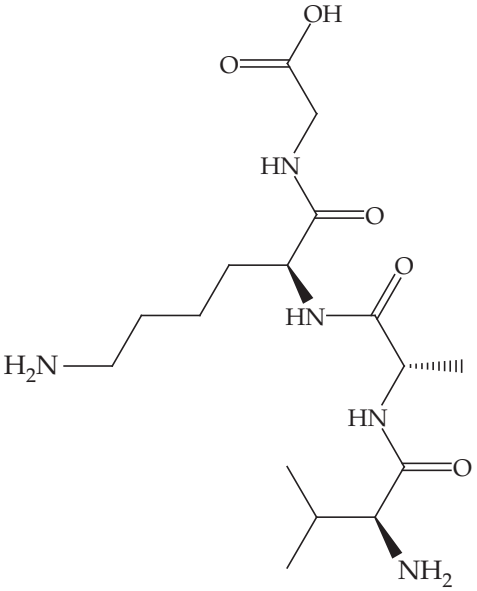
31.9



31.11



31.14 α-alanine and β-alanine both share the same molecular formula and have the same functional groups. They are structural isomers (also known as constitutional isomers). **31.16** (**a**) Both amino and carboxyl groups in acidic form. (**b**) Carboxyl group in basic form, amino group in acidic form. (**c**) pI = 3.22 (Halfway between the first two pK_a values). **31.19** A has an overall neutral charge. B is negatively charged. C is positively charged. The 2nd electrophoresis result (from the left) is expected. **31.26** Glu-Cys-Gly
31.27 Glutamyltyrosine, Gln-Tyr, Q-Y **31.29** (**a**) Val-Ala-Lys-Gly

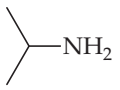


valyl alanyl lysyl glycine

(**b**) basic (**c**) Gly and Val-Ala-Lys (**d**) Valine **31.32** TGAGCT **31.33** CAGTCCTTAGAA **31.36** (**a**) CTAATGT (**b**) CTAATGT transcribed into mRNA would be GAUUACA. GATTACA transcribed into mRNA would be CUAAUCU **31.38** (**a**) molecule (i) disaccharide (maltose) (**b**) molecule (iii) amino acid (phenylalanine) (**c**) molecule (ii) organic base (guanine) **31.40** Ala-His-Tyr-Ser, AHYS **31.42** (**a**) Alanine (**b**) S **31.44** Asn-Pro-stop **31.45** (**a**) Pyrimidine (**b**) 2-ethylpiperidine (**c**) Triethylamine (**d**) 1,4-diaminobutane or 1,4-butanediamine

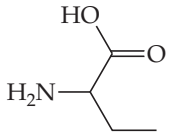
31.46

(a)



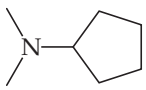
2-propanamine

(b)



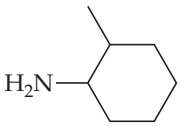
2-aminobutanoic acid

(c)



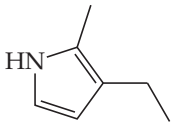
N,N-dimethylcyclopentanamine

(d)



2-methylcyclohexylamine

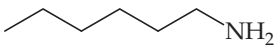
(e)



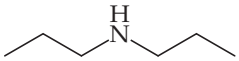
2-methyl-3-ethylpyrrole

31.47 (**a**)

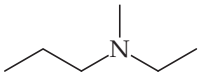
Primary amine:



Secondary amine:



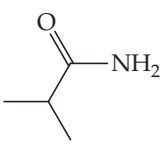
Tertiary amine:



All three amines are constitutional isomers. (**b**) The boiling point of an amine will depend on the strength of intermolecular interactions, *i.e.*, H-bonding, dipole-dipole and Van der Waals dispersion forces. For primary, secondary and tertiary amines with the same molecular formula: tertiary amines do not have a hydrogen attached to the nitrogen atom hence tertiary amines are not able to form H-bonds with each other. Their boiling point is normally much lower than secondary and primary amines. The primary amine has two hydrogen bond donor atoms and one hydrogen bond acceptor atom, while the secondary amine has one atom that can act as a hydrogen bond donor and one that can act as an acceptor. The primary amine will form the strongest intermolecular bonds and hence have a higher boiling point. (**c**) Both propylamine and triethylamine can form H-bonds with water. Propylamine can act as both a hydrogen bond donor and acceptor, while triethylamine can only act as a hydrogen bond acceptor through the lone pair on nitrogen. Triethylamine is therefore slightly less soluble than propylamine. Isobutane cannot form H-bonds and is far less soluble in water. **31.48** For a cyclic structure to be classed as aromatic it must have an odd number of pairs of π electrons. The lone pair on N has a low K_b indicating that these electrons form part of the aromatic π-system. The nitrogen will only be weakly basic - the lone pair is not concentrated on N, decreasing its ability to accept protons. Indole can be considered aromatic only if N contributes a lone pair to the delocalised π system.

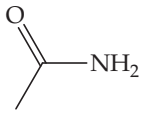
31.50

(a)



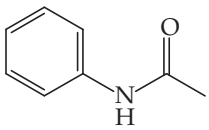
2-methylpropanamide

(b)



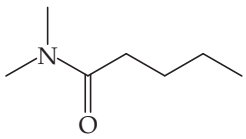
acetamide

(c)



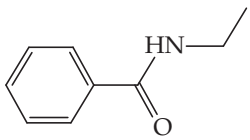
N-phenylacetamide

(d)



N,N-dimethylpentanamide

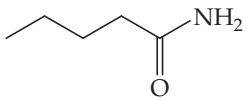
(e)



N-ethylbenzamide

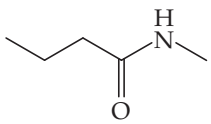
31.51

Primary amide:



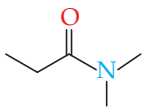
Chemical Formula: $C_5H_{11}NO$

Secondary amide:



Chemical Formula: $C_5H_{11}NO$

Tertiary amide:

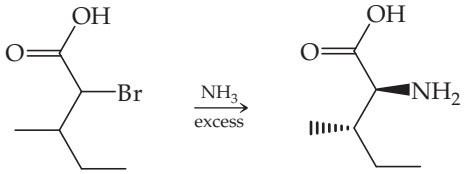


All three molecules are constitutional isomers. **31.54** The charge, basicity, acidity, shape, specific functionality and hydrophobic/hydrophilic character of the amino acid side chain can have a profound affect on the structure and function of proteins in which they are incorporated. For example, aspartic acid and lysine both have side chains that can form charged species under biological conditions, so they will tend to be on the exposed parts of proteins. Aspartic acid, as its name suggests, is an acid, while lysine is a base, and hence they will tend to react with different substrates. Proline, as the only cyclic member of the 20 amino acids in the genetic code, introduces a 'kink' in

a protein chain, so cannot be incorporated into most of the ordered motifs (secondary structure) in proteins; and glycine, with the smallest side chain, is required to be every third amino acid along the collagen chain because it is the only one small enough to fit this structure. Only cysteine can give rise to the disulfide bonds which provide covalent links between and within protein chains, making very large structural proteins like keratin possible. Hydrophobic amino acids, like isoleucine, are commonly found in the interior of proteins, far from water. **31.56** pK_a 2-3: carboxyl group pK_a 3-4: side chain pK_a 9-10: amino group (**a**) +0.97 (rounded) (**b**) 0 (**c**) −0.06

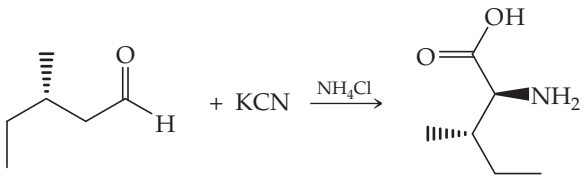
31.60

(a)

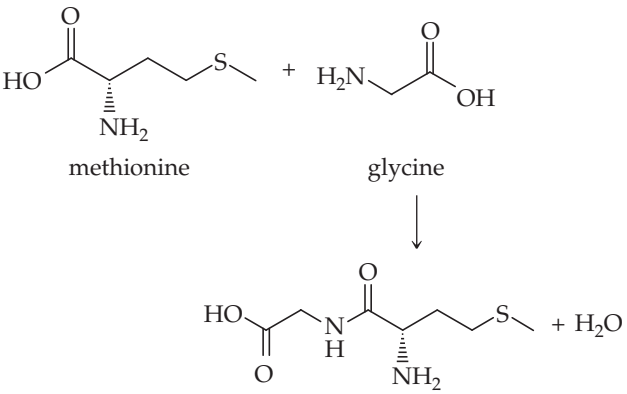


2-bromo-3-methylpentanoic acid isoleucine

(b)



31.61 (**a**)

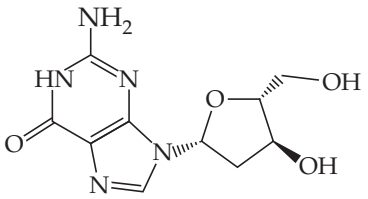


methionine glycine

methionyl glycine

(**b**) 4 **31.62** (**a**) Valine, serine and glutamate. (**b**) 6: Val-Ser-Glu VSE Val-Glu-Ser VES Ser-Val-Glu SVE Ser-Glu-Val SEV Glu-Ser-Val ESV Glu-Val-Ser EVS **31.63** (**a**) H-bonds form between amino acids four residues apart in an α-helix. This stabilises the alpha-helical structure. (**b**) Proline forms a secondary rather than primary amide. It cannot participate in hydrogen bonding therefore destabilises the alpha-helix. Proline is more rigid than other amino acids because of its cyclic nature and cannot adopt the ideal bond angles required for an alpha helix when it is incorporated in a protein. This would also distort the structure of the helix. **31.67** (**a**) The native form of the protein has a lower free energy. (**b**) The entropy change in going from the denatured to the folded form will be negative for the protein. (**c**) The disulfide bridges will decrease the free energy and the entropy of the system. (**d**) The protein is likely to unfold without the disulfide bridges to maintain its structure.

31.68

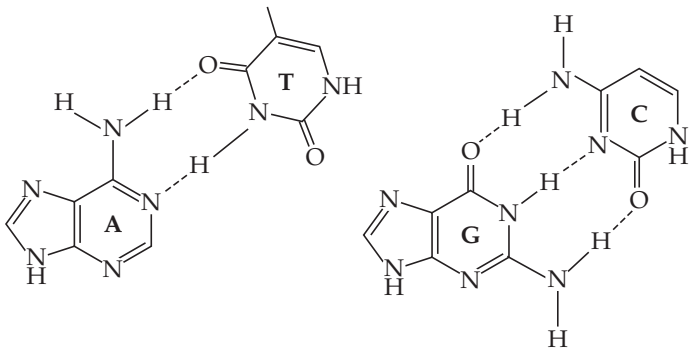


dexyguanosine

31.71 Use pH = pK_a + log([base]/[acid]) 7.4 = 7.21 + log([base]/[acid]) 0.19 = log([base]/[acid]) [base]/[acid] = $10^{0.19}$ = 1.55 The ratio of AMP-OH$^-$ (acid) to AMP-O^{2-} (conjugate base) will be approximately 2 to 3.

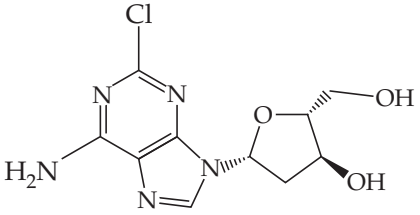
31.72

(a) **(b)**



Guanine does not base pair with thymine because guanine has two hydrogen bond donor groups and one hydrogen bond acceptor group, while thymine has one of each. This imbalance in the number of hydrogen bonds each base can form and their differing sizes means they do not base-pair in DNA.

31.74



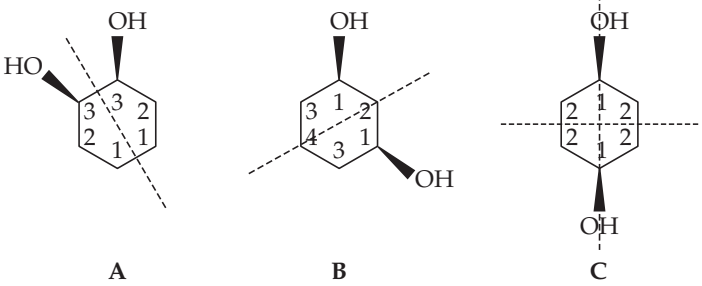
2-chloro-2′-dexyadenosine

31.75 (**a**) Arg-Thr-Ala-Ser-Gln (**b**) UCC UGA CGU AGC GUU **31.77** (**a**) seven (**b**) *N*-glycoside (**c**) furanose form **31.79** (**a**) Quinine is a basic amine and not very soluble in water. Salts of amines are usually more stable and water soluble than their corresponding amines and therefore easier to administer as medicine. (**b**) With a pK_a of 4.32 quinine hydrochloride counts as weak acid. Therefore, the pH can be calculated as follows: pH = ½ (pK_a – log[c_0]) pH = ½ (4.32 – log 0.053) pH = 2.8

Chapter 32

32.3 (**a**) OH (**b**) C=O (**c**) C=C (**d**) COOH (**e**) primary or secondary amide, $CONH_2$ or CONH **32.5** (**a**) OH stretch present for $CH_3CH_2CH_2CH_2OH$ (**b**) OH stretch present for CH_2=$CHCH_2OH$ (**c**) C=O stretch present for pyridone (**d**) C=C stretch present for CH_3CH=$CHCH_2CH_3$ (**e**) N–H stretch present for $CH_3CH_2NHCH_3$ **32.10** CD_3OD and CCl_4 are suitable solvents for use in ^{1}H NMR spectroscopy as they do not contain any ^{1}H nuclei, which would mask the signal from the analyte.

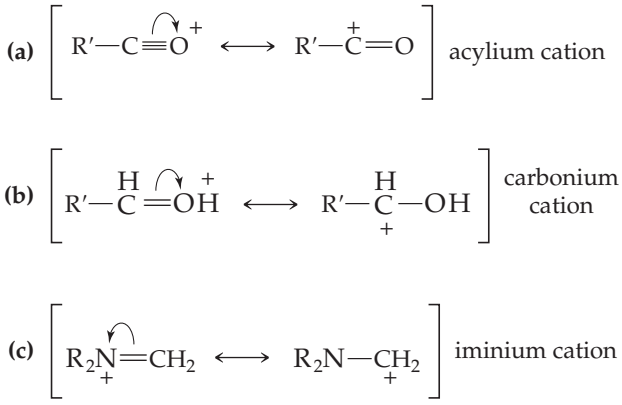
32.12 (**a**) 4 (**b**) 2 (**c**) 2 (**d**) 2 (**e**) 1 (**f**) 4 (**g**) 3 **32.16** Each product below has a different ^{13}C NMR spectrum, and they all have an element of symmetry, which simplifies spectra. Compound C is the most symmetric and has only two different carbons, which means there are two signals in its spectrum. Compound A and B have 3 and 4 signals respectively. *dotted lines indicate lines of symmetry



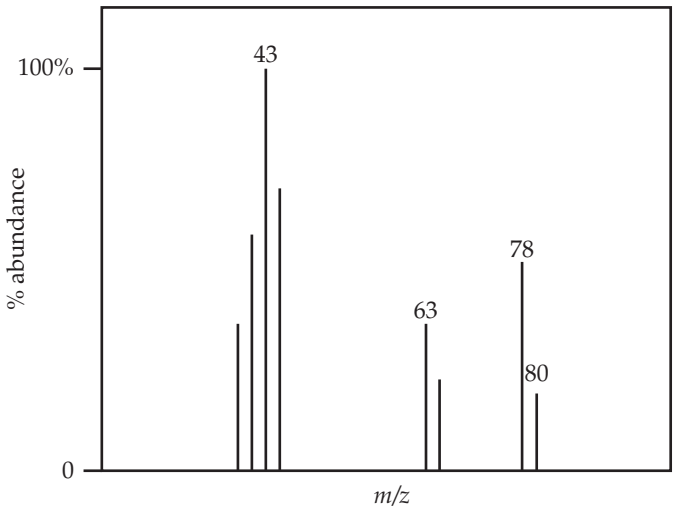
A **B** **C**

It can therefore be inferred that bottle A contains compound C and bottle B contains compound B.

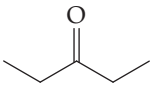
32.23



32.25



The spectrum for chloropropane has an M^+ peak at 78 and an $[M+2]^+$ peak at 80. The relative abundance of these two peaks is expected to be 3:1 respectively, due to the relative abundance of ^{35}Cl to ^{37}Cl. The fragmentation peaks at 63 and 65 amu corresponds to the mass of a methyl radical (15 amu) from M^+ and $[M+2]^+$. The loss of Cl from the structure results in the base peak at 43 amu. **32.28** The product of the oxidation (using chromic acid) can be a ketone or aldehyde (which can react further to a carboxylic acid). Because there are only 2 signals in the ^1H NMR spectrum, it can be inferred that the molecule is symmetric with only two different 'environments' for the hygrogens. The presence of a triplet and quartet with same coupling indicates a $-CH_2CH_3$ (ethyl) group. The quartet at 2.35 ppm is more downfield than the triplet, which indicates that it is close to an electron withdrawing group – in this case, a carbonyl. The functionality must therefore be a ketone, as aldehydes and carboxylic acids are terminal. The structure of the molecule is shown below, and consists of the ketone and two ethyl groups.



3-pentanone

32.30 Chemical Evidence:

The Lassaigne test is used to detect the presence of nitrogen, sulfur and halogens in organic compounds. From the empirical formula, it is known that there is nitrogen in the compound. In this case the Lassaigne test is positive for nitrogen.

Microanalysis:

	C	H	N
% composition	71.22	14.94	13.84
relative atomic mass	12.01	1.01	14.01
Divide by relative atomic mass	5.89	14.79	0.99
Divide by	0.99	0.99	0.99
Ratio of atoms	5.95	14.94	1
Round to nearest whole number	6	15	1

Empirical formula = $C_6H_{15}N$

Mass spectrum:

From the mass spectrum the molecular ion peak appears at *m/z* 101. Peak at 86 represents a loss of 15 mass units ($-CH_3$). Mass of empirical formula: $C_6H_{15}N$ = 101 g mol^{-1}. Therefore molecular formula is $C_6H_{15}N$.

IR spectrum:

No signal for N–H, so there must be a tertiary amine present.

^{1}H NMR

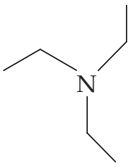
There are only two signals in the proton NMR, which indicates some symmetry in the molecule. The presence of a triplet and quartet with same coupling indicates a $-CH_2CH_3$ (ethyl) group. The quartet at 2.5 ppm is more downfield than the triplet, which indicates that it is close to an electron withdrawing group (the nitrogen). In addition to this, there are only 5 hydrogens accounted for in the spectrum, which means that the triplet and quartet actually integrate for 9 and 6 hydrogens (*i.e.,* three ethyl groups).

^{13}C NMR

There are two signals, which indicate two different types of carbons in the molecule. The signal at 16 ppm is that of the $-CH_3$ groups, and the more downfield signal (at 47 ppm, due to neighboring N atom) is of the $-CH_2$ groups

Putting it all together:

The likely structure of the unknown is:



Triethylamine

32.32 Chemical Evidence:

Reaction with Brady's reagent forming a highly coloured compound suggests the presence of a ketone or aldehyde in the molecule.

Microanalysis:

	C	H	O
% composition	58.32	8.39	33.29
Atomic mass	12.01	1.01	16.00
Divide by relative atomic mass	4.86	8.31	2.08
Divide by	2.08	2.08	2.08
Ratio of atoms	2.33	3.99	1
Whole number ratio of atoms	7	12	3

Empirical formula = $C_7H_{12}O_3$

Mass spectrum:

From the mass spectrum the $[M + H]^+$ peak appears at m/z 145. Mass of empirical formula: $C_7H_{12}O_3$ = 144 g/mol. Therefore molecular formula is $C_7H_{12}O_3$.

IR spectrum:

Strong peak at 1700 cm^{-1}: C = O

^{1}H NMR

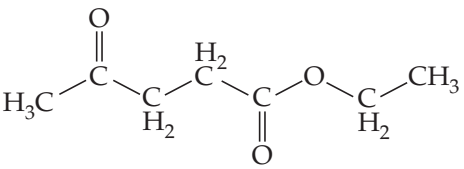
The presence of a triplet and quartet with same coupling indicates a $-CH_2CH_3$ group. The $-CH_2$ appears as a quartet since it is next to a $-CH_3$ group. Since the quartet for the $-CH_2$ group appears at 3.97 ppm, this indicates it is bonded next to an oxygen. The two triplets around 2.5 ppm have the same coupling, which implies that they are next to each other and also as they have similar chemical shifts, it is expected that they are in a similar chemical environment. The signal at 2.0 ppm integrating for three protons is not in close proximity to other hydrogens, so is a singlet.

^{13}C NMR

The signals at 208 and 172 ppm are both indicative of –C=O carbons, suggesting two such groups are present. The downfield carbonyl signal is consistent with an ester (due to the electronegativity of the adjoining oxygen).

Putting it all together:

The likely structure of the unknown is:



Ethyl 4-oxopentanoate

32.33 (**a**) $A = -\log_{10}T = 0.21$ $T = 10^{-0.21} = 0.617$ %T = 61.7% (**b**) $A = \varepsilon \times c \times l$ 0.48 = 300 $dm^3\ mol^{-1}\ cm^{-1} \times c \times 1.0$ cm c = 0.48 / (300 × 1.0) mol dm^{-3} 1.6×10^{-3} M **32.35** (**a**) The label of 600 MHz indicates radio frequency (RF) radiation or operating frequency. The higher this number the better the spatial resolution and image that the instrument can obtain. This number is important for calculating chemical shift. (**b**) The stronger the applied magnetic field the greater the population difference between the two spin states (parallel and anti-parallel) of the ^{1}H nucleus. Increasing this difference leads to greater sensitivity, increased resolution, decreased acquisition time and a better signal-to-noise ratio. (**c**) Superconducting magnets emit a magnetic field. Implants and other foreign bodies made of ferromagnetic materials (those that are magnetic or respond to a magnetic field) can move or heat up if such a strong field is applied to the body. As such many implants are made from titanium that do not exhibit ferromagnetism. The strong magnetic field required for MRI is known to interfere with artificial pacemakers and hence the technique can not be used on a person that has had one implanted. Other safety concerns relate to potential projectiles in the room and the use of cryogens. Current superconducting magnets require cooling to very low temperatures to be able to superconduct. The cold liquids used (liquid He and liquid N_2) possess their own safety concerns, one of which is the risk of asphyxiation. **32.37** These two compounds can be distinguished using mass spectrometry by: i) The distinct isotopic pattern of Cl in a mass spectrum ($[M]^+$: $[M+2]^+$ peaks with a ratio of 3:1. ii) By studying the fragmentation peaks and looking for characteristic mass losses of 35 and 37 atomic mass units (amu) for Cl. **32.40** If picric acid were a carboxylic acid it would contain stretches at around 1700 cm^{-1} and 3500 cm^{-1}. As a phenol, it contains an absorption at 3500 cm^{-1}. **32.41** (**a**) Bioimaging using the functional group would allow the mapping of water in the body, distinguishing between different sorts of tissues. For bioimaging of molecules other than water, the C=O group would probably be most useful because it occurs in all proteins, while water would mask the O–H signal of other molecules containing this functional group and C≡N is rare in biological systems. (**b**) The amide and amine functional groups are widely distributed in biological systems so bioimaging based on N–H might be useful. Because of the similarity between the O–H and N–H functional groups behaviour in the infrared, a bioimaging technique based on infrared using N–H would probably run into problems with masking of signal by water.

32.44 (**a**)



2-propanol 1-propanol

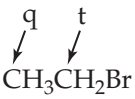
(**b**) The ^{1}H NMR for 2-propanol should give three signals with integration 1:6:1:

1. A broad singlet for the –OH
2. A doublet for the 6 $-CH_3$ protons
3. A septet for the 1H on the central carbon

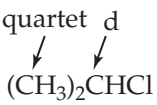
The ^{1}H NMR for 1-propanol should give four signals with integration 1:2:2:3:

1. A broad singlet for the –OH
2. A triplet for the 2 $-CH_2-O$ protons
3. A multiplet for the 2 $C-CH_2-C$ protons
4. A triplet for the 3 $-CH_3$ protons

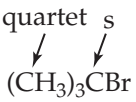
32.45 (**a**) s = singlet, d = doublet, t = triplet, q = quartet



(**b**)



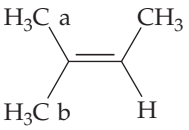
(**c**)



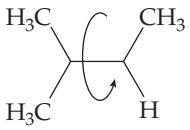
32.46 (**a**) The direction of electron spin does not affect the energy of the electron unless it is in a strong applied magnetic field. Hence strong magnets were needed to discover electron spin as they produced a small, but measurable, change in electron energy. The

detection of two different energy states in a magnetic field led to the formulation of the electron spin concept. (**b**) An ESR experiment requires greater energy than an NMR experiment. Microwave radiation is at a higher frequency than radio frequency radiation and photon energy is directly proportional to frequency: E=hν.

32.47



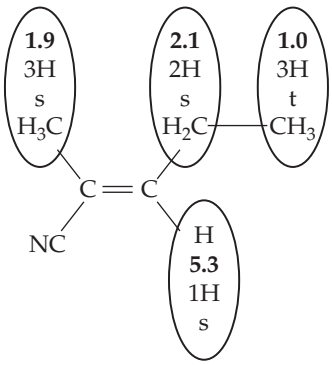
2-methyl-2-butene



2-methylbutane

Due to the inability to rotate around the C=C double bond, the two –CH_3 groups in 2-methyl-2-butene labelled 'a' and 'b' are in different magnetic environments. As such they each produce a distinct ^{13}C signal, as do all the other carbons in the compound, leading to 5 signals being observed. When the double bond is broken to form the alkane, free rotation about the C–C single bond makes the two –CH_3 groups magnetically and chemically equivalent and hence only one signal is observed for the two carbons. **32.49** (**a**) 3 (**b**) 4 (**c**) 3 (**d**) 5 **32.50** Spin ½ nuclei such as ^{31}P and ^{1}H couple to each other and cause splitting according to the n+1 rule. Hence for PH_2Cl we have two magnetically and chemically equivalent H that will not couple to each other. We would expect the following: ^{1}H NMR: A doublet integrating for 2 protons ^{31}P NMR: A triplet integrating for 1 phosphorus

32.51



32.52 Boron occurs naturally as two isotopes ^{10}B (19.9%) and ^{11}B (80.1%). Triethylborane [$(CH_3CH_2)_3B$] has a mass of (6×12)+(15×1)+10 = 97 amu or (6×12)+(15×1)+11 = 98 amu depending on which isotope of boron is present in the molecule. **32.53** Microanalysis determines the empirical formula, which then needs to be multiplied by a factor to get the correct molecular weight to give the molecular formula. In this case, the molecular and empirical formulas are the same. From TABLE 32.4, it can be seen that chlorine and bromine both exist as two isotopes ($[M]^+$ and $[M+2]^+$, each of which are of significant abundance). The two isotopes of bromine however, are almost of equal abundance so by calculating the extra 52.90% of the elemental analysis as bromine of average atomic weight 80 and following the procedure of 32.38, the following is found: Empirical formula = $C_5H_{11}Br$ From the mass spectrum the molecular ion peak appears at m/z 150, and the $[M+2]^+$ peak appears at m/z 152 Mass of empirical formula: $C_5H_{11}{}^{79}Br$ = 150 amu. Mass of empirical formula: $C_5H_{11}{}^{81}Br$ = 152 amu. Therefore, molecular formula is $C_5H_{11}Br$. **32.55** (**a**) Molecular ion peak (**b**) Molecular ion peak plus 2 mass units (**c**) The peak in the mass spectrum that has the greatest intensity (**d**) Mass to charge ratio (**e**) Electron impact mass spectrometry **32.56** If we study the compounds below we notice that oxygen does not change the ratio of C:H as it requires two bonds. This means effectively it inserts between a C–C bond or C–H bond without changing the ratio. Nitrogen atoms require 3 bonds so incorporating into a C–C bond or C–H bond requires the addition of an extra H to complete the valence of nitrogen.

$H_3C—CH_3$	$H_3C—CH_2—OH$	$H_3C—O—CH_3$	$H_3C—CH_2—NH_2$
C_nH_{2n+2}	C_nH_{2n+2}	C_nH_{2n+2}	C_nH_{2n+3}

32.58 Chemical Evidence:
Amino acids contain oxygen and nitrogen atoms, so the missing atom in the elemental analysis is oxygen.

Microanalysis:

	C	H	N	O
% composition	46.59	8.80	13.58	31.03
relative atomic mass	12.01	1.01	14.01	16.00
Divide by relative atomic mass	3.88	8.71	0.97	1.94
Divide by	0.97	0.97	0.97	0.97
Ratio of atoms rounded to nearest whole number	4	9	1	2

Empirical formula = $C_4H_9NO_2$

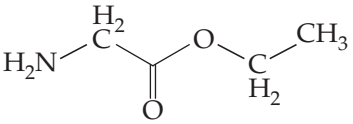
Mass spectrum:
From the mass spectrum the molecular ion peak appears at m/z 103. Peak at 74 represents a loss of 29 mass units (–CH_2CH_3). Mass of empirical formula: $C_4H_9NO_2$ = 103 g mol^{-1}. Therefore molecular formula is $C_4H_9NO_2$.

IR spectrum:
Strong peak at 1700 cm^{-1}: C = O Broad peak from 3000–3100 cm^{-1}: N–H

^{1}H NMR
The presence of a triplet and quartet with same coupling indicates a –CH_2CH_3 (ethyl) group. The –CH_2 appears as a quartet since it is next to a –CH_3 group. Since the quartet for the –CH_2 group appears at 4.16 ppm, this indicates it is bonded next to an oxygen group. The broad singlet at 3.4 ppm indicated an –NH_2 group, while the singlet at 2.15 ppm is indicative of the –CH_2 group next to the amine.

^{13}C NMR
The signal at 175 ppm is indicative of a carbonyl carbon, while the signal at 61 ppm for the –CH_2 group next to the amine. The –CH_2 and –CH_3 groups of the ethyl groups have signals at 43 and 15 ppm respectively. The –CH_2 signal is more downfield because it is in close proximity to the oxygen.

Putting it all together:
The likely structure of the unknown is:



Ethyl 2-aminoacetate or glycine ethyl ester

32.60 Chemical Evidence:
Reaction with aqueous sodium bicarbonate indicates that the organic unknown possesses a carboxylic acid.

Microanalysis:

	C	H	O
% composition	48.64	8.16	43.2
Divide by relative atomic mass	12.01	1.01	16.00
	4.04	8.08	2.7
Divide by lowest	2.7	2.7	2.7
Ratio of atoms	1.5	3	1
Multiply by 2	3	6	2

Empirical formula = $C_3H_6O_2$

Mass spectrum:

From the mass spectrum the molecular ion peak appears at *m/z* 74. Peak at 57 represents a loss of 17 mass units (–OH). Mass of empirical formula: $C_3H_6O_2 = 74$ g mol^{-1}. Therefore molecular formula is $C_3H_6O_2$.

IR spectrum:

Strong peak at 1700 cm^{-1}: C = O Broad peak from 3000–3200 cm^{-1}: O–H

^{1}H NMR

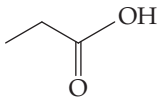
The presence of a triplet and quartet with same coupling indicates a $-CH_2CH_3$ group. The $-CH_2$ appears as a quartet since it is next to a $-CH_3$ group. Since the quartet for the $-CH_2$ group appears at 2.3 ppm, this indicates it is bonded next to a –C=O group.

^{13}C NMR

There are three peaks indicating the presence of 3 different types of carbon atoms. The peak at approximately 182 ppm is indicative of a –C=O carbon.

Putting it all together:

The likely structure of the unknown is:



CH_3CH_2COOH

Propionic acid

ANSWERS TO GO FIGURE

Chapter 1

Figure 1.1 Aspirin. It contains 9 carbon atoms. ***Figure 1.4*** Vapor (gas) ***Figure 1.5*** Molecules of a compound are composed of more than one type of atom, and molecules of an element are composed of only one type of atom. ***Figure 1.6*** It would get larger because hydrogen atoms are lighter than the atoms of any other element. ***Figure 1.7*** (**c**) Each water molecule contains one oxygen atom and two hydrogen atoms. ***Figure 1.14*** The separations are due to physical processes of adsorption of the materials onto the column ***Figure 1.18*** True ***Figure 1.19*** 1000 ***Figure 1.23*** The darts would be scattered widely (poor precision) but their average position would be at the center (good accuracy).

Chapter 2

Figure 2.2 Cathode rays would still be generated but without the fluorescent screen you would not be able to see them. ***Figure 2.3*** The electron beam would be deflected downward because of repulsion by the upper negative plate and attraction toward the positive plate. ***Figure 2.4*** No, the electrons are of negligible mass compared with an oil drop. ***Figure 2.6*** Beta rays are equivalent to electrons. (**a**) They are lighter. ***Figure 2.8*** The beam consists of alpha particles, which carry a +2 charge. They are repelled from the positively charged gold nuclei. ***Figure 2.9*** 10^{-2} pm ***Figure 2.12*** Based on the periodic trend, we expect that elements that precede a nonreactive gas, as F does, will also be reactive nonmetals. The elements fitting this pattern are H and Cl. ***Figure 2.14*** All of the metals shown here are solids, that exhibit varying degrees of luster to their appearance. In contrast, bromine is a liquid and none of the nonmetals shown here are lustrous. ***Figure 2.16*** The ball-and-stick model. ***Figure 2.17*** The elements are in the following groups: Ag^+ is 11, Zn^{2+} is 12, and Sc^{3+} is 3. Only Sc^{3+} has the same number of electrons as a noble gas, Ar (element 18). ***Figure 2.18*** No it is not, ionic solids like NaCl do not contain discrete molecules. ***Figure 2.21*** Removing one O atom from the perbromate ion gives the bromate ion, BrO_3^-.

Chapter 3

Figure 3.3 There are two CH_4 and four O_2 molecules on the reactant side, which contain 2 C atoms, 8 H atoms and 8 O atoms. The number of each type of atom remains the same on the product side as it must. ***Figure 3.7*** The flame gives off heat and therefore the reaction must release heat. ***Figure 3.8*** Avogadro's number ***Figure 3.10*** g/mol and mol^{-1} ***Figure 3.16*** If the amount of H_2 is doubled then O_2 becomes the limiting reactant. In that case $(7\ mol\ O_2) \times (2\ mol\ H_2O/1\ mol\ O_2) =$ 14 mol H_2O would be produced.

Chapter 4

Figure 4.2 NaCl(*aq*) ***Figure 4.3*** K^+ and NO_3^- ***Figure 4.7*** Mg$(NO_3)_2$ and water ***Figure 4.10*** Two. Each O atom becomes an O^{2-} ion. ***Figure 4.11*** One, based on the reaction stoichiometry. ***Figure 4.12*** Because the Cu(II) ion produces a blue color in aqueous solution. ***Figure 4.16*** The volume needed to reach the end point if $Ba(OH)_2(aq)$ were used would be one-half the volume needed for titration with NaOH(*aq*), because there are two hydroxide ions for every barium ion.

Chapter 5

Figure 5.2 The electrostatic potential energy of two oppositely charged particles is negative (Equation 5.2). As the particles become closer, the electrostatic potential energy becomes even more negative—that is, it decreases. ***Figure 5.3*** Attractions between oppositely charged ions would cause the ions to move closer together reducing the potential energy of the system. The lost potential energy is converted to kinetic energy needed to move the ions. ***Figure 5.4*** The number of molecules will change because three reactant molecules (2 H_2 and 1 O_2) are needed to make two product (H_2O) molecules. However, in a closed system like this one the total mass will not change. ***Figure 5.5*** If $E_{final} = E_{initial}$, then $\Delta E = 0$. ***Figure 5.6***

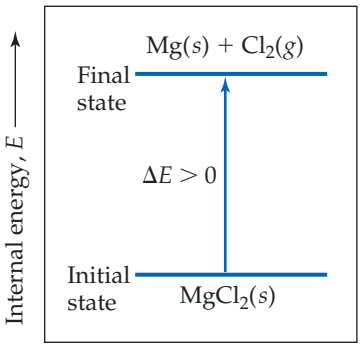


Figure 5.7 $\Delta E = 50\ J + (-85\ J) = -35\ J$ ***Figure 5.10*** The battery is doing work on the surroundings, so $w < 0$. ***Figure 5.11*** The system does work on the surroundings to move the piston upward, so $w < 0$. ***Figure 5.17*** Endothermic—heat is being added to the system to raise the temperature of the water. ***Figure 5.18*** Two cups provide more thermal insulation so less heat will escape the system. ***Figure 5.19*** In a calorimeter the system is defined as the reactants and products, so the water inside the calorimeter is part of the surroundings. ***Figure 5.21*** The condensation of 2 $H_2O(g)$ to 2 $H_2O(l)$ ***Figure 5.22*** Yes, ΔH_3 would remain the same as it is the enthalpy change for the process $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$. ***Figure 5.24*** Exothermic, because the enthalpy of the products is lower than that of the reactants. ***Figure 5.25*** Grams of fat

Chapter 6

Figure 6.3 Wavelength = 1.0 m, frequency = 3.0×10^8 cycles/s. ***Figure 6.4*** Longer by 3 to 5 orders of magnitude (depending on what part of the microwave spectrum is considered). ***Figure 6.5*** The part of the nail glowing yellow is hotter than the part glowing red. ***Figure 6.7*** As the frequency of the incoming light is increased the photon energy will increase and the kinetic energy of the ejected electrons will increase. ***Figure 6.11*** The $n = 2$ to $n = 1$ transition involves a larger energy change than the $n = 3$ to $n = 2$ transition. (Compare the lengths of the arrows connecting the states in the figure.) If the $n = 3$ to $n = 2$ transition produces visible light, the $n = 2$ to $n = 1$ transition must produce radiation of greater energy. Of the two choices only ultraviolet radiation has higher frequency and greater energy than visible light. ***Figure 6.12*** The $n = 4$ to $n = 3$ transition involves a smaller energy difference and will therefore emit light of longer wavelength. ***Figure 6.16*** The region of highest electron density is where the density of dots

is highest, which is near the nucleus. ***Figure 6.17*** For a single electron atom like hydrogen the energies of the orbitals are the same as the energies of the orbits in the Bohr model. ***Figure 6.18*** There would be four maxima and three nodes. ***Figure 6.22*** The p_x orbital. ***Figure 6.23*** There are two nodal planes for each of the *d*-orbitals. For the d_{xy} orbital the nodal planes are the *xz* and *yz* planes. ***Figure 6.24*** The 4*d* and 4*f* subshells are not shown. ***Figure 6.30*** Osmium

Chapter 7

Figure 7.1 These three metals do not readily react with other elements, especially oxygen, so they are often found in nature in the elemental form as metals (such as gold nuggets) ***Figure 7.4*** Because of the peak near the nucleus in the 2*s* curve there is a higher probability of finding a 2*s* within 50 pm of the nucleus. In a multielectron atom an electron in a 2*s* orbital will have a lower energy than one in a 2*p* orbital. ***Figure 7.7*** Bottom and left ***Figure 7.8*** They get larger, just like the atoms do. ***Figure 7.10*** 900 kJ/mol ***Figure 7.11*** There is more electron–electron repulsion in the case of oxygen because two electrons have to occupy the same orbital. ***Figure 7.12*** The added electron for the Group 14 elements leads to a half-filled np^3 configuration. For the Group 15 elements, the added electron leads to an np^4 configuration, so the electron must be added to an orbital that already has one electron in it, and thus experiences more electron-electron repulsion. ***Figure 7.13*** They are opposite: As ionization energy increases, metallic character decreases, and vice versa. ***Figure 7.15*** Anions are above and to the right of the line; cations are below and to the left of the line. ***Figure 7.16*** No. The Na^+ and NO_3^- ions will simply be spectator ions. The H^+ ions of an acid are needed in order to dissolve NiO. ***Figure 7.17*** No. As seen in the photo, sulfur crumbles as it is hit with a hammer, typical of a solid nonmetal. ***Figure 7.21*** Because Rb is below K in the periodic table, and has a lower first ionization energy we expect Rb to be more reactive with water than K. ***Figure 7.23*** Lilac (see ***Figure 7.22***). ***Figure 7.25*** The bubbles are due to $H_2(g)$. This could be confirmed by carefully testing the bubbles with a flame—there should be popping as the hydrogen gas ignites. ***Figure 7.26*** A regular octagon. ***Figure 7.27*** I_2 is a solid whereas Cl_2 is a gas. Molecules are more closely packed together in a solid than they are in a gas, as will be discussed in detail in Chapter 11.

Chapter 8

Figure 8.1 We would draw the chemical structure of sugar molecules (which have no charges and have covalent bonding between atoms in each molecule) and indicate weak intermolecular forces (especially hydrogen bonding) between sugar molecules. ***Figure 8.3*** Yes. ***Figure 8.4*** Cations have a smaller radius than their neutral atoms and anions have a larger radius. Because Na and Cl are in the same row of the periodic table, we would expect Na^+ to have a smaller radius than Cl^-, so we would infer that the larger green spheres represent the chloride ions and the smaller purple spheres represent the sodium ions. ***Figure 8.5*** The distance between ions in KF should be larger than that in NaF and smaller than that in KCl. We would thus expect the lattice energy of KF to be between 701 and 910 kJ/mol. ***Figure 8.7*** The repulsions between the nuclei would decrease, the attractions between the nuclei and the electrons would decrease, and the repulsions between the electrons would be unaffected. ***Figure 8.8*** The electronegativity decreases with increasing atomic number. ***Figure 8.10*** μ will decrease. ***Figure 8.11*** The bonds are not polar enough to cause enough excess electron density on the halogen atom to lead to a red shading. ***Figure 8.13*** The lengths of the bonds of the outer O atoms to the inner O atom are the same. ***Figure 8.14*** Yes. The electron densities on the left and right parts of the molecule are the same, indicating that resonance has made the two O — O bonds equivalent to one another. ***Figure 8.15*** It should be halfway between the values for single and double bonds, which we can estimate to be about 280 kJ/mol from the graph.

Chapter 9

Figure 9.1 The radii of the atoms involved (see Section 7.3). ***Figure 9.2*** NF_3 ***Figure 9.3*** Octahedral. ***Figure 9.4*** No. We will get the same bent-shaped geometry regardless of which two atoms we remove. ***Figure 9.8*** 90°. ***Figure 9.9*** The C — O — H bond involving the right O because of the greater repulsions due to the nonbonding electron domains. The angle should be less than the ideal value of 109.5°. ***Figure 9.10*** Zero. Because they are equal in magnitude but opposite in sign, the vectors cancel upon addition. ***Figure 9.13*** 74 pm is the bond length, 436 kJ/mol is the bond strength. ***Figure 9.16*** 120° ***Figure 9.17*** The p_z orbital. ***Figure 9.18*** No. All four hybrids are equivalent and the angles between them are all the same, so we can use any of the two to hold the nonbonding pairs. ***Figure 9.19*** Because the P 3*p* orbitals are larger than the N 2*p* orbitals, we would expect somewhat larger lobes on the hybrid orbitals in the right-most drawing. Other than that, the molecules are entirely analogous. ***Figure 9.22*** They have to lie in the same plane in order to allow the overlap of the π orbitals to be effective in forming the π bond. ***Figure 9.23*** Acetylene should have the higher carbon-carbon bond energy because it has a triple bond as compared to the double bond in ethylene. ***Figure 9.25*** It has six C — C σ and six C — H σ bonds. ***Figure 9.31*** σ_{1s}^2, $\sigma^*_{1s}{}^1$. ***Figure 9.32*** σ^*_{1s} and σ^*_{2s}. ***Figure 9.33*** The end-on overlap in the σ_{2p} MO is greater than the sideways overlap in the π_{2p}. ***Figure 9.39*** The σ_{2p} and π_{2p} MOs have switched order. ***Figure 9.40*** O_2 and F_2 ***Figure 9.42*** N_2 is diamagnetic so it would not be attracted to the magnetic field. The liquid nitrogen would simply pour through the poles of the magnet without "sticking." ***Figure 9.43*** 11. All the electrons in the $n = 2$ level are valenceshell electrons.

Chapter 10

Figure 10.2 It will increase. ***Figure 10.5*** Decreases ***Figure 10.6*** 1520 torr or 203 kPa ***Figure 10.9*** One ***Figure 10.10*** Chlorine, Cl_2. ***Figure 10.12*** About one-sixth ***Figure 10.13*** O_2 has the largest molar mass, 32 g/mol, and H_2 has the smallest, 2.0 g/mol. ***Figure 10.16*** *n*, moles of gas ***Figure 10.20*** True ***Figure 10.22*** It would increase.

Chapter 11

Figure 11.1 The density in a liquid is much closer to a solid than it is to a gas. ***Figure 11.3*** The distance within the molecule (the covalent bond distance) represented by the solid black line is smaller than the intermolecular distance represented by the red dotted line. ***Figure 11.5*** The halogens are diatomic molecules and have much greater size and mass, and therefore greater polarizability, than the noble gases, which are monatomic. ***Figure 11.8*** They stay roughly the same because the molecules have roughly the same molecular weights. Thus, the change in boiling point moving left to right is due mainly to the increasing dipole-dipole attractions. ***Figure 11.9*** Both compounds are nonpolar and incapable of forming hydrogen bonds. Therefore, the boiling point is determined by the dispersion forces, which are stronger for the larger,

heavier AsH_3. ***Figure 11.10*** The non-hydrogen atom must possess a nonbonding electron pair. ***Figure 11.11*** There are four electron pairs surrounding oxygen in a water molecule. Two of the electron pairs are used to make covalent bonds to hydrogen within the H_2O molecule, while the other two are available to make hydrogen bonds to neighboring molecules. Because the electron-pair geometry is tetrahedral (four electron domains around the central atom), the H — O · · · H bond angle is approximately 109°. ***Figure 11.13*** The O atom is the negative end of the polar H_2O molecule; the negative end of the dipole is attracted to the positive ion. ***Figure 11.14*** Yes, although not likely. ***Figure 11.19*** Wax is a hydrocarbon that cannot form hydrogen bonds. Therefore, coating the inside of tube with wax will dramatically decrease the adhesive forces between water and the tube and change the shape of the water meniscus to an inverted U-shape. Neither wax nor glass can form metallic bonds with mercury so the shape of the mercury meniscus will be qualitatively the same, an inverted U-shape. ***Figure 11.20*** Because energy is a state function, the energy to convert a gas to a solid is the same regardless of whether the process occurs in one or two steps. Thus, the energy of deposition equals the energy of condensation plus the energy of freezing. ***Figure 11.21*** Because water has stronger intermolecular interactions. ***Figure 11.22*** The temperature of the liquid water is increasing. ***Figure 11.24*** Increases, because the molecules have more kinetic energy as the temperature increases and can escape more easily ***Figure 11.25*** All liquids including ethylene glycol reach their normal boiling point when their vapor pressure is equal to atmospheric pressure, 101.3 kPa. ***Figure 11.27*** It must be lower than the temperature at the triple point.

Chapter 12

Figure 12.5 There is not a centered square lattice, because if you tile squares and put lattice points on the corners and the center of each square it would be possible to draw a smaller square (rotated by 45°) that only has lattice points on the corners. Hence a "centered square lattice" would be indistinguishable from a primitive square lattice with a smaller unit cell. ***Figure 12.12*** Face-centered cubic, assuming similar size spheres and cell edge lengths, since there are more atoms per volume for this unit cell compared to the other two. ***Figure 12.13*** A hexagonal lattice ***Figure 12.15*** The solvent is the majority component and the solute the minority component. Therefore, there will be more solvent atoms than solute atoms. ***Figure 12.17*** The samarium atoms sit on the corners of the unit cell so there is only $8 \times (1/8) = 1$ Sm atom per unit cell. Eight of the nine cobalt atoms sit on faces of the unit cell, and the other sits in the middle of the unit cell so there are $8 \times (1/2) + 1 = 5$ Co atoms per unit cell. ***Figure 12.19*** P_4, S_8, and Cl_2 are all molecules, because they have strong chemical bonds between atoms and have well-defined numbers of atoms per molecule. ***Figure 12.21*** In the fourth period, vanadium and chromium have very similar melting points. Molybdenum and tungsten have the highest melting points in the fifth and sixth periods, respectively. All of these elements are located near the middle of the period where the bonding orbitals are mostly filled and the antibonding orbitals mostly empty. ***Figure 12.22*** The molecular orbitals become more closely spaced in energy. ***Figure 12.23*** Potassium has only one valence electron per atom ($4s^1$). Therefore we expect the 4*s* band to be approximately half full. If we fill the 4*s* band halfway a small amount of electron density might leak over and start to fill the 3*d* orbitals as well. The 4*p* orbitals should be empty. ***Figure 12.24*** Ionic substances cleave because the nearest neighbor interactions switch from attractive to repulsive if the atoms slide so that ions of like charge (cation–cation and anion–anion) touch each other. Metals don't cleave because the atoms are attracted to all other atoms in the crystal through metallic bonding. ***Figure 12.25*** No, ions of like charge do not touch in an ionic compound because they are repelled from one another. In an ionic compound the cations touch the anions. ***Figure 12.27*** In NaF there are four Na^+ ions ($12 \times 1/4$) and four F^- ions ($8 \times 1/8 + 6 \times 1/2$) per unit cell. In MgF_2 there are two Mg^{2+} ions ($8 \times 1/8 + 1$) and four F^- ions ($4 \times 1/2 + 2$) per unit cell. In ScF_3 there is one Sc^{3+} ion ($8 \times 1/8$) and three F^- ions ($12 \times 1/4$) per unit cell. ***Figure 12.28*** The intermolecular forces are stronger in toluene, as shown by its higher boiling point. The molecules pack more efficiently in benzene, which explains its higher melting point, even though the intermolecular forces are weaker. ***Figure 12.30*** The band gap for an insulator would be larger than the one for a semiconductor. ***Figure 12.31*** If you doubled the amount of doping in panel (**b**), the amount of blue shading the conduction band would also double. ***Figure 12.44*** Decrease. As the quantum dots get smaller, the band gap increases and the emitted light shifts to shorter wavelength. ***Figure 12.48*** Each carbon atom in C_{60} is bonded to three neighboring carbon atoms through covalent bonds. Thus, the bonding is more like graphite, where carbon atoms also bond to three neighbors, than diamond, where carbon atoms bond to four neighbors.

Chapter 13

Figure 13.1 Gas molecules move in constant random motion. ***Figure 13.2*** Opposite charges attract. The electron-rich O atom of the H_2O molecule, which is the negative end of the dipole, is attracted to the positive Na^+ ion. ***Figure 13.4*** For exothermic solution processes the magnitude of ΔH_{mix} will be larger than the magnitude of $\Delta H_{solute} + \Delta H_{solvent}$ ***Figure 13.6*** 46 g. ***Figure 13.11*** If the partial pressure of a gas over a solution is doubled, the concentration of gas in the solution would double. ***Figure 13.12*** The highest. ***Figure 13.14*** Looking at where the solubility curves for KCl and NaCl intersect the 80 °C line, we see that the solubility of KCl is about 51 g/100 g H_2O, whereas NaCl has a solubility of about 39 g/100 g H_2O. Thus, KCl is more soluble than NaCl at this temperature. ***Figure 13.15*** N_2 has the same molecular weight as CO but is nonpolar, so we can predict that its curve will be just below that of CO. ***Figure 13.21*** The water will move through the semipermeable membrane toward the more concentrated solution. Thus, the liquid level in the left arm will increase. ***Figure 13.22*** Water will move toward the more concentrated solute solution, which is inside the red blood cells, causing them to undergo hemolysis. ***Figure 13.25*** The negatively charged groups both have the composition $—CO_2^-$. ***Figure 13.27*** Recall the rule that likes dissolve likes. The oil drop is composed of nonpolar molecules, which interact with the nonpolar part of the stearate ion via dispersion forces.

Chapter 14

Figure 14.1 No. The surface area of a steel nail is much smaller than that for the same mass of steel wool, so the reaction with O_2 would not be as vigorous. Depending on how hot it is, it might not burn at all. ***Figure 14.2*** Our first guess might be half way between the values at 20 s and 40 s, namely 0.42 mol A. However, we also see that the change in the number of moles of A between 0 s and 20 s is greater than that between 20 s and 40 s—in other words, the rate of

conversion gets smaller as the amount of A decreases. So we would guess that the change from 20 s to 30 s is greater than the change from 30 s to 40 s, and we would estimate that the number of moles of A is between 0.42 and 0.30 mol. ***Figure 14.3*** The instantaneous rate decreases as the reaction proceeds. ***Figure 14.7*** The reaction is first order. ***Figure 14.9*** At the beginning of the reaction when both plots are linear or nearly so. ***Figure 14.13*** No, it will not turn down. The rate constant increases monotonically with increasing temperature because the kinetic energy of the colliding molecules continues to increase. ***Figure 14.15*** The difference in height between the ball and the top of the barrier. ***Figure 14.16*** As shown, the magnitude of energy needed to overcome the energy barrier is greater than the magnitude of the energy change in the reaction. ***Figure 14.17*** It would be more spread out, the maximum of the curve would be lower and to the right of the maximum of the red curve, and a greater fraction of molecules would have kinetic energy greater than E_a than for the red curve. ***Figure 14.19*** The rate of converting intermediates to products will be faster, because this reaction has a lower barrier than the reaction that converts intermediates back to reactants. ***Figure 14.20*** No, because the bottleneck, or rate determining step, is passing through toll plaza A. ***Figure 14.21*** The color is characteristic of molecular bromine, Br_2, which is an intermediate in this reaction. ***Figure 14.22*** There is one valley corresponding to the formation of intermediates, so the reaction has a total of two steps. ***Figure 14.25*** Grinding increases the surface area, exposing more of the catalase to react with the hydrogen peroxide. ***Figure 14.26*** Substrates must be held more tightly so that they can undergo the desired reaction. Products are released from the active site.

Chapter 15

Figure 15.1 The same because once the system reaches equilibrium the concentrations of NO_2 and N_2O_4 stop changing. ***Figure 15.2*** Because the concentration of reactants is decreasing, which reduces the frequency of collisions and hence the rate of the forward reaction. ***Figure 15.3*** Yes. The reaction stoichiometry dictates that H_2 disappears at three times the rate that N_2 disappears. ***Figure 15.5*** Experiment 4 ***Figure 15.6*** The boxes would be approximately the same size. ***Figure 15.7*** It would decrease. To reestablish equilibrium the concentration of $CO_2(g)$ would need to return to its previous value. The only way to do that would be for more $CaCO_3$ to decompose to produce enough $CO_2(g)$ to replace what was lost. ***Figure 15.9*** High pressure and low temperature, 500 atm and 400 °C in this figure. ***Figure 15.10*** Nitrogen must react with some of the added hydrogen to create ammonia and restore equilibrium. ***Figure 15.15*** (**a**) the energy difference between the initial state and the transition state. ***Figure 15.16*** About 5×10^{-4}

Chapter 16

Figure 16.1 Hydrogen bonds. ***Figure 16.3*** $O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq)$. ***Figure 16.4*** Basic. The mixture of the two solutions will still have $[H^+] < [OH^-]$. ***Figure 16.5*** Lemon juice. It has a pH of about 2 whereas black coffee has a pH of about 5. The lower the pH, the more acidic the solution. ***Figure 16.7*** Phenolphthalein changes from colorless, for pH values less than 8, to pink for pH values greater than 10. A pink color indicates pH $>$ 10. ***Figure 16.8*** Bromthymol blue would be most suitable because it changes pH over a range that brackets pH $=$ 7. Methyl red is not sensitive to pH changes when pH $>$ 6, while phenolphthalein is not sensitive to pH changes when pH $<$ 8, so neither changes color at pH $=$ 7. ***Figure 16.12*** Yes. The equilibrium of interest is $H_3CCOOH \rightleftharpoons H^+ + H_3CCOO^-$. If the percent dissociation remained constant as the acid concentration increased, the concentration of all three species would increase at the same rate. However, because there are two products and only one reactant, the product of the concentrations of products would increase faster than the concentration of the reactant. Because the equilibrium constant is constant, the percent dissociation decreases as the acid concentration increases. ***Figure 16.13*** 3. ***Figure 16.15*** The nitrogen atom in hydroxylamine accepts a proton to form NH_3OH^+. As a general rule, nonbonding electron pairs on nitrogen atoms are more basic than nonbonding electron pairs on oxygen atoms. ***Figure 16.17*** The range of pH values is so large that we can't show the effects using a single indicator (see Figure 16.8). ***Figure 16.20*** The HOY molecule on the left because it is a weak acid. Most of the HOY molecules remain undissociated.

Chapter 17

Figure 17.6 The pH will increase upon addition of the base. ***Figure 17.7*** 25.00 mL. The number of moles of added base needed to reach the equivalence point remains the same. Therefore, by doubling the concentration of added base the volume needed to reach the equivalence point is halved. ***Figure 17.9*** The volume of base needed to reach the equivalence point would not change because this quantity does not depend on the strength of the acid. However, the pH at the equivalence point, which is greater than 7 for a weak acid–strong base titration, would decrease to 7 because hydrochloric acid is a strong acid. ***Figure 17.11*** The pH at the equivalence point increases (becomes more basic) as the acid becomes weaker. The volume of added base needed to reach the equivalence point remains unchanged. ***Figure 17.12*** No; it would change color by pH 6 and miss pH 7. ***Figure 17.15*** $H_2PO_3^-$ at first equivalence point, HPO_3^{2-} at the second. ***Figure 17.22*** Because the solution is basic. ***Figure 17.23*** Yes. CuS would precipitate in step 2 on addition of H_2S to an acidic solution, while the Zn^{2+} ions remained in solution.

Chapter 18

Figure 18.1 About 85 km, at the mesopause. ***Figure 18.3*** The atmosphere absorbs a significant fraction of solar radiation. ***Figure 18.4*** (**c**) UV ***Figure 18.5*** The peak value is about 5×10^{12} molecules per cm^3. If we use Avogradro's number to convert molecules to moles, and the conversion factor of $1000\ cm^3 = 1000\ mL = 1\ L$, we find that the concentration of ozone at the peak is 8×10^{-9} mol/L. ***Figure 18.8*** $CaSO_3(s)$ ***Figure 18.10*** The Earth's surface absorbs 492 W/m^2. Of that amount 390 W/m^2 or 79% is radiated back toward the atmosphere. ***Figure 18.12*** The increasing slope corresponds to an increasing *rate* of addition of CO_2 to the atmosphere, probably as a result of ever-increasing burning of fossil fuels worldwide. ***Figure 18.14*** Evaporation from sea water, evaporation from freshwater; evaporation and transpiration from land. ***Figure 18.15*** As the temperature of water goes down its density increases. Therefore, density increases as depth increases (note the pressure also increases which also results in an increase in density). ***Figure 18.19*** To reduce concentrations of dissolved iron and manganese, remove H_2S and NH_3, and reduce bacterial levels.

Chapter 19

Figure 19.1 Yes, the potential energy of the eggs decreases as they fall. ***Figure 19.3*** To be truly reversible, the temperature change δT must be infinitesimally small. ***Figure 19.5*** Because the final volume would be less than twice the volume of Flask A, the final pressure would be greater than 50.7 kPa. ***Figure 19.8*** There are two other independent rotational motions of the H_2O molecule:

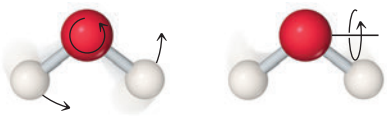


Figure 19.9 Ice, because it is the phase in which the molecules are held most rigidly ***Figure 19.11*** The decrease in the number of molecules due to the formation of new bonds. ***Figure 19.12*** During a phase change, the temperature remains constant but the entropy change can be large as molecules increase their degrees of freedom and motion. ***Figure 19.13*** Based on the three molecules shown, the addition of each C increases $S°$ by 40–45 J/mol K. Based on this observation, we would predict that $S°(C_4H_{10})$ would 310–315 J/mol K. Appendix C confirms that this is a good prediction: $S°(C_4H_{10}) = 310.0\,J/mol\,K$. ***Figure 19.14*** Spontaneous ***Figure 19.15*** If we plot progress of the reaction versus free energy, equilibrium is at a minimum point in free energy, as shown in the figure. In that sense, the reaction runs "downhill" until it reaches that minimum point.

Chapter 20

Figure 20.1 Exothermic. ***Figure 20.2*** The permanganate ion, MnO_4^-, is reduced, as the half-reactions in the text show. The oxalate ion, $C_2O_4^{2-}$, acts as the reducing agent. ***Figure 20.3*** The blue color is due to $Cu^{2+}(aq)$. As this ion is reduced, forming $Cu(s)$, its concentration decreases and the blue color fades. ***Figure 20.4*** The Zn is oxidized and, therefore, serves as the anode of the cell. ***Figure 20.5*** The electrical balance is maintained in two ways: Anions migrate into the half-cell, and cations migrate out via the salt bridge. ***Figure 20.9*** As the cell operates, H^+ is reduced to H_2 in the cathode half-cell. As H^+ is depleted, the positive Na^+ ions are drawn into the half-cell to maintain electrical balance in the solution. ***Figure 20.11*** Yes. ***Figure 20.13*** The variable n is the number of moles of electrons transferred in the process. ***Figure 20.14*** The cathode. ***Figure 20.19*** The cathode consists of $PbO_2(s)$. Because each oxygen has an oxidation state of −2, lead must have an oxidation state of +4 in this compound. ***Figure 20.20*** Zn ***Figure 20.21*** Co^{3+}. The oxidation number increases as the battery charges. ***Figure 20.24*** $O_2(g) + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O(g)$ ***Figure 20.25*** The oxidizing agent of $O_2(g)$ from the air. ***Figure 20.29*** 0 V

Chapter 21

Figure 21.1 From Figure 21.1 we see that the belt of stability for a nucleus containing 70 protons lies at approximately 102 neutrons. ***Figure 21.2*** $^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e$ ***Figure 21.3*** Only three of the elements with an even number of protons have fewer than three isotopes: He, Be, and C. Note that these three elements are the lightest elements that have an even atomic number. Because they are so light, any change in the number of neutrons will change the neutron/proton ratio significantly. This helps to explain why they do not have more stable isotopes. None of the elements in Figure 21.3 that have an odd number of protons have more than two stable isotopes. ***Figure 21.6*** 6.25 g. After one half-life, the amount of the radioactive material will have dropped to 25.0 g. After two half-lives, it will have dropped to 12.5 g. After three half-lives, it will have dropped to 6.25 g. ***Figure 21.7*** Plants convert $^{14}CO_2$ to ^{14}C-containing sugars via photosynthesis. When mammals eat the plants, they metabolize the sugars, thereby incorporating ^{14}C in their bodies. ***Figure 21.8*** Gamma rays. Both X rays and gamma rays consist of high-energy electromagnetic radiation, whereas alpha and beta rays are streams of particles. ***Figure 21.9*** Ionization energy. Detection depends on the ability of the radiation to cause ionization of the gas atoms. ***Figure 21.14*** The mass numbers are equal on both sides. Remember that this does not mean that mass is conserved—mass is lost during the reaction, which appears as energy released. ***Figure 21.15*** 16. Each of the eight neutrons would split another uranium-235 nucleus, releasing two more neutrons. ***Figure 21.16*** Critical without being supercritical so that the release of energy is controlled. ***Figure 21.23*** Alpha rays are less dangerous when outside the body because they cannot penetrate the skin. However, once inside the body they can do great harm to any cells that are nearby.

Chapter 22

Figure 22.5 Beaker on the right is warmer. ***Figure 22.6*** HF is the most stable, SbH_3 the least stable. ***Figure 22.8*** More soluble in CCl_4 — the colors are deeper. ***Figure 22.9*** CF_2 ***Figure 22.12*** No ***Figure 22.14*** Based on this structure—yes, it would have a dipole moment. In fact, if you look it up, hydrogen peroxide's dipole moment is larger than water's! ***Figure 22.19*** Formally they could both be +2. If we consider that the central sulfur is like SO_4^{2-}, however, then the central sulfur would be +6, like SO_4^{2-}, and the terminal sulfur would be −2. ***Figure 22.21*** Nitrite ***Figure 22.22*** Longer. (There is a triple bond in N_2.) ***Figure 22.24*** The NO double bond ***Figure 22.26*** In both compounds the electron domains around the P atoms are tetrahedral. In P_4O_{10} all the electron domains around the P atoms are bonding. In P_4O_6 one of the electron domains about each P atom is nonbonding. ***Figure 22.30*** The minimum temperature should be the melting point of silicon; the temperature of the heating coil should not be so high that the silicon rod starts to melt outside the zone of the heating coil.

Chapter 23

Figure 23.3 No. The radius decreases first and then flattens out before increasing on moving past group 8B, while the effective nuclear charge increases steadily on moving left to right across the transition metal series. ***Figure 23.4*** Zn^{2+}. ***Figure 23.5*** The 4*s* orbitals are always empty in transition metal ions, so all of the ions shown in this table have empty 4*s* orbitals. The 3*d* orbitals are only empty for those ions that have lost all of their valence electrons: Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, and Mn^{7+}. ***Figure 23.6*** The electron spins would tend to align with the direction of the magnetic field. ***Figure 23.8*** No. If you start with a chloride ion on one vertex of the octahedron and then generate structures by placing the second chloride ion on any of the other five vertices you will get one complex that is the *trans* isomer and four complexes that are equivalent to the *cis* isomer shown in this figure. ***Figure 23.9*** Neither the coordination number nor the oxidation state of iron change in this reaction. ***Figure 23.10*** The solid wedge represents a bond coming out of the plane of the page. The dashed wedge

represents a bond that is going into the plane of the page. ***Figure 23.13*** There are 20 carbon atoms in porphine, all of which have sp^2 hybridization. ***Figure 23.15*** The coordination number is 6. The blue atoms in the heme are nitrogen atoms. ***Figure 23.16*** The peak at 660 nm. ***Figure 23.20*** $[Fe(NH_3)_5(NO_2)]^{2+}$ and pentaammi-nenitroiron(III) ion for the complex on the left. $[Fe(NH_3)_5(ONO)]^{2+}$ and pentaamminenitritoiron(III) ion for the complex on the right. ***Figure 23.21*** The *cis* isomer. ***Figure 23.24*** Larger, since ammonia can displace water. ***Figure 23.26*** The peak would stay in the same position in terms of wavelength, but its absorbance would decrease. ***Figure 23.28*** $d_{x^2-y^2}$ and d_{z^2}. ***Figure 23.29*** Convert the wavelength of light, 495 nm, into energy in joules using the relationship $E = hc/\lambda$. ***Figure 23.30*** The absorption peak would shift to shorter wavelengths absorbing green light and the color of the complex ion would become red. An even larger shift would move the absorption peak into the blue region of the spectrum and the color would become orange. ***Figure 23.34*** Only the $d_{x^2-y^2}$ orbital points directly at the ligands.

Chapter 24

Figure 24.5 Four. ***Figure 24.12*** Staggered = chair, eclipsed = boat.

Chapter 25

Figure 25.1 No, there are no other ways of positioning three C–C bonds. ***Figure 25.12*** There is one that appears at the sharp end of the wedge.

Chapter 26

Figure 26.5 To achieve maximum overlap of the unhybridised orbitals thereby creating a π-bond. ***Figure 26.6*** Acetylene, since it has a triple bond. ***Figure 26.11*** None. ***Figure 26.14*** Z. ***Figure 26.20*** Exothermic.

Chapter 27

Figure 27.3 Three, one from the hydrogen attached to the oxygen and two involving the lone pairs on the oxygen. ***Figure 27.7*** Butan-2-ol is chiral. It has one stereocentre and so can exist as *R* or *S* stereoisomers. ***Figure 27.17*** The distributed alkenes; the 1,1-disubstituted alkene is a constitutional isomer of the 1,2-disubstituted alkenes and the two 1,2-disubstituted alkenes are stereoisomers (geometric isomers) of one another.

Chapter 28

Figure 28.1 O=C=O. ***Figure 28.2*** Propanoic acid, propanone. ***Figure 28.5*** Being a salt, $NaBH_4$ would not be very soluble in common organic solvents. It is slightly soluble in polar solvents like methanol where ion pairing can be disrupted. ***Figure 28.6*** Benzaldehyde. ***Figure 28.7*** Three. ***Figure 28.8*** Because of a plane of symmetry. ***Figure 28.13*** Four. There are four hydroxyl groups attached directly to the ring, all of which are in an equatorial position.

Chapter 29

Figure 29.1 Lactic acid and citric acid. ***Figure 29.2*** Non-polar solvents as polar solvents compete for hydrogen bonding. ***Figure 29.6*** Long-chain fatty acids. ***Figure 29.13*** They are nucleophiles. ***Figure 29.14*** It acts to cross-link the polymers.

Chapter 30

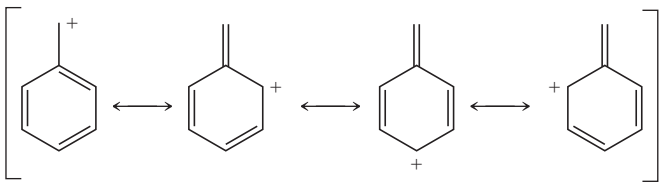
Figure 30.1 Apart from each having six carbons and both being hydrocarbons, there are no similarities. Their shape, electronic characteristics and reactivity are very different. ***Figure 30.4*** Vanillin: aldehyde, phenol, ether; styrene: alkene; asprin: carboxylic acid, ester; terephthalic acid: carboxylic acid; BHT: phenol; benzoic acid: carboxylic acid. ***Figure 30.9*** Two *ortho,* two *meta* and one *para*. ***Figure 30.14*** The nitro groups are converted to the very stable N_2 upon reaching the activation energy barrier, thereby releasing heat due to the exothermic nature of the reaction.

Chapter 31

Figure 31.1 The number of C–N bonds. ***Figure 31.2*** The pyridine N is 3°, the aliphatic amine is 1°. ***Figure 31.5*** The lone pair in cyclohexylamine cannot be redistributed and so is concentrated on the nitrogen. ***Figure 31.11*** All but glycine. ***Figure 31.18*** At pH 5.66, tyrosine has no net overall charge and will not move in an electrophoresis experiment. At pH 9, tyrosine will be deprotonated and attracted to the positive electrode. ***Figure 31.25*** A molecule of specific shape is required to unlock the activity the enzyme, similar to a specific key needed to unlock a lock. ***Figure 31.28*** Negatively charged. ***Figure 31.30*** G–C. There are three hydrogen bonds holding this base pair together and there are two hydrogen bonds binding adenine to thymine.

Chapter 32

Figure 32.2 Dark-coloured cars absorb electromagnetic radiation within the visible region while light-coloured cars reflect it. ***Figure 32.5*** Lower. ***Figure 32.13*** An applied magnetic field increases the energy difference between spin-aligned and spin-not-aligned nuclei. Thermodynamically, most nuclei would like to minimise their energy and so would populate the lower energy state. ***Figure 32.18*** Deshielded. ***Figure 32.19*** Top to bottom, left to right: 2, 5, 2, 3, 1, 4, 5 signals. ***Figure 32.23*** The solvent. There is a small amount of $CHCl_3$ in the $CDCl_3$ solvent. ***Figure 32.26*** $(CH_3)_2CH$–. ***Figure 32.30*** The magnetic field only influences charged particles and so it is only the charged particles that are bent towards the detector. ***Figure 32.32***



ANSWERS TO SELECTED PRACTICE EXERCISES

Chapter 1

Sample Exercise 1.1
Practice Exercise: It is a compound because it has constant composition and can be separated into several elements.

Sample Exercise 1.2
Practice Exercise: (**a**) 10^{12} pm, (**b**) 6.0 km, (**c**) 4.22×10^{-3} g, (**d**) 0.00422 g.

Sample Exercise 1.3
Practice Exercise: (**c**) selenium, Se

Sample Exercise 1.4
Practice Exercise: (**a**) 8.96 g/cm^3, (**b**) 19.0 mL, (**c**) 340 g.

Sample Exercise 1.5
Practice Exercise: (**a**) a 500-kg motorcycle moving at 100 km/h

Sample Exercise 1.6
Practice Exercise: No. The number of cm^3 in a liter is a defined quantity and is therefore exact, but the volume represented by one cm^3 is not exact, although it is known to high accuracy.

Sample Exercise 1.7
Practice Exercise: (**c**) 4

Sample Exercise 1.8
Practice Exercise: 9.52 m/s (three significant figures).

Sample Exercise 1.9
Practice Exercise: (**e**) 2.9×10^2 g

Sample Exercise 1.10
Practice Exercise: 1.496×10^8 km

Sample Exercise 1.11
Practice Exercise: 12 km/L.

Sample Exercise 1.12
Practice Exercise: $2.24/gal

Chapter 2

Sample Exercise 2.1
Practice Exercise: (**a**) 154 pm, (**b**) 1.3×10^6 C atoms

Sample Exercise 2.2
Practice Exercise: (**d**) ^{162}Ho, (**e**) ^{159}Gd

Sample Exercise 2.3
Practice Exercise: $^{208}_{82}$Pb

Sample Exercise 2.4
Practice Exercise: 28.09 u

Sample Exercise 2.5
Practice Exercise: Na, atomic number 11, is a metal; Br, atomic number 35, is a nonmetal.

Sample Exercise 2.6
Practice Exercise: (**d**) C_4O_2, C_2O

Sample Exercise 2.7
Practice Exercise: (**b**) P^{3-}, (**d**) Se^{2-}

Sample Exercise 2.8
Practice Exercise: (**a**) Ti^{4+}, (**d**) Te^{2-}

Sample Exercise 2.9
Practice Exercise: (**a**) Rb is from Group 1, and readily loses one electron to attain the electron configuration of the nearest noble gas element, Kr. (**b**) Nitrogen and the halogens are all nonmetallic elements, which form molecular compounds with one another. (**c**) Krypton, Kr, is a noble gas element and is chemically inactive except under special conditions. (**d**) Na and K are both from Group 1 and adjacent to one another in the periodic table. They would be expected to behave very similarly. (**e**) Calcium is an active metal and readily loses two electrons to attain the noble gas configuration of Ar.

Sample Exercise 2.10
Practice Exercise: (**d**) N

Sample Exercise 2.11
Practice Exercise: (**a**) ClO^{2-}, chlorate

Sample Exercise 2.12
Practice Exercise: (**c**) Fe_2O_3, diiron oxide

Sample Exercise 2.13
Practice Exercise: (**b**) nitrous acid, (**d**) iodic acid

Sample Exercise 2.14
Practice Exercise: (**a**) carbon disulfide (**b**) carbon monoxide (**c**) tricarbon dioxide (**d**) carbon tetrabromide (**e**) carbon monofluoride.

Sample Exercise 2.15
Practice Exercise: (**a**) C_6H_{14}, (**b**) hexanol, C–6H_{14}O

Chapter 3

Sample Exercise 3.1
Practice Exercise: (**d**) 6

Sample Exercise 3.2
Practice Exercise: (**a**) 4, 3, 2; (**b**) 2, 6, 2, 3; (**c**) 1, 2, 1, 1, 1

Sample Exercise 3.3
Practice Exercise: (**d**) $2\,Ag_2O(s) \longrightarrow 4\,Ag(s) + O_2(g)$

Sample Exercise 3.4
Practice Exercise: (**b**) $2\,C_2H_4(OH)_2(l) + 5\,O_2(g) \longrightarrow 4\,CO_2(g) + 6\,H_2O(g)$

Sample Exercise 3.5
Practice Exercise: (**a**) 78.0 u, (**b**) 32.0 u, (**c**) 211.0 u

Sample Exercise 3.6
Practice Exercise: (**b**) 17.1%

Sample Exercise 3.7
Practice Exercise: (**c**) 50 g sodium chloride

Sample Exercise 3.8
Practice Exercise: (**a**) 9.0×10^{23}, (**b**) 2.71×10^{24}

Sample Exercise 3.9
Practice Exercise: (**b**) 2+

Sample Exercise 3.10
Practice Exercise: 6.05 mol

Sample Exercise 3.11
Practice Exercise: 532 g

Sample Exercise 3.12
Practice Exercise: (**c**) 1.91×10^{23}

Sample Exercise 3.13
Practice Exercise: (**b**) $COCl_2$

Sample Exercise 3.14
Practice Exercise: (**d**) C_6H_{12}

Sample Exercise 3.15
Practice Exercise: (**d**) $C_4H_8O_2$

Sample Exercise 3.16
Practice Exercise: (**a**) 3.18 g

Sample Exercise 3.17
Practice Exercise: (**d**) 3.63 g

Sample Exercise 3.18
Practice Exercise: (**a**) Al, (**b**) 1.50 mol, (**c**) 0.75 mol Cl_2

Sample Exercise 3.19
Practice Exercise: (**a**) 1.20 g As

Sample Exercise 3.20
Practice Exercise: (**b**) 96%

Chapter 4

Sample Exercise 4.1
Practice Exercise: (**a**) 6, (**b**) 12, (**c**) 2, (**d**) 9

Sample Exercise 4.2
Practice Exercise: (**b**) $CaCO_3$

Sample Exercise 4.3
Practice Exercise: (**a**) $Fe(OH)_3$,
(**b**) $Fe_2(SO_4)_3(aq) + 6\,LiOH(aq) \longrightarrow 2\,Fe(OH)_3(s) + 3\,Li_2SO_4(aq)$

Sample Exercise 4.4
Practice Exercise: $3\,Ag^+(aq) + PO_4^{3-}(aq) \longrightarrow Ag_3PO_4(s)$

Sample Exercise 4.5
Practice Exercise: (**d**) both chloric acid and hydrobromic acid

Sample Exercise 4.6
Practice Exercise: (**d**) sodium nitrate

Sample Exercise 4.7
Practice Exercise: (**d**) $NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$

Sample Exercise 4.8
Practice Exercise: (**d**) H_2O_2

Sample Exercise 4.9
Practice Exercise: (**b**) Zinc is reduced, and copper ion is oxidized.

Sample Exercise 4.10
Practice Exercise: (**d**) sodium

Sample Exercise 4.11
Practice Exercise: (**c**) $3.91 \times 10^{-2}\,M$

Sample Exercise 4.12
Practice Exercise: (**e**) 2:1

Sample Exercise 4.13
Practice Exercise: (**a**) 1.1 g, (**b**) 76 mL

Sample Exercise 4.14
Practice Exercise: (**b**) 8.75 mL

Sample Exercise 4.15
Practice Exercise: (**b**) 19.5 mg

Sample Exercise 4.16
Practice Exercise: (**c**) 0.163 *M*

Sample Exercise 4.17
Practice Exercise: (**e**) 81.0%

Chapter 5

Sample Exercise 5.1
Practice Exercise: (**c**) $q < 0, w > 0$, the sign of ΔE cannot be determined from the information given

Sample Exercise 5.2
Practice Exercise: 70 J

Sample Exercise 5.3
Practice Exercise: (**d**) exothermic, negative

Sample Exercise 5.4
Practice Exercise: −14.4 kJ

Sample Exercise 5.5
Practice Exercise: (**a**) 4.9×10^5 J,
(**b**) 11 K decrease = 11 °C decrease

Sample Exercise 5.6
Practice Exercise: −68,000 J/mol = −68 kJ/mol

Sample Exercise 5.7
Practice Exercise: (**a**) −15.2 kJ/g, (**b**) −1370 kJ/mol

Sample Exercise 5.8
Practice Exercise: (**d**) −171.0 kJ

Sample Exercise 5.9
Practice Exercise: −304.1 kJ

Sample Exercise 5.10
Practice Exercise: $C(graphite) + 2\,Cl_2(g) \longrightarrow CCl_4(l)$;
$\Delta H_f^\circ = -106.7$ kJ/mol.

Sample Exercise 5.11
Practice Exercise: (**b**) −196.0 kJ

Sample Exercise 5.12
Practice Exercise: (**c**) $2\Delta H_f^\circ[SO_3] = \Delta H_{rxn}^\circ + 2\Delta H_f^\circ[SO_2]$

Sample Exercise 5.13
Practice Exercise: −1255 kJ

Sample Exercise 5.14
Practice Exercise: (**a**) 15 kJ/g, (**b**) 100 min

Chapter 6

Sample Exercise 6.1
Practice Exercise: 34.5 μm

Sample Exercise 6.2
Practice Exercise: (**a**) $1.43 \times 10^{14}\,s^{-1}$, (**b**) 2.899 m

Sample Exercise 6.3
Practice Exercise: (**e**) $E = N_A \frac{hc}{\lambda}$

Sample Exercise 6.4
Practice Exercise: (**a**) 3

Sample Exercise 6.5
Practice Exercise: (**a**) i < iii < ii

Sample Exercise 6.6
Practice Exercise: (**a**) $5p$; (**b**) 3; (**c**) 1, 0, −1

Sample Exercise 6.7
Practice Exercise: (**a**) $1s^2 2s^2 2p^6 3s^2 3p^2$, (**b**) two

Sample Exercise 6.8
Practice Exercise: Group 14

Sample Exercise 6.9
Practice Exercise: (**b**) Te

Chapter 7

Sample Exercise 7.1
Practice Exercise: P−Br

Sample Exercise 7.2
Practice Exercise: C < Be < Ca < K

Sample Exercise 7.3
Practice Exercise: (**b**) F < Cl < S^{2-} < Se^{2-}

Sample Exercise 7.4
Practice Exercise: (**a**) $Sr^{2+} < Rb^+ < Br^- < Se^{2-} < Te^{2-}$

Sample Exercise 7.5
Practice Exercise: (**e**) $Br^{2+}(g) \longrightarrow Br^{3+}(g) + e^-$

Sample Exercise 7.6
Practice Exercise: (**d**) Statements (ii) and (iii) are true.

Sample Exercise 7.7
Practice Exercise: (**a**) $[Kr]4d^4$

Sample Exercise 7.8
Practice Exercise: (**e**) $M(OH)_3(aq)$

Sample Exercise 7.9
Practice Exercise: (**c**) 3

Sample Exercise 7.10
Practice Exercise: (**e**) All three statements are true.

Chapter 8

Sample Exercise 8.1
Practice Exercise: (**b**) ScN > MgO > NaCl > CsI

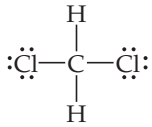
Sample Exercise 8.2
Practice Exercise: Mg^{2+} and N^{3-}

Sample Exercise 8.3
Practice Exercise: (**b**) H_2S

Sample Exercise 8.4
Practice Exercise: (**a**) H—F

Sample Exercise 8.5
Practice Exercise: (**a**) F, (**b**) 0.11−

Sample Exercise 8.6
Practice Exercise: (**a**) 20, (**b**)



Sample Exercise 8.7
Practice Exercise: (**a**) zero

Sample Exercise 8.8
Practice Exercise: (**b**) 6

Sample Exercise 8.10
Practice Exercise: (**d**) The cyanide ion has only one dominant resonance structure.

Sample Exercise 8.11
Practice Exercise: (**a**) C, (**b**)

Chapter 9

Sample Exercise 9.1
Practice Exercise: (**a**) tetrahedral, bent; (**b**) trigonal planar, trigonal planar

Sample Exercise 9.2
Practice Exercise: (**d**) Statements (ii) and (iii) are true.

Sample Exercise 9.3
Practice Exercise: (**a**) 109.5° and 109.5°

Sample Exercise 9.4
Practice Exercise: (**b**) Trigonal planar

Sample Exercise 9.5
Practice Exercise: (**c**) O_3

Sample Exercise 9.6
Practice Exercise: (**e**) All three statements are true.

Sample Exercise 9.7
Practice Exercise: (**b**) 4

Sample Exercise 9.8
Practice Exercise: (**c**) 2

Sample Exercise 9.9
Practice Exercise: (**e**) $F_2^- < C_2^{2+} < O_2^- < N_2^-$

Chapter 10

Sample Exercise 10.1
Practice Exercise: (**d**) 10.3 m

Sample Exercise 10.2
Practice Exercise: 107.6 kPa

Sample Exercise 10.3
Practice Exercise: 5.30×10^3 L

Sample Exercise 10.4
Practice Exercise: 202.65 kPa

Sample Exercise 10.5
Practice Exercise: $3.83 \times 10^3\ m^3$

Sample Exercise 10.6
Practice Exercise: 27 °C

Sample Exercise 10.7
Practice Exercise: 5.9 g/L

Sample Exercise 10.8
Practice Exercise: (**c**) 44.1 g/mol

Sample Exercise 10.9
Practice Exercise: 14.8 L

Sample Exercise 10.10
Practice Exercise: 289.8 kPa

Sample Exercise 10.11
Practice Exercise: (**b**) 0.33

Sample Exercise 10.12
Practice Exercise: (**b**) The C_3H_8 and CH_4 molecules have the same average kinetic energy

Sample Exercise 10.13
Practice Exercise: (**a**) four, will not change

Sample Exercise 10.14
Practice Exercise: $r_{N_2}/r_{O_2} = 1.07$

Sample Exercise 10.15
Practice Exercise: (**a**) 756.6 kPa, (**b**) 727.1 kPa

Chapter 11

Sample Exercise 11.1
Practice Exercise: (**d**) hydrogen peroxide, H_2O_2

Sample Exercise 11.2
Practice Exercise: (**d**) $CH_3COOH < Cl_2 < Ar < CH_4$

Sample Exercise 11.3
Practice Exercise: (**d**) heat of vaporization and specific heat of $H_2O(l)$

Sample Exercise 11.4
Practice Exercise: about 45 kPa

Sample Exercise 11.5
Practice Exercise: (**a**) −162 °C; (**b**) It sublimes whenever the pressure is less than 10 kPa; (**c**) The highest temperature at which a liquid can exist is defined by the critical temperature. So we do not expect to find liquid methane when the temperature is higher than −80 °C.

Sample Exercise 11.6
Practice Exercise: (**e**) rod-shaped molecules

Chapter 12

Sample Exercise 12.1
Practice Exercise: (**e**) 78.5%

Sample Exercise 12.2
Practice Exercise: $a = 402$ pm and density $= 4.31\ g/cm^3$

Sample Exercise 12.3
Practice Exercise: smaller.

Sample Exercise 12.4
Practice Exercise: A Group 15 element could be used to replace Se.

Chapter 13

Sample Exercise 13.2
Practice Exercise: (**d**) There are twice as many gas molecules in the liquid.

Sample Exercise 13.3
Practice Exercise: (**d**) 2.91%

Sample Exercise 13.4
Practice Exercise: (**c**) It is unchanged.

Sample Exercise 13.5
Practice Exercise: (**b**) 1.80×10^{-5}

Sample Exercise 13.6
Practice Exercise: (**a**) 10.9 *m*, (**b**) $X_{C_3H_8O_3} = 0.163$, (**c**) 5.97 *M*

Sample Exercise 13.7
Practice Exercise: 0.290

Sample Exercise 13.8
Practice Exercise: (**b**) 0.15 *m* NaCl

Sample Exercise 13.9
Practice Exercise: (**d**) increasing the temperature

Sample Exercise 13.10
Practice Exercise: (**d**) norfenefrine

Sample Exercise 13.11
Practice Exercise: 4.20×10^4 g/mol

Chapter 14

Sample Exercise 14.1
Practice Exercise: (**e**) All three statements are true.

Sample Exercise 14.2
Practice Exercise: (**d**) $2.7 \times 10^{-5}\ M/s$

Sample Exercise 14.3
Practice Exercise: (**c**) $2\ A \longrightarrow B + 3\ C$

Sample Exercise 14.4
Practice Exercise: (**e**) $3 < 1 < 2$

Sample Exercise 14.5
Practice Exercise: (**a**) $M^{-1/2}s^{-1}$

Sample Exercise 14.7
Practice Exercise:

Sample Exercise 14.8
Practice Exercise: (**b**) Statements (i) and (ii) are true.

Sample Exercise 14.9
Practice Exercise: (**a**) 0.478 yr = 1.51×10^7 s, (**b**) it takes two half-lives, 2(0.478 yr) = 0.956 yr

Sample Exercise 14.10
Practice Exercise: (**a**) Only one—(i), or (ii), or (iii)—increases the reaction rate.

Sample Exercise 14.12
Practice Exercise: (**c**) Statements (i) and (iii) are true.

Sample Exercise 14.13
Practice Exercise: (**e**) $A + B \longrightarrow X + Z$

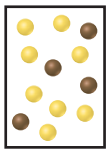
Sample Exercise 14.15
Practice Exercise: (**c**) Rate $= k[P]^2[Q]$

Chapter 15

Sample Exercise 15.1
Practice Exercise: (**c**) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

Sample Exercise 15.2
Practice Exercise: (**c**) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$

Sample Exercise 15.3
Practice Exercise:



(b)

Sample Exercise 15.4
Practice Exercise: (**d**) 1.8×10^2

Sample Exercise 15.5
Practice Exercise: (**e**) neither $[Ag^+]$ nor $[Cl^-]$ will change

Sample Exercise 15.6
Practice Exercise: (**d**) Increasing the volume of the vessel

Sample Exercise 15.7
Practice Exercise: 1.79×10^{-5}

Sample Exercise 15.8
Practice Exercise: (**d**) 1.4

Sample Exercise 15.9
Practice Exercise: (**c**) The direction of this reaction does not depend on the volume of the container.

Sample Exercise 15.10
Practice Exercise: 127.5 kPa

Sample Exercise 15.11
Practice Exercise: $P_{PCl_5} = 97.94$ kPa, $P_{PCl_3} = P_{Cl_2} = 70.26$ kPa

Sample Exercise 15.12
Practice Exercise: (**a**) right, (**b**) left, (**c**) right, (**d**) left

Chapter 16

Sample Exercise 16.1
Practice Exercise: (**b**) HSO_4^- and H_2O

Sample Exercise 16.2
Practice Exercise: (**c**) i and iii

Sample Exercise 16.3
Practice Exercise: (**e**) iii < ii < i

Sample Exercise 16.4
Practice Exercise: (**a**) $1.0 \times 10^{-8}\,M$

Sample Exercise 16.5
Practice Exercise: (**c**) $2.5 \times 10^{-7}\,M$

Sample Exercise 16.6
Practice Exercise: (**d**) 11.83

Sample Exercise 16.7
Practice Exercise: (**e**) All three statements are true.

Sample Exercise 16.8
Practice Exercise: (**c**) iii < i < ii

Sample Exercise 16.9
Practice Exercise: (**e**) iii < ii < i

Sample Exercise 16.10
Practice Exercise: (**c**) 6.6×10^{-5}

Sample Exercise 16.11
Practice Exercise: (**e**) 9.0%

Sample Exercise 16.12
Practice Exercise: (**a**) 2.30

Sample Exercise 16.13
Practice Exercise: (**e**) 2.64

Sample Exercise 16.14
Practice Exercise: (**b**) 2.32

Sample Exercise 16.15
Practice Exercise: (**c**) 9.52

Sample Exercise 16.16
Practice Exercise: (**a**) 0.38

Sample Exercise 16.17
Practice Exercise: (**d**) ii < iii < i

Sample Exercise 16.18
Practice Exercise: (**e**) iii < ii < i

Sample Exercise 16.19
Practice Exercise: (**c**) 2

Sample Exercise 16.20
Practice Exercise: (**b**) $HOI < HIO_2 < HBrO_2 < HClO_2 < HClO_3$

Chapter 17

Sample Exercise 17.1
Practice Exercise: (**d**) If you add the soluble salt KA to a solution of HA that is at equilibrium, the pH would increase.

Sample Exercise 17.2
Practice Exercise: (**e**) $1.73 \times 10^{-4}\,M$

Sample Exercise 17.3
Practice Exercise: (**c**) The acid and base concentrations must be equal.

Sample Exercise 17.4
Practice Exercise: (**b**) 0.174

Sample Exercise 17.5
Practice Exercise: (**a**) 60.7 g

Sample Exercise 17.6
Practice Exercise: (**e**) In order to do calculations in which a strong acid or base is added to a buffer, you need to calculate the amounts of substances from the neutralization reaction and then equilibrate.

Sample Exercise 17.7
Practice Exercise: (**e**) At the equivalence point, the OH^- concentration in the solution is $3.67 \times 10^{-3}\,M$.

Sample Exercise 17.8
Practice Exercise: (**b**) Halfway to the equivalence point, $pH = pK_a$.

Sample Exercise 17.9
Practice Exercise: (**d**) The conjugate base that is formed at the equivalence point reacts with water.

Sample Exercise 17.10
Practice Exercise: (**c**) $[Ag^+]^3[PO_4^{3-}]$

Sample Exercise 17.11
Practice Exercise: (**e**) 1.40×10^{-37}

Sample Exercise 17.12
Practice Exercise: (**b**) cobalt(II) hydroxide, $K_{sp} = 1.3 \times 10^{-15}$

Sample Exercise 17.13
Practice Exercise: (**d**) Raising the temperature of the solution.

Sample Exercise 17.14
Practice Exercise: (**e**) none of these

Sample Exercise 17.15
Practice Exercise: (**c**) The precipitate was chromium hydroxide, which then reacted with more hydroxide to produce a soluble complex ion, $Cr(OH)_4^-(aq)$.

Sample Exercise 17.16
Practice Exercise: (**a**) Yes

Sample Exercise 17.17
Practice Exercise: (**c**) when Q exceeds K_{sp}

Chapter 18

Sample Exercise 18.1
Practice Exercise: 4.0×10^{-4} kPa

Sample Exercise 18.2
Practice Exercise: (**a**) 620 nm

Sample Exercise 18.3
1.5×10^4 g CO_2 or 15 kg CO_2

Chapter 19

Sample Exercise 19.1
Practice Exercise: (**d**) Equilibrium is achieved in a closed system when the rate of iron oxidation is equal to the rate of iron(III) oxide reduction.

Sample Exercise 19.2
Practice Exercise: (**a**) Yes, because the heat transferred from the system has a negative sign.

Sample Exercise 19.3
Practice Exercise: (**a**) $CO_2(s) \longrightarrow CO_2(g)$

Sample Exercise 19.4
Practice Exercise: (**a**) 1 mol of $SO_2(g)$ at STP, (**b**) 2 mol of $NO_2(g)$ at STP

Sample Exercise 19.5
Practice Exercise: (**a**) 326.3 J/K

Sample Exercise 19.6
Practice Exercise: (**d**) All spontaneous reactions have a negative free-energy change

Sample Exercise 19.7
Practice Exercise: (**b**) $\Delta G_1^\circ = 2\,\Delta G_2^\circ$

Sample Exercise 19.8
Practice Exercise: (**b**) The reaction is nonspontaneous at all temperatures

Sample Exercise 19.9
Practice Exercise: (**d**) 193 °C

Sample Exercise 19.10
Practice Exercise: (**c**) +34,000 J

Sample Exercise 19.11
Practice Exercise: (**e**) If $Q > 1$, $\Delta G > \Delta G^\circ$.

Sample Exercise 19.12
Practice Exercise: (**e**) +265 kJ/mol

Chapter 20

Sample Exercise 20.1
Practice Exercise: (**a**) $Br^-(aq)$

Sample Exercise 20.2
Practice Exercise: (**d**) Seven on the product side

Sample Exercise 20.3
Practice Exercise: (**a**) One on the reactant side

Sample Exercise 20.4
Practice Exercise: (**b**) The electrode is gaining mass and cations from the salt bridge are flowing into the half-cell.

Sample Exercise 20.5
Practice Exercise: (**a**) −0.35 V

Sample Exercise 20.6
Practice Exercise: (**e**) +0.80 V

Sample Exercise 20.7
Practice Exercise: (**d**) Cells 1 and 2

Sample Exercise 20.8
Practice Exercise: (**b**) $Cl_2(g)$

Sample Exercise 20.9
Practice Exercise: **d**) Cl_2 and Br_2

Sample Exercise 20.10
Practice Exercise: (**d**) −0.13 V

Sample Exercise 20.11
Practice Exercise:(**b**) 0.56 V

Sample Exercise 20.12
Practice Exercise: (**e**) $7.6 \times 10^{-3}\,M$

Sample Exercise 20.13
Practice Exercise: (**a**) The anode is the half-cell in which $[Zn^{2+}] = 3.75 \times 10^{-4}\,M$. (**b**) The emf is 0.105 V.

Sample Exercise 20.14
Practice Exercise: (**c**) 62 min

Chapter 21

Sample Exercise 21.1
Practice Exercise: (**b**) Uranium-234

Sample Exercise 21.2
Practice Exercise: (**a**) Alpha decay followed by beta emission

Sample Exercise 21.3
Practice Exercise: (**d**) iodine-131

Sample Exercise 21.4
Practice Exercise: (**e**) $^{239}_{93}Np$

Sample Exercise 21.5
Practice Exercise: (**b**) 6.0 h

Sample Exercise 21.6
Practice Exercise: (**d**) 45.5 yr

Sample Exercise 21.7
Practice Exercise: (**e**) 178 yr

Sample Exercise 21.8
Practice Exercise: -3.19×10^{-3} g

Chapter 22

Sample Exercise 22.1
Practice Exercise: (**d**) Oxygen is better able to form π bonds than sulfur.

Sample Exercise 22.2
Practice Exercise: (**d**) C_2H_2

Sample Exercise 22.3
Practice Exercise: (**c**) trigonal bipyramidal, T shaped

Sample Exercise 22.4
Practice Exercise: (**a**) F_2

Sample Exercise 22.5
Practice Exercise: $N_2H_4(aq) + O_2 \longrightarrow N_2(g)_2 + H_2O(l)$

Sample Exercise 22.6
Practice Exercise: (**d**) $BeAl_2Si_6O_{15}$?

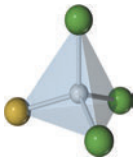
Chapter 23

Sample Exercise 23.1
Practice Exercise: (**b**) $[Rh(NH_3)_4Cl_2]Cl$

Sample Exercise 23.2
Practice Exercise: (**c**) $Rb_3[MoO_3F_3]$

Sample Exercise 23.3
Practice Exercise: (**c**) Tetraamminedichloridorhodium(III) chloride

Sample Exercise 23.4
Practice Exercise:



$[MX_3Y]$
(a)

Sample Exercise 23.5
Practice Exercise: (**d**) Tetrahedral $[Co(NH_3)BrClI]^-$

Sample Exercise 23.6
Practice Exercise: (**d**) orange

Sample Exercise 23.7
Practice Exercise: (**d**) $[RhCl_6]^{3-}$

Sample Exercise 23.8
Practice Exercise: (**e**) 5

Chapter 24

Sample Exercise 24.1
Practice Exercise: 2,4-dimethylpentane

Sample Exercise 24.2
Practice Exercise:

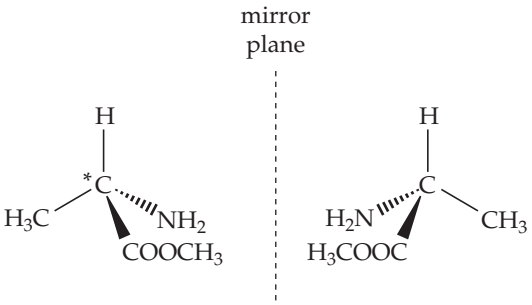
$CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$ or $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$

Sample Exercise 24.3
Practice Exercise: $2\ C_6H_{14}(g) + 19\ O_2(g)$: $12\ CO_2(g) + 14\ H_2O(l)$

Chapter 25

Sample Exercise 25.1
Practice Exercise: *trans*-1,3-dimethylcyclopentanes

Sample Exercise 25.2
Practice Exercise:



Sample Exercise 25.3
Practice Exercise: $[\alpha]_D = +30°$. This value is lower than that listed in Table 25.1; hence the sample contains a small amount of the other enantiomer.

Sample Exercise 25.4
Practice Exercise: (**a**) *R*, (**b**) *S*

Chapter 26

Sample Exercise 26.1
Practice Exercise: (**a**) Approximately 109° around the left C and 180° on the right C; (**b**) sp^3, sp; (**c**) five σ-bonds and two π-bonds

Sample Exercise 26.2
Practice Exercise: (**a**) The molecule has $2 \times sp$, $2 \times sp^2$ and $1 \times sp^3$ hybridised carbon atoms. (**b**) The molecule has $5 \times sp^3$ and $1 \times sp^2$ hybridised carbon atoms.

Sample Exercise 26.3
Practice Exercise: Five (hex-1-ene, *cis*-hex-2-ene, *trans*-hex-2-ene, *cis*-hex-3-ene, *trans*-hex-3-ene)

Sample Exercise 26.4
Practice Exercise:

$CH_3—C{\equiv}C—CH(CH_3)—CH_3$

Sample Exercise 26.5
Practice Exercise: SO_3^{2-} and O_3, as indicated by the presence of two or more resonance structures involving π-bonding for each of these molecules.

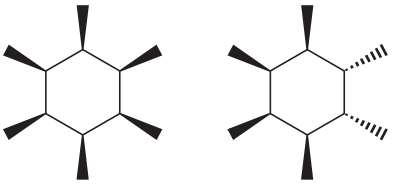
Sample Exercise 26.6
Practice Exercise: 3-methylbut-1-ene

Sample Exercise 26.7
Practice Exercise:



major minor

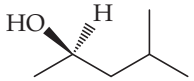
Sample Exercise 26.8
Practice Exercise: There are two products which, as line drawings, are:

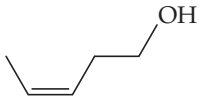


Chapter 27

Sample Exercise 27.1
Practice Exercise: $C_5H_{12} < C_5H_{11}Cl < C_5H_{11}OH < C_5H_{10}(OH)_2$ (in order of increasing polarity and hydrogen-bonding ability)

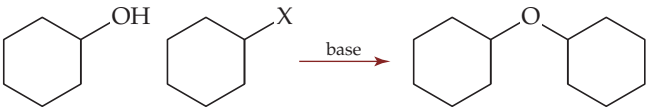
Sample Exercise 27.2
Practice Exercise:

(a) 

(b) 

Sample Exercise 27.3
Practice Exercise: There are four 2° and one 3° OH groups (around the ring), and one 1° OH group.

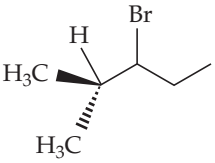
Sample Exercise 27.4
Practice Exercise: There are two parts to answering this question. Disconnection of the ether leads to the following reaction:



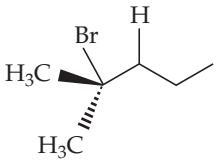
X = Cl, Br, I

The haloalkane can be synthesised from cyclohexanol by treatment with a haloacid (HCl, HBr, HI, respectively) or use of $SOCl_2$ in the case where X = Cl.

Sample Exercise 27.5
Practice Exercise: There are two answers but only one is realistic. Both these haloalkanes will yield the desired product:



III



IV

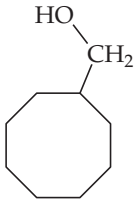
However, in the case of III, the *β*-hydrogen that leads to the product is sterically hindered by the two methyl groups on one carbon atom and the bromine atom and ethyl group on the adjacent carbon atom. This steric concern is further enhanced by the use of potassium *tert*-butoxide which is also very bulky. Compound IV is not hindered as much and so is the better choice of haloalkane.

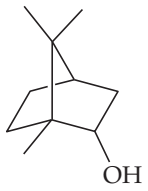
Sample Exercise 27.6
Practice Exercise: 2-methylpropene

Chapter 28

Sample Exercise 28.1
Practice Exercise: (**a**) (*S*)-2-methylcyclohexanone, (**b**) (*S*)-4-hydroxypentan-2-one

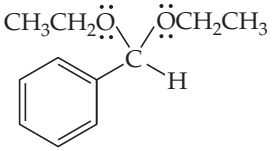
Sample Exercise 28.2
Practice Exercise:

(a) 

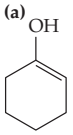
(b) 

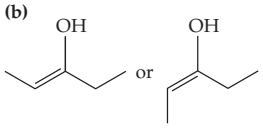
Sample Exercise 28.3
Practice Exercise: (**a**) Mg in diethyl ether, (**b**) formaldehyde

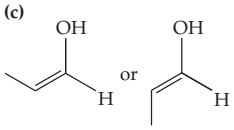
Sample Exercise 28.4
Practice Exercise:



Sample Exercise 28.5
Practice Exercise:

(a) 

(b) 

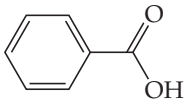
(c) 

Sample Exercise 28.6
Practice Exercise: (**a**) L-aldopentose, (**b**) L-ketopentose, (**c**) D-aldohexose

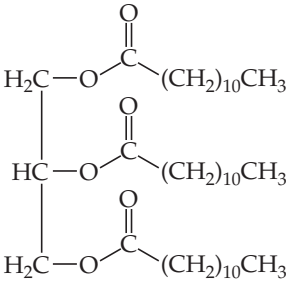
Chapter 29

Sample Exercise 29.1
Practice Exercise: a < e < b < c < d

Sample Exercise 29.2
Practice Exercise:

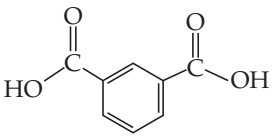


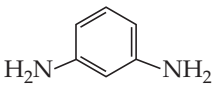
Sample Exercise 29.4
Practice Exercise:



Sample Exercise 29.5
Practice Exercise: In both cases a hydrophobic tail and polar head group are present. The difference lies in both the nature of the head group (negatively or positively charged) and in its functionality.

Sample Exercise 29.6
Practice Exercise: This is a polyamide, a step-growth polymer. The monomers that are used to prepare it are:





Chapter 30

Sample Exercise 30.1
Practice Exercise: phenol < 2,4-dichlorophenol < 4-nitro- 2-chlorophenol < 2,6-dinitrophenol

Sample Exercise 30.2
Practice Exercise: chlorobenzene

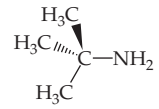
Sample Exercise 30.3
Practice Exercise: (**a**) Being an alkyl group, the *tert*-butyl group would be activating. In this case the rate is ~15 times faster than that for benzene. (**b**) The *para* position is favoured for nitration. Being an alkyl group means the *tert*-butyl group is *o, p*-directing. However, because of its bulk, *para* substitution is more likely.

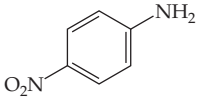
Sample Exercise 30.4
Practice Exercise: anisole

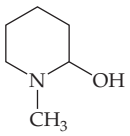
Chapter 31

Sample Exercise 31.1
Practice Exercise: Spermine contains primary and secondary amines. The primary amines occupy positions at the end of the chain. The secondary amines appear within the chain.

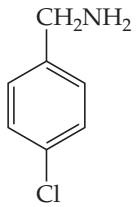
Sample Exercise 31.2
Practice Exercise:

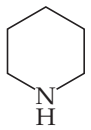
(a)


(b)


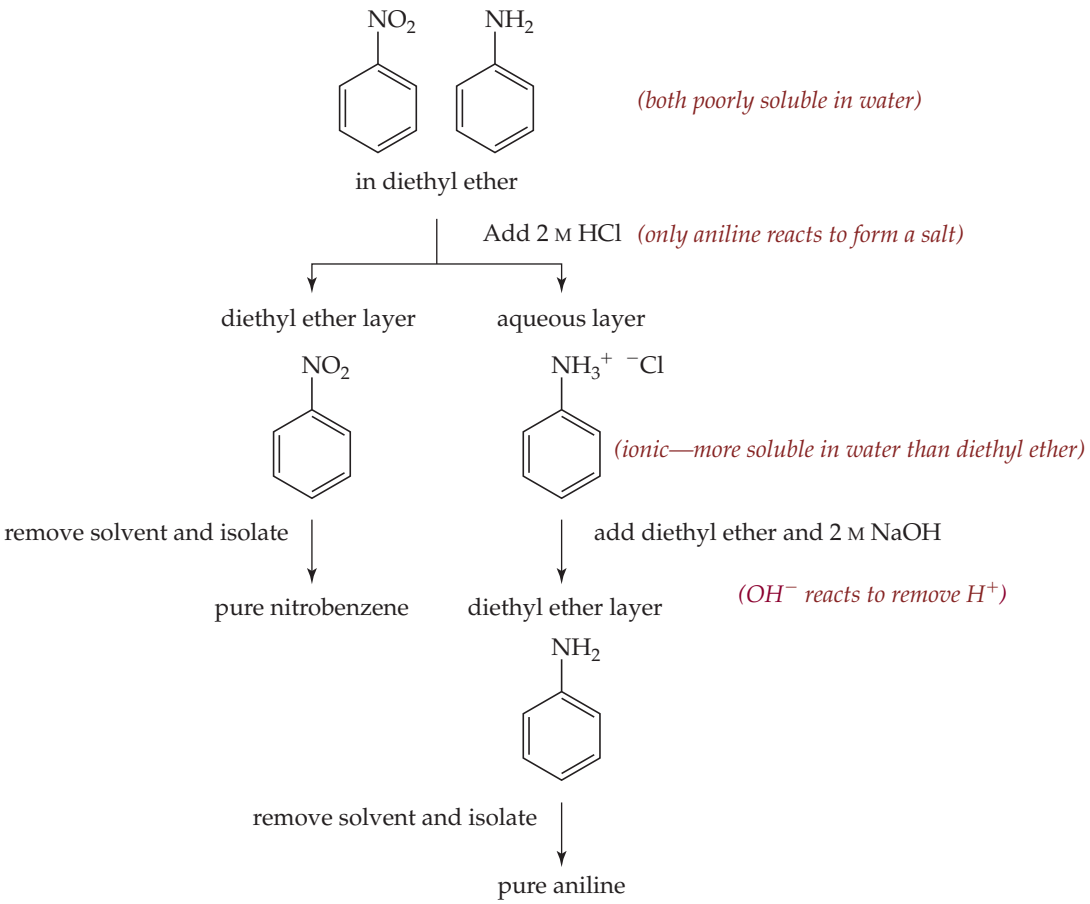
(c)


Sample Exercise 31.3
Practice Exercise:

(a)


(b)


Sample Exercise 31.4
Practice Exercise: The easiest way to achieve the separation is to take advantage of the basicity of aniline and the solubility of the resultant ammonium salt (**Comment:** This method is quite general. Any basic organic compound can be separated from a non-basic one in this way).



Sample Exercise 31.5
Practice Exercise:

At pH 2 $^{+}H_3NCHRCO_2H$

At pH 7 $^{+}H_3NCHRCO_2^{-}$

At pH 10 $H_2NCHRCO_2^{-}$

R = CH_2OH

Sample Exercise 31.7
Practice Exercise: Serylaspartic acid: Ser-Asp, SD

Sample Exercise 31.8
Practice Exercise: Gly-Ala-Phe-Tyr-His-Glu

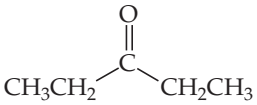
Chapter 32

Sample Exercise 32.1
Practice Exercise: (**a**) Cyclohexene shows a weak but characteristic C=C stretching absorption at 1600–1680 cm–1. (**b**) Both show an N–H absorption, but acetamide (being an amide) has a C=O absorption at 1600–1680 cm-1.

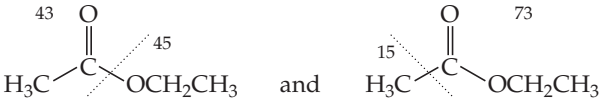
Sample Exercise 32.2
Practice Exercise: (**a**) 4, (**b**) 5

Sample Exercise 32.3
Practice Exercise: Draw the two possibilities. The Markovnikov product is symmetrical, which leads to only two absorptions in either the ^{1}H or ^{13}C NMR spectrum.

Sample Exercise 32.4
Practice Exercise: Check for symmetry by comparing the integration with the number of hydrogens in the molecular formula. The structure is



Sample Exercise 32.5
Practice Exercise: Fragmentation around the carbonyl group yielding acylium cations is extremely likely. For example:



Sample Exercise 32.6
Practice Exercise: (**a**) C_3H_8O, (**b**) $C_4H_8O_2$

GLOSSARY

absolute configuration The configuration of a molecule defined unambiguously using the Cahn–Ingold–Prelog rules. (Section 25.5)

absolute zero The temperature at which all thermal motion ceases: 0 K on the Kelvin scale and −273.15 °C on the Celsius scale. (Section 1.5)

absorption spectrum A pattern of variation in the amount of light absorbed by a sample as a function of wavelength. (Section 23.5)

accuracy A measure of how closely individual measurements agree with the correct, or "true," value. (Section 1.6)

acetals The product formed by the reaction of an aldehyde or ketone with two moles of an alcohol. (Section 28.3)

achiral A term used to describe molecules with a plane of symmetry that is superimposable on its mirror image. (Section 25.3)

acid A substance that is able to donate a H^+ ion (a proton) and, hence, increases the concentration of $H^+(aq)$ when it dissolves in water. (Section 4.3)

acid anhydrides An organic compound that has two carbonyl groups linked by a single oxygen. (Section 29.5)

acid halides A compound with molecular formula RCOX, where R = alkyl, aryl and X = halogen substituent. (Section 29.5)

activated (Section 30.5)

activating group A substituent that increases the reactivity of an aromatic ring. (Section 30.5)

active site Specific site on a heterogeneous catalyst or an enzyme where catalysis occurs. (Section 31.3)

acyl groups The group R—C(=O)—, where R = alkyl, aryl. (Section 29.5)

acid-dissociation constant (K_a) An equilibrium constant that expresses the extent to which an acid transfers a proton to solvent water. (Section 16.5)

acidic anhydride (acidic oxide) An oxide that forms an acid when added to water; soluble nonmetal oxides are acidic anhydrides. (Section 22.5)

acidic oxide (acidic anhydride) An oxide that reacts either with a base to form a salt or with water to form an acid. (Section 22.5)

acid rain Rainwater that has become excessively acidic because of absorption of pollutant oxides, notably SO_3, produced by human activities. (Section 18.2)

actinide element Element in which the 5*f* orbitals are only partially occupied. (Section 6.8)

activated complex (transition state) The particular arrangement of atoms found at the top of the potential-energy barrier as a reaction proceeds from reactants to products. (Section 14.5)

activation energy (E_a) The minimum energy needed for reaction; the height of the energy barrier to formation of products. (Section 14.5)

active site Specific site on a heterogeneous catalyst or an enzyme where catalysis occurs. (Section 14.7)

activity The decay rate of a radioactive material, generally expressed as the number of disintegrations per unit time. (Section 21.3)

activity series A list of metals in order of decreasing ease of oxidation. (Section 4.4)

addition polymerization Polymerization in which monomers are coupled through their multiple bonds. (Section 12.5)

addition polymerizations Polymerisation that occurs through coupling of monomers with one another, with no other products formed in the reaction. (Section 26.6)

addition polymer A polymer formed from alkenes by a free-radical process. (Section 26.6)

addition reaction A reaction in which a reagent adds to the two carbon atoms of a carbon–carbon multiple bond. (Section 24.3)

addition reactions A reaction in which a reagent adds to the two carbon atoms of a carbon–carbon multiple bond. (Section 26.4)

adsorption The binding of molecules to a surface. (Section 14.7)

alcohols An organic compound obtained by substituting a hydroxyl group (—OH) for a hydrogen on a hydrocarbon. (Sections 2.9, 24.4, 24.6 and 27.1)

aldehyde An organic compound that contains a carbonyl group (C=O) to which at least one hydrogen atom is attached. (Section 24.4)

aldehyde An organic compound that contains a carbonyl group to which at least one hydrogen atom is attached. (Section 28.1)

aldoses A carbohydrate that contains an aldehyde group when in its open-chain form. (Section 28.4)

aliphatic amines An amine in which alkyl chains are bonded to nitrogen. (Section 31.1)

alkali metals Members of group 1 in the periodic table. (Section 7.7)

alkaloids A large class of naturally occurring compounds with biological activity. Alkaloids are cyclic amines derived from plant material and contain a basic nitrogen atom. (Section 31.1)

alkaline earth metals Members of group 2 in the periodic table. (Section 7.7)

alkanes Compounds of carbon and hydrogen containing only carbon–carbon single bonds. (Sections 2.9 and 24.2)

alkenes Hydrocarbons containing one or more carbon–carbon double bonds. (Section 26.1)

alkoxide The conjugate base of an alcohol. (Section 27.4)

alkoxy (–OR) **group** A group of the form –OR, where R is generally alkyl or aryl. (Section 27.3)

alkyl ammonium salt An ionic class of molecule containing four groups around nitrogen, of which one is an alkyl group; for example, R_3NH^+, $R_2NH_2^+$, RNH_3^+, where R = alkyl group. (Section 27.5 and 31.1)

alkyl group A group that is formed by removing a hydrogen atom from an alkane. (Section 24.2)

alkynes Hydrocarbons containing one or more carbon–carbon triple bonds. (Section 24.2)

alloy A substance that has the characteristic properties of a metal and contains more than one element. Often there is one principal metallic component, with other elements present in smaller amounts. Alloys may be homogeneous or heterogeneous. (Section 12.2)

alpha emission A type of radioactive decay in which an atomic nucleus emits an alpha particle and thereby transforms (or "decays") into an atom with a mass number 4 less and atomic number 2 less. (Section 21.1)

alpha (α) helix A protein structure in which the protein is coiled in the form of a helix with hydrogen bonds between C=O and N—H groups on adjacent turns. (Section 24.7)

alpha particles Particles that are identical to helium-4 nuclei, consisting of two protons and two neutrons, symbol ^4_2He or $^4_2\alpha$. (Section 21.1)

amide An organic compound that has an NR_2 group attached to a carbonyl. (Section 29.5)

amides An organic compound that has an NR_2 group attached to a carbonyl, where R may be H or a hydrocarbon group. (Section 24.4)

amines A compound that has the general formula R_3N, where R may be H or a hydrocarbon group. (Section 16.6, 27.5 and 30.1)

amino acid A carboxylic acid that contains an amino (—NH_2) group attached to the carbon atom adjacent to the carboxylic acid (—COOH) functional group. (Section 24.7 and Section 31.2)

α-amino acid An amino acid in which the carboxylic acid and amine groups are bonded through the same carbon atom. (Section 31.2)

amino group A nitrogen-containing group of the type –NH_2, –NHR or –NR_2. (Section 31.1)

amorphous solid A solid whose molecular arrangement lacks the order (regularly repeating long-range pattern) of a crystal. (Section 12.1)

amphiprotic Refers to the capacity of a substance to either add or lose a proton (H^+). (Section 16.1)

amphiprotic Refers to the capacity of a substance to either lose or gain a proton; that is, to act as an acid or a base. (Section 31.2)

amphoteric oxides and hydroxides Oxides and hydroxides that are only slightly soluble in water but that dissolve in either acidic or basic solutions. (Section 17.5)

amylopectins A branched derivative of starch, a polysaccharide. (Section 28.4)

amyloses An unbranched derivative of starch, a polysaccharide. (Section 28.4)

angstrom A common non-SI unit of length, denoted Å, that is used to measure atomic dimensions: $1Å = 10^{-10}$ m. (Section 2.3)

anion A negatively charged ion. (Section 2.7)

anode An electrode at which oxidation occurs. (Section 20.3)

anomeric carbon The new stereocentre formed in a monosaccharide as a result of intramolecular hemiacetal formation. (Section 28.4)

anomers Diastereoisomers that are formed about the anomeric carbon upon hemiacetal formation. The two forms are α and β anomers. (Section 28.4)

antibonding molecular orbital A molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ^* or π^*, are less stable (of higher energy) than bonding molecular orbitals. (Section 9.7)

antiferromagnetism A form of magnetism in which unpaired electron spins on adjacent sites point in opposite directions and cancel each other's effects. (Section 23.1)

antioxidants Compounds able to terminate the harmful effects of naturally occurring free radicals. (Section 24.7)

aqueous solution A solution in which water is the solvent. (Section 4.1)

arene Hydrocarbon compounds that contain a planar, cyclic arrangement of carbon atoms linked by both σ-bonds and delocalised π-bonds. (Section 30.1)

aromatic amines An amine in which at least one aryl group is bonded to nitrogen, or the nitrogen forms part of the aromatic unit, as in pyridine. (Section 31.1)

aromatic hydrocarbons Hydrocarbon compounds that contain a planar, cyclic arrangement of carbon atoms linked by both σ and delocalized π bonds. (Section 24.2)

aromatic hydrocarbon Hydrocarbon compounds that contain a planar, cyclic arrangement of carbon atoms linked by both σ-bonds and delocalised π-bonds. (Section 30.1)

Arrhenius equation An equation that relates the rate constant for a reaction to the frequency factor, A, the activation energy, E_a, and the temperature, T: $k = Ae^{-E_a/RT}$. In its logarithmic form it is written $\ln k = -E_a/RT + \ln A$. (Section 14.5)

atmosphere (atm) A unit of pressure equal to 760 torr; 1 atm = 101.325 kPa. (Section 10.2)

atom The smallest representative particle of an element. The almost infinitesimally small building blocks of matter. (Sections 1.1 and 2.1)

atomic mass unit (amu) A unit based on the value of exactly 12 amu for the mass of the isotope of carbon that has six protons and six neutrons in the nucleus; 1 amu = 1.66054×10^{-24} g. (Sections 2.3 and 2.4)

atomic number The number of protons in the nucleus of an atom of an element. (Section 2.3)

atomic radius An estimate of the size of an atom. See bonding atomic radius. (Section 7.3)

atomic weight The average mass of the atoms of an element in atomic mass units (amu); it is numerically equal to the mass in grams of one mole of the element. (Section 2.4)

autoionization The process whereby water spontaneously forms low concentrations of $H^+(aq)$ and $OH^-(aq)$ ions by proton transfer from one water molecule to another. (Section 16.2)

Avogadro's hypothesis A statement that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. (Section 10.3)

Avogadro's law A statement that the volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas. (Section 10.3)

Avogadro's number (N_A) The number of ^{12}C atoms in exactly 12 g of ^{12}C; it equals $6.022 \times 10^{23}\ mol^{-1}$. (Section 3.4)

axial hydrogens Those hydrogens on a chair conformation that extend perpendicular to the rough plane of the ring. (Section 24.5)

ball-and-stick model Model that depicts atoms as spheres and bonds as sticks. (Section 2.6)

band An array of closely spaced molecular orbitals occupying a continuous range of energy. (Section 12.2)

band gap The energy gap between a fully occupied valence band and an empty conduction band. (Section 12.4)

band structure The electronic structure of a bulk solid. (Section 12.2)

bar A unit of pressure equal to 10^5 Pa. (Section 10.2)

base A substance that is an H^+ acceptor; a base produces an excess of $OH^-(aq)$ ions when it dissolves in water. (Section 4.3)

base-dissociation constant (K_b) An equilibrium constant that expresses the extent to which a base reacts with solvent water, accepting a proton and forming $OH^-(aq)$. (Section 16.6)

basic anhydride (basic oxide) An oxide that forms a base when added to water; soluble metal oxides are basic anhydrides. (Section 22.5)

basic oxide (basic anhydride) An oxide that either reacts with water to form a base or reacts with an acid to form a salt and water. (Section 22.5)

base peak The peak within the mass spectrum that has 100% relative intensity. This does not necessarily correspond to the molecular ion. (Section 32.4)

battery A portable, self-contained electrochemical power source that contains one or more voltaic cells. (Section 20.7)

becquerel The SI unit of radioactivity. It corresponds to one nuclear disintegration per second. (Section 21.3)

Beer's law The light absorbed by a substance (A) equals the product of its extinction coefficient (ε), the path length through which the light passes (b), and the molar concentration of the substance (c): $A = \varepsilon bc$. (Section 14.3)

Beer–Lambert's law The light absorbed by a substance (A) equals the product of its molar absorption coefficient (ε), the path length through which the light passes (l) and the molar concentration of the substance (c): $A = \varepsilon \times c \times l$. (Section 32.1)

benzyl group A hydrocarbon group with formula $C_6H_5CH_2$. (Section 30.2)

beta emission A nuclear decay process where a beta particle is emitted from the nucleus; also called beta decay. (Section 21.1)

beta particles Energetic electrons emitted from the nucleus, symbol $^0_{-1}e$ or β^-. (Section 21.1)

beta sheet A structural form of protein in which sheets are made of two or more strands of peptides that hydrogen-bond from an amide H in one strand to a carbonyl O in the other strand. (Section 24.7)

bidentate ligand A ligand in which two linked coordinating atoms are bound to a metal. (Section 23.3)

bimolecular reaction An elementary reaction that involves two molecules. (Section 14.6)

biochemistry The study of the chemistry of living systems. (Section 24.1)

biodegradable Organic material that bacteria are able to oxidize. (Section 18.4)

biopolymers Three broad categories of polymers: proteins, polysaccharides (carbohydrates), and nucleic acids. (Section 24.6)

boat conformation The least stable conformation of a cyclohexane ring. (Section 24.5)

body-centered lattice A crystal lattice in which the lattice points are located at the center and corners of each unit cell. (Section 12.1)

bomb calorimeter A device for measuring the heat evolved in the combustion of a substance under constant-volume conditions. (Section 5.5)

bond angles The angles made by the lines joining the nuclei of the atoms in a molecule. (Section 9.1)

bond dipole The dipole moment that is due only to unequal electron sharing between two atoms in a covalent bond. (Section 9.3)

bond enthalpy The enthalpy change, ΔH, required to break a particular bond when the substance is in the gas phase. (Section 5.8)

bonding atomic radius The radius of an atom as defined by the distances separating it from other atoms to which it is chemically bonded. (Section 7.3)

bonding molecular orbital A molecular orbital in which the electron density is concentrated in the internuclear region. The energy of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms. (Section 9.7)

bonding pair In a Lewis structure, a pair of electrons that is shared by two atoms. (Section 8.3)

bond length The distance between the centers of two bonded atoms. (Section 8.3)

bond order The number of bonding electron pairs shared between two atoms, minus the number of antibonding electron pairs: bond order = (number of bonding electrons − number of antibonding electrons)/2. (Section 9.7)

bond polarity A measure of the degree to which the electrons are shared unequally between two atoms in a chemical bond. (Section 8.4)

boranes Molecules containing only boron and hydrogen; covalent hydrides of boron. (Section 22.11)

Born–Haber cycle A thermodynamic cycle based on Hess's law that relates the lattice energy of an ionic substance to its enthalpy of formation and to other measurable quantities. (Section 8.2)

Boyle's law A law stating that at constant temperature, the product of the volume and pressure of a given amount of gas is a constant. (Section 10.3)

Brønsted–Lowry acid A substance (molecule or ion) that acts as a proton donor. (Section 16.1)

Brønsted–Lowry base A substance (molecule or ion) that acts as a proton acceptor. (Section 16.1)

Brownian motion The random motion of colloidal particles in solution due to collisions with solvent molecules. (Section 13.6)

buffer capacity The amount of acid or base a buffer can neutralize before the pH begins to change appreciably. (Section 17.2)

buffered solution (buffer) A solution that undergoes a limited change in pH upon addition of a small amount of acid or base. (Section 17.2)

Cahn–Ingold–Prelog *R,S* notation Use of *R,S* notation to describe the configuration of a stereocentre as defined by a set of sequence priority rules. (Section 25.5)

calorie A unit of energy; it is the amount of energy needed to raise the temperature of 1 g of water by 1 °C from 14.5 °C to 15.5 °C. A related unit is the joule: 1 cal = 4.184 J. (Section 1.5)

calorimeter An apparatus that measures the heat released or absorbed in a chemical or physical process. (Section 5.5)

calorimetry The experimental measurement of heat produced in chemical and physical processes. (Section 5.5)

capillary action The process by which a liquid rises in a tube because of a combination of adhesion to the walls of the tube and cohesion between liquid particles. (Section 11.3)

carbanions A species containing a carbon atom that bears a negative charge. (Section 28.3)

carbide A binary compound of carbon with a metal or metalloid. (Section 22.9)

carbocations A species containing a carbon atom that bears a positive charge. (Section 26.4)

carbohydrates A class of substances formed from polyhydroxy aldehydes or ketones. (Section 24.8)

carbohydrate A class of substances formed from polyhydroxy aldehydes or ketones, typically with a molecular formula in the form $Cr(H_2O)_m$. (Section 28.4)

carbon black An amorphous form of carbon. (Section 22.9)

carbonyl group The C=O double bond, a characteristic feature of several organic functional groups, such as ketones and aldehydes. (Section 24.4)

carbonyl group The C=O double bond, a characteristic feature of several organic functional groups, such as ketones and aldehydes. (Section 28.1)

carboxylic acid An acid that contains the —COOH functional group. (Sections 16.8 and 24.4)

carboxylic acids A compound that contains the —COOH functional group. (Section 29.1)

carboxylate anion The conjugate base of a carboxylic acid. (Section 29.1)

catalyst A substance that changes the speed of a chemical reaction without itself undergoing a permanent chemical change in the process. (Section 14.7)

catalytic hydrogenation A reaction used to add molecular hydrogen to a molecule in the presence of a catalyst. Most commonly used for the conversion of unsaturated hydrocarbons to saturated hydrocarbons. (Section 26.5)

cathode An electrode at which reduction occurs. (Section 20.3)

cathode rays Streams of electrons that are produced when a high voltage is applied to electrodes in an evacuated tube. (Section 2.2)

cathodic protection A means of protecting a metal against corrosion by making it the cathode in a voltaic cell. This can be achieved by attaching a more easily oxidized metal, which serves as an anode, to the metal to be protected. (Section 20.8)

cation A positively charged ion. (Section 2.7)

cell potential The potential difference between the cathode and anode in an electrochemical cell; it is measured in volts: 1 V = 1 J/C. Also called electromotive force. (Section 20.4)

cellulose A polysaccharide of glucose; it is the major structural element in plant matter. (Section 24.8)

cellulose polysaccharide of glucose; it is the major structural element in plant matter. (Section 28.4)

Celsius scale A temperature scale on which water freezes at 0° and boils at 100° at sea level. (Section 1.5)

chain reaction A series of reactions in which one reaction initiates the next. (Section 21.5)

changes of state Physical changes of matter from one state to a different one, for example, from a gas to a liquid. (Section 1.3)

chair conformation The most stable conformation of a cyclohexane ring. (Section 24.5)

charcoal An amorphous form of carbon produced when wood is heated strongly in a deficiency of air. (Section 22.9)

Charles's law A law stating that at constant pressure, the volume of a given quantity of gas is proportional to absolute temperature. (Section 10.3)

chelate effect The generally larger formation constants for bidentate and polydentate ligands as compared with the corresponding *monodentate* ligands. (Section 23.3)

chelating agent Bidentate and polydentate ligands capable of occupying two or more sites in the coordination sphere. (Section 23.3)

chemical bond A strong attractive force that exists between atoms in a molecule. (Section 8.1)

chemical changes Processes in which a substance is transformed into a chemically different substance; also called chemical reactions. (Section 1.3)

chemical equation A representation of a chemical reaction using the chemical formulas of the reactants and products; a balanced chemical equation contains equal numbers of atoms of each element on both sides of the equation. (Section 3.1)

chemical equilibrium A state of dynamic balance in which the rate of formation of the products of a reaction from the reactants equals the rate of formation of the reactants from the products; at equilibrium the concentrations of the reactants and products remain constant. (Section 4.1; Section 15.1)

chemical formula A notation that uses chemical symbols with numerical subscripts to convey the relative proportions of atoms of the different elements in a substance. (Section 2.6)

chemical kinetics The area of chemistry concerned with the speeds, or rates, at which chemical reactions occur. (Section 14.1)

chemical nomenclature The rules used in naming substances. (Section 2.8)

chemical properties Properties that describe the way a substance may change, or *react*, to form other substances. (Section 1.3)

chemical reactions Processes in which a substance is transformed into a chemically different substance; also called chemical changes. (Section 1.3)

chemical shift (δ) The frequency of a signal, expressed in parts per million (ppm), from tetramethylsilane divided by the operating frequency of the spectrometer. (Section 32.3)

chemistry The scientific discipline that studies matter, its properties, and the changes that matter undergoes. (Section 1.1)

chiral A term describing a molecule or an ion that cannot be superimposed on its mirror image. (Section 25.3)

chiral center A tetrahedral atom, usually carbon, bearing four different substituents. (Section 25.3)

chlorofluorocarbons Ozone-damaging substances, principally $CFCl_3$ and CF_2Cl_2, that were once widely used as propellants in spray cans. They do not occur in nature. (Section 18.2)

chlorophyll A plant pigment that plays a major role in conversion of solar energy to chemical energy in photosynthesis. (Section 23.3)

cholesteric liquid crystal A liquid crystal having molecules arranged in layers, with their long axes parallel to the other molecules within the same layer. Moving from one layer to the next, the orientation of the molecules rotates by a fixed angle, resulting in a spiral pattern. (Section 11.7)

cis A geometric isomer in which two substituents attached to a cyclic compound are orientated on different sides of the plane of the ring. (Section 25.2)

coal A naturally occurring solid containing hydrocarbons of high molecular weight, as well as compounds containing sulfur, oxygen, and nitrogen. (Section 5.9)

codon The sets of three successive nucleotides in mRNA that are encoded for amino acids. Used in translation. (Section 31.4)

colligative property A property of a solvent (vapor-pressure lowering, freezing-point lowering, boiling-point elevation, osmotic pressure) that depends on the total concentration of solute particles present. (Section 13.5)

collision model A model of reaction rates based on the idea that molecules must collide to react; it explains the factors influencing reaction rates in terms of the frequency of collisions, the number of collisions with energies exceeding the activation energy, and the probability that the collisions occur with suitable orientations. (Section 14.5)

colloids (colloidal dispersions) Mixtures containing particles larger than normal solutes but small enough to remain suspended in the dispersing medium. (Section 13.6)

combination reaction A chemical reaction in which two or more substances combine to form a single product. (Section 3.2)

combustion A chemical reaction that proceeds with evolution of heat and usually also a flame; most combustion involves reaction with oxygen, as in the burning of a match. (Section 24.7)

combustion reaction A chemical reaction that proceeds with evolution of heat and usually also a flame; most combustion involves reaction with oxygen, as in the burning of a match. (Section 3.2)

common-ion effect A shift of an equilibrium induced by an ion common to the equilibrium. Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution. (Section 17.1)

complementary colors Colors that, when mixed in proper proportions, appear white or colorless. For example, orange and blue are complementary colors that form white light when mixed; when blue is removed, the light looks orange. (Section 23.5)

complete ionic equation A chemical equation in which dissolved strong electrolytes (such as dissolved ionic compounds) are written as separate ions. (Section 4.2)

complex ion (complex) An assembly of a metal ion and the Lewis bases bonded to it. (Section 17.5)

compound A substance composed of two or more elements united chemically in definite proportions. (Section 1.2)

complex lipids Lipids that can be broken down into smaller constituents, usually by hydrolysis. (Section 29.4)

concentration The quantity of solute present in a given quantity of solvent or solution. (Section 4.5)

concentration cell A voltaic cell containing the same electrolyte and the same electrode materials in both the anode and cathode compartments. The emf of the cell is derived from a difference in the concentrations of the same electrolyte solutions in the compartments. (Section 20.6)

condensation polymerization Polymerization in which two molecules are joined to form a larger molecule by elimination of a small molecule, such as H_2O. (Section 12.5)

condensation polymerization Polymerisation in which molecules are joined together through condensation reactions. (Section 29.5)

condensation reaction A reaction in which two molecules are joined to form a larger molecule by elimination of a small molecule, such as H_2O. (Section 12.8)

conduction band A band of unoccupied antibonding molecular orbitals lying higher in energy than the occupied valence band and distinctly separated from it. (Section 12.4)

conformation (Section 24.3)

conformational isomers Isomers which are differentiated by their three-dimensional shape at any instance by rotation about a C–C bond. (Section 24.3)

conjugate acid A substance formed by addition of a proton to a Brønsted–Lowry base. (Section 16.1)

conjugate acid–base pair An acid and a base, such as H_2O and OH^-, that differ only in the presence or absence of a proton. (Section 16.1)

conjugate base A substance formed by the loss of a proton from a Brønsted–Lowry acid. (Section 16.1)

conjugated proteins A protein that yields compounds, such as carbohydrates, lipids, metal complexes and so on, as well as amino acids on hydrolysis. (Section 31.3)

continuous spectrum A spectrum that contains radiation distributed over all wavelengths. (Section 6.3)

conversion factor A fraction whose numerator and denominator are the same quantity expressed in different units. (Section 1.7)

coordination compound A compound containing a complex. (Section 23.2)

coordination number The number of adjacent atoms in a crystal structure to which an atom is directly bonded. In a complex, the coordination number of the metal ion is the number of atoms bonded to the metal ion. (Sections 12.2 and 23.2)

coordination sphere The central metal ion and its surrounding ligands. (Section 23.2)

coordination-sphere isomers Structural isomers that differ in which species in the complex are ligands and which are outside the coordination sphere in the solid. (Section 23.4)

copolymer A complex polymer resulting from the polymerization of two or more chemically different monomers. (Section 12.5)

copolymers A complex polymer resulting from the polymerisation of two or more chemically different monomers. (Section 29.5)

core electrons The electrons that are not in the outermost shell of an atom. (Section 6.8)

corrosion Spontaneous redox reactions in which a metal is attacked by some substance in its environment and converted to an unwanted compound. (Section 20.8)

coupling constant A measure of the spin–spin interactions between two coupled nuclei. (Section 32.3)

covalent bond A bond formed between two or more atoms by a sharing of electrons. (Section 8.1)

covalent-network solids Solids that are held together by an extended network of covalent bonds. (Sections 12.1 and 12.4)

critical mass The amount of fissionable material necessary to maintain a nuclear chain reaction. (Section 21.5)

critical point The temperature and pressure beyond which the liquid and gas phases are indistinguishable from each other. (Section 11.6)

critical pressure The pressure at which a gas at its critical temperature is converted to a liquid state. (Section 11.4)

critical temperature The highest temperature at which a distinct liquid phase can form. The critical temperature increases with an increase in the magnitude of intermolecular forces. (Section 11.4)

cross-linking A method of stiffening polymers by introducing chemical bonds between chains. (Section 12.5)

crown ethers Cyclic compounds containing three or more ether linkages. (Section 27.3)

crystal-field theory A theory that accounts for the colors and the magnetic and other properties of transition-metal complexes in terms of the splitting of the energies of metal ion *d* orbitals by the electrostatic interaction with the ligands. (Section 23.6)

crystal lattice The geometrical pattern of points on which the unit cells are arranged; in effect, an abstract (that is, not real) scaffolding for the crystal structure. (Section 12.1)

crystalline solid (crystal) A solid whose internal arrangement of atoms, molecules, or ions possesses a regularly repeating pattern in any direction through the solid. (Section 12.1)

crystallinity A measure of the extent of short-range ordering in a polymer where chains line up in regular arrays. (Section 12.5)

crystallinity A measure of the extent of crystalline character (order) in a polymer. (Section 26.6)

crystallization The process in which molecules, ions, or atoms come together to form a crystalline solid. The opposite of the solution process. (Section 13.2)

cross-linking The formation of bonds between polymer chains. (Section 26.6)

cubic close packing A crystal structure where the atoms are packed together as close as possible, and the close-packed layers of atoms adopt a three-layer repeating pattern that leads to a face-centered cubic unit cell. (Section 12.2)

curie A measure of radioactivity: $1\text{ curie} = 3.7 \times 10^{10}$ nuclear disintegrations per second. (Section 21.3)

cyanohydrins Compounds containing both a hydroxy (OH) and nitrile (CN) group typically on the same carbon atom. (Section 28.3)

cyclic amines A cycloalkane in which at least one of the carbons within the ring is replaced by nitrogen. A heterocyclic compound. (Section 31.1)

cyclic polyethers A cyclic compound containing more than one ether group within the ring. (Section 27.3)

cycloalkanes Saturated hydrocarbons of general formula C_nH_{2n} in which the carbon atoms form a closed ring. (Section 24.5)

Dalton's law of partial pressures A law stating that the total pressure of a mixture of gases is the sum of the pressures that each gas would exert if it were present alone. (Section 10.5)

***d–d* transition** The transition of an electron in a transition-metal compound from a lower-energy *d* orbital to a higher-energy *d* orbital. (Section 23.6)

deactivating group A substituent that makes the functional group to which it is attached less reactive. Often applied to substituents on aromatic rings undergoing an electrophilic aromatic substitution reaction. (Section 30.5)

decomposition reaction A chemical reaction in which a single compound reacts to give two or more products. (Section 3.2)

decoupling An experiment where information on coupling between two nuclei is lost by saturation. (Section 32.3)

deoxyribonucleic acids (DNA) A polynucleotide in which the sugar component is deoxyribose. (Section 31.4)

degenerate A situation in which two or more orbitals have the same energy. (Section 6.7)

delocalized electrons Electrons that are spread over a number of atoms in a molecule or a crystal rather than localized on a single atom or a pair of atoms. (Section 9.6)

density The amount of mass in a unit volume of a substance. (Section 1.5)

dextrorotatory A term used to label a chiral molecule that rotates the plane of polarisation of plane-polarised light to the right (clockwise). (Section 25.4)

deoxyribonucleic acid (DNA) A polynucleotide in which the sugar component is deoxyribose. (Section 24.10)

derived unit An SI unit obtained by multiplication or division of one or more of the SI base units. (Section 1.5)

desalination The removal of salts from seawater, brine, or brackish water to make it fit for human consumption. (Section 18.4)

deuterium The isotope of hydrogen whose nucleus contains a proton and a neutron: ${}^{2}_{1}\text{H}$. (Section 22.2)

dextrorotatory, or merely dextro or *d* A term used to label a chiral molecule that rotates the plane of polarization of plane-polarized light to the right (clockwise). (Section 23.4)

diamagnetism A type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field. (Section 9.8)

diatomic molecule A molecule composed of only two atoms. (Section 2.6)

1,3-diaxial interactions Interactions between two groups in an axial position on the same side of a chair conformation of a cyclohexane ring separated by three carbon atoms. (Section 24.5)

diffusion The spreading of one substance throughout a space or throughout a second substance. (Section 10.7)

dilution The process of preparing a less concentrated solution from a more concentrated one by adding solvent. (Section 4.5)

dimensional analysis A method of problem solving in which units are multiplied together or divided into each other along with the numerical values. Dimensional analysis ensures that the final answer of a calculation has the desired units. (Section 1.7)

dipole A molecule with one end having a partial negative charge and the other end having a partial positive charge; a polar molecule. (Section 8.4)

dipole–dipole interactions A force that becomes significant when polar molecules come in close contact with one another. The force is attractive when the positive end of one polar molecule approaches the negative end of another. (Section 11.2)

dipole moment A measure of the separation and magnitude of the positive and negative charges in polar molecules. (Section 8.4)

disaccharide Two monosaccharide units linked together by a condensation reaction. (Section 24.8)

diastereomers Stereoisomers that have a non-mirror-image relationship. (Sections 25.1 and 25.6)

dispersion forces Intermolecular forces resulting from attractions between induced dipoles. Also called London dispersion forces. (Section 11.2)

displacement reaction A reaction in which an ion in solution is displaced (replaced) through oxidation of an element. (Section 4.4)

disproportionation reaction A reaction in which an element is simultaneously oxidized and reduced. (Section 22.5)

distillation A separation process that depends on the different abilities of substances to form gases. (Section 1.3)

donor atom The atom of a ligand that bonds to the central metal ion in a coordination complex. (Section 23.3)

doping The process of adding controlled amounts of impurity atoms to a material. For example, incorporation of P into Si. (Section 12.4)

double bond A covalent bond involving two electron pairs. (Section 8.3)

double helix The structure for DNA that involves the winding of two DNA polynucleotide chains together in a helical arrangement. The two strands of the double helix are complementary in that the organic bases on the two strands are paired for optimal hydrogen bond interaction. (Section 24.10)

double helix The structure for DNA that involves the winding of two DNA polynucleotide chains together in a helical arrangement. The two strands of the double helix are complementary in that the organic bases on the two strands are paired for optimal hydrogen bond interaction. (Section 31.4)

dynamic equilibrium A state of balance in which opposing processes occur at the same rate. (Section 11.5)

E1 An elimination reaction displaying second order kinetics. (Section 27.7)

E2 An elimination reaction displaying second order kinetics. (Section 27.6)

***E, Z* system** A system used to distinguish between geometrical isomers in alkenes. The term *E* for *entgegen* means opposite. The term *Z* for *zusammen* means together (or same side). (Section 26.2)

eclipsed A conformation in which all groups around a C–C single bond are as close as possible. This arrangement results in the bonds about a C–C single bond being behind each other when viewed as a Newman projection. (Section 24.3)

Edman degradation A systematic process designed to cleave and identify one amino acid at a time from the *N*-terminus of the peptide chain. (Section 31.3)

effective nuclear charge The net positive charge experienced by an electron in a many-electron atom; this charge is not the full nuclear charge because there is some shielding of the nucleus by the other electrons in the atom. (Section 7.2)

effusion The escape of a gas through an orifice or hole. (Section 10.7)

elastomer A material that can undergo a substantial change in shape via stretching, bending, or compression and return to its original shape upon release of the distorting force. (Section 12.5)

electrochemistry The branch of chemistry that deals with the relationships between electricity and chemical reactions. (Section 20.1)

electrolysis reaction A reaction in which a nonspontaneous redox reaction is brought about by the passage of current under a sufficient external electrical potential. The devices in which electrolysis reactions occur are called electrolytic cells. (Section 20.9)

electrolyte A solute that produces ions in solution; an electrolytic solution conducts an electric current. (Section 4.1)

electrolytic cell A device in which a nonspontaneous oxidation–reduction reaction is caused to occur by passage of current under a sufficient external electrical potential. (Section 20.9)

electron-withdrawing groups A group that has an attraction for electrons that it shares in a chemical bond with other atoms. (Section 30.4)

electron impact ionization (EI) mass spectrometry (EIMS) A popular technique used to determine the molecular weight of a compound through bombardment with high-energy electrons. (Section 32.4)

electromagnetic radiation (radiant energy) A form of energy that has wave characteristics and that propagates through a vacuum at the characteristic speed of 3.00×10^8 m/s. (Section 6.1)

electrometallurgy The use of electrolysis to reduce or refine metals. (Section 20.9)

electromotive force (emf) A measure of the driving force, or *electrical pressure*, for the completion of an electrochemical reaction. Electromotive force is measured in volts: $1\text{ V} = 1\text{ J/C}$. Also called the cell potential. (Section 20.4)

electron A negatively charged subatomic particle found outside the atomic nucleus; it is a part of all atoms. (Section 2.2)

electron affinity The energy change that occurs when an electron is added to a gaseous atom or ion. (Section 7.5)

electron capture A mode of radioactive decay in which an inner-shell orbital electron is captured by the nucleus. (Section 21.1)

electrophilic aromatic substitution (EAS) The mechanism by which benzene and its derivatives react to form more highly substituted compounds. (Section 30.5)

electrophoresis A method for separating compounds based on their electric charge at a given pH. (Section 31.2)

electron configuration The arrangement of electrons in the orbitals of an atom or molecule (Section 6.8)

electron density The probability of finding an electron at any particular point in an atom; this probability is equal to ψ^2, the square of the wave function. Also called the probability density. (Section 6.5)

electron domain In the VSEPR model, a region about a central atom in which an electron pair is concentrated. (Section 9.2)

electron-domain geometry The three-dimensional arrangement of the electron domains around an atom according to the VSEPR model. (Section 9.2)

electronegativity A measure of the ability of an atom that is bonded to another atom to attract electrons to itself. (Section 8.4)

electronic charge The negative charge carried by an electron; it has a magnitude of 1.602×10^{-19} C. (Section 2.3)

electronic structure The arrangement of electrons in an atom or molecule. (Section 6.1)

electron-sea model A model for the behavior of electrons in metals. (Section 12.2)

electron shell A collection of orbitals that have the same value of n. For example, the orbitals with $n = 3$ (the 3*s*, 3*p*, and 3*d* orbitals) comprise the third shell. (Section 6.5)

electron spin A property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized. (Section 6.7)

electrophiles Any atom, molecule or ion that accepts a pair of electrons from a nucleophile to form a new covalent bond. (Section 26.4)

element A substance that cannot be decomposed into simpler substances. (Sections 1.1 and 1.2)

elemental composition The percentage composition of an element in a substance. (Section 3.3)

elementary reaction A process in a chemical reaction that occurs in a single step. An overall chemical reaction consists of one or more elementary reactions or steps. (Section 14.6)

***β*-elimination reaction** A reaction that produces an unsaturated hydrocarbon by the loss of atoms from adjacent carbons in a molecule. (Section 27.6)

elimination reaction A reaction that proceeds by the loss of atoms or groups of atoms, resulting in the formation of multiple bonds. (Section 27.6)

empirical formula A chemical formula that shows the kinds of atoms and their relative numbers in a substance in the smallest possible whole-number ratios. (Section 2.6)

enantiomers Two mirror-image molecules of a chiral substance. The enantiomers are non-superimposable. (Section 25.1)

enantiomerically pure A term used to describe a sample containing 100% of a single enantiomer. (Section 25.4)

endothermic process A process in which a system absorbs heat from its surroundings. (Section 5.2)

energy The capacity to do work or to transfer heat. (Section 1.4)

energy-level diagram A diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived. Also called a **molecular-orbital diagram**. (Section 9.7)

enthalpy A quantity defined by the relationship $H = E + PV$; the enthalpy change, ΔH, for a reaction that occurs at constant pressure is the heat evolved or absorbed in the reaction: $\Delta H = q_p$. (Section 5.3)

enthalpy of formation The enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. (Section 5.7)

enthalpy of reaction The enthalpy change associated with a chemical reaction. (Section 5.4)

entropy A measure of the tendency for energy to spread or disperse, thereby reducing its ability to accomplish work. In a general sense, it reflects the degree of *randomness* or *disorder* associated with the particles that carry the energy. (Section 19.2)

enzyme A protein molecule that acts to catalyze specific biochemical reactions. (Section 14.7)

enzymes A protein molecule that acts to catalyse specific biochemical reactions. (Section 31.3)

equatorial hydrogens Those hydrogens on a chair conformation that radiate out in the rough plane of the ring. (Section 24.5)

equilibrium constant The numerical value of the equilibrium-constant expression for a system at equilibrium. The equilibrium constant is most usually denoted by K_p for gas-phase systems or K_c for solution-phase systems. (Section 15.2)

equilibrium-constant expression The expression that describes the relationship among the concentrations (or partial pressures) of the substances present in a system at equilibrium. The numerator is obtained by multiplying the concentrations of the substances on the product side of the equation, each raised to a power equal to its coefficient in the chemical equation. The denominator similarly contains the concentrations of the substances on the reactant side of the equation. (Section 15.2)

equivalence point The point in a titration at which the added solute reacts completely with the solute present in the solution. (Section 4.6)

ester An organic compound that has an OR group attached to a carbonyl; it is the product of a reaction between a carboxylic acid and an alcohol. (Section 24.4)

ethers A compound in which two hydrocarbon groups are bonded to one oxygen. (Section 24.4 and 27.3)

esters An organic compound that has an –OR group attached to a carbonyl; it is the product of a reaction between a carboxylic acid and an alcohol. (Section 29.3)

exchange (metathesis) reaction A reaction between compounds that when written as a molecular equation appears to involve the exchange of ions between the two reactants. (Section 4.2)

excited state A higher energy state than the ground state. (Section 6.3)

exothermic process A process in which a system releases heat to its surroundings. (Section 5.2)

extensive property A property that depends on the amount of sample considered; for example, mass or volume. (Section 1.3)

face-centered lattice A crystal lattice in which the lattice points are located at the faces and corners of each unit cell. (Section 12.1)

Faraday constant (*F*) The magnitude of charge of one mole of electrons: 96,500 C/mol. (Section 20.5)

fats Triglycerides that are solids or semi-solids at room temperature. They are usually rich in saturated fatty acids. (Section 26.5 and 29.4)

fatty acids Carboxylic acids with > C12 alkyl chains. (Section 29.4)

***f*-block metals** Lanthanide and actinide elements in which the 4*f* or 5*f* orbitals are partially occupied. (Section 6.9)

ferrimagnetism A substance that has both ferromagnetic and antiferromagnetic characteristics. A form of magnetism in which unpaired electron spins on different-type ions point in opposite directions but do not fully cancel out. (Section 23.1)

ferromagnetism A form of magnetism in which unpaired electron spins align parallel to one another. (Section 23.1)

fibrous proteins Proteins that are arranged like filaments or fibres, for example collagen. (Section 31.3)

fingerprint region Usually defined as the most complex region of the IR spectrum (300–1400 cm^{-1}). (Section 32.2)

first law of thermodynamics A statement that energy is conserved in any process. One way to express the law is that the change in internal energy, ΔE, of a system in any process is equal to the heat, q, added to the system, plus the work, w, done on the system by its surroundings: $\Delta E = q + w$. (Section 5.2)

first-order reaction A reaction in which the reaction rate is proportional to the concentration of a single reactant, raised to the first power. (Section 14.4)

fission The splitting of a large nucleus into two smaller ones. (Section 21.5)

Fischer projections A convention for representing the configuration of a stereocentre in two dimensions. (Section 28.4)

folding The process by which a protein adopts its biologically active shape. (Section 24.7)

folding The process by which a protein adopts the biologically active form. (Section 31.3)

force A push or a pull. (Section 1.4)

formal charge The charge an atom (in a molecule) would have if each bonding electron pair in the molecule were shared equally between its two atoms. (Section 8.5)

formation constant For a metal ion complex, the equilibrium constant for formation of the complex from the metal ion and base species present in solution. It is a measure of the tendency of the complex to form. (Section 17.5)

formula weight The sum of the atomic weights (AW) of the atoms in the chemical formula of the substance. For example, the formula weight of NO_2 (46.0 amu) is the sum of the masses of one nitrogen atom and two oxygen atoms. (Section 3.3)

fossil fuels Coal, oil, and natural gas, which are presently our major sources of energy. (Section 5.9)

fracking The practice in which water laden with sand and other materials is pumped at high pressure into rock formations to release natural gas and other petroleum materials. (Section 18.4)

fragment A chemical species produced by the cleavage of a covalent bond. Usually associated with mass spectrometry. (Section 32.4)

free energy (Gibbs free energy, *G*) A thermodynamic state function that gives a criterion for spontaneous change in terms of enthalpy and entropy: $G = H - TS$. (Section 19.5)

free radical A substance with one or more unpaired electrons. (Section 21.6)

free radicals A substance with one or more unpaired electrons. (Section 24.7)

frequency The number of times per second that one complete wavelength passes a given point. (Section 6.1)

frequency factor (*A*) A term in the Arrhenius equation that is related to the frequency of collision and the probability that the collisions are favorably oriented for reaction. (Section 14.5)

fuel cell A voltaic cell that utilizes the oxidation of a conventional fuel, such as H_2 or CH_4, in the cell reaction. (Section 20.7)

fuel value The energy released when 1 g of a substance is combusted. (Section 5.9)

functional group An atom or group of atoms that imparts characteristic chemical properties to an organic compound. (Section 24.1 and 24.6)

fusion The joining of two light nuclei to form a more massive one. (Section 21.5)

galvanic cell See **voltaic (galvanic) cell**. (Section 20.3)

gamma radiation Energetic electromagnetic radiation emanating from the nucleus of a radioactive atom. (Section 21.1)

gas Matter that has no fixed volume or shape; it uniformly fills its container. (Section 1.2)

gas constant (*R*) The constant of proportionality in the ideal-gas equation. (Section 10.4)

geometric isomerism A form of isomerism in which compounds with the same type and number of atoms and the same chemical bonds have different spatial arrangements of these atoms and bonds. (Sections 23.4 and 24.3)

geometric isomers Compounds with the same type and number of atoms and the same chemical bonds but different spatial arrangements of these atoms and bonds. (Section 25.1)

Gibbs free energy A thermodynamic state function that combines enthalpy and entropy, in the form $G = H - TS$. For a change occurring at constant temperature and pressure, the change in free energy is $\Delta G = \Delta H - T\Delta S$. (Section 19.5)

glass An amorphous solid formed by fusion of SiO_2, CaO, and Na_2O. Other oxides may also be used to form glasses with differing characteristics. (Section 22.10)

globular proteins Tightly bundled proteins, so named because of their globular or spherical shape. (Section 31.3)

glucose A polyhydroxy aldehyde whose formula is $CH_2OH(CHOH)_4CHO$; it is the most important of the monosaccharides. (Section 24.8)

glucose A polyhydroxy aldehyde whose formula is $CH_2OH(CHOH)_4CHO$; it is the most important of the monosaccharides. (Section 28.4)

glycogen The general name given to a group of polysaccharides of glucose that are synthesized in mammals and used to store energy from carbohydrates. (Section 24.8)

glycoside A carbohydrate derivative in which the hydroxy group (–OH) located at the anomeric carbon is replaced by another group, typically an alkoxy group (–OR) or amine. (Section 28.4)

glycogen The general name given to a group of polysaccharides of glucose that are synthesised in mammals and used to store energy from carbohydrates. (Section 28.4)

glycosidic bond The bond from the anomeric carbon to the OR group in a glycoside. (Section 28.4)

Graham's law A law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight. (Section 10.7)

gray (Gy) The SI unit for radiation dose corresponding to the absorption of 1 J of energy per kilogram of biological material; 1 Gy = 100 rads. (Section 21.6)

green chemistry Chemistry that promotes the design and application of chemical products and processes that are compatible with human health and that preserve the environment. (Section 18.5)

greenhouse gases Gases in an atmosphere that absorb and emit infrared radiation (radiant heat), "trapping" heat in the atmosphere. (Section 18.2)

Grignard Reagent A class of reagent with general formula RMgX, where R = alkyl, aryl and X = halide. (Section 28.3)

ground state The lowest-energy, or most stable, state. (Section 6.3)

group Elements that are in the same column of the periodic table; elements within the same group or family exhibit similarities in their chemical behavior. (Section 2.5)

Haber process The catalyst system and conditions of temperature and pressure developed by Fritz Haber and coworkers for the formation of NH_3 from H_2 and N_2. (Section 15.2)

half-life The time required for the concentration of a reactant substance to decrease to half its initial value; the time required for half of a sample of a particular radioisotope to decay. (Sections 14.4 and 21.3)

half-reaction An equation for either an oxidation or a reduction that explicitly shows the electrons involved, for example, $Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$. (Section 20.2)

halogens Members of group 17 in the periodic table. (Section 7.8)

halogenation A reaction in which at least one halide is added. In the case of addition reactions to alkenes, two halogen atoms are added across the double bond. (Section 24.7 and 26.4)

haloalkanes Of general formula R–X, where X = F, Cl, Br, I. A haloalkane is any hydrocarbon containing one or more halo groups. (Section 27.2)

haloforms Compounds of the form CHX_3, for example chloroform.(Section 27.1)

hardening A term used to describe the conversion of oils to fats by hydrogenation of unsaturated triglycerides. (Section 26.5 and 29.4)

Haworth projection A convention for representing the configuration of functional groups around a furanose or pyranose ring. (Section 28.4)

heat The energy that causes the temperature of an object to increase. The flow of energy from a body at higher temperature to one at lower temperature when they are placed in thermal contact. (Sections 1.4 and 1.5)

heat capacity The quantity of heat required to raise the temperature of a sample of matter by 1 °C (or 1 K). (Section 5.5)

heat of fusion The enthalpy change, ΔH, for melting a solid. (Section 11.4)

heat of sublimation The enthalpy change, ΔH, for vaporization of a solid. (Section 11.4)

heat of vaporization The enthalpy change, ΔH, for vaporization of a liquid. (Section 11.4)

α-helix A protein structure in which the protein is coiled in the form of a helix, with hydrogen bonds between C=O and N–H groups on adjacent turns. (Section 31.3)

hemiacetals The product formed by the reaction of an aldehyde or ketone with one mole of alcohol. (Section 28.3)

Henderson–Hasselbalch equation The relationship among the pH, pK_a, and the concentrations of acid and conjugate base in an aqueous solution: $pH = pK_a + \log\frac{[base]}{[acid]}$. (Section 17.2)

Henry's law A law stating that the concentration of a gas in a solution, S_g, is proportional to the pressure of gas over the solution: $S_g = kP_g$. (Section 13.3)

Hess's law If a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps. (Section 5.6)

Heteroatom An atom other than carbon or hydrogen used to form functional groups in organic compounds. (Section 24.6)

heterocyclic compounds A cyclic compound in which one or more carbon atoms within the ring are replaced by heteroatoms. (Section 27.3)

heterogeneous alloy An alloy in which the components are not distributed uniformly; instead, two or more distinct phases with characteristic compositions are present. (Section 12.2)

heterogeneous catalyst A catalyst that is in a different phase from that of the reactant substances. (Section 14.7)

heterogeneous equilibrium The equilibrium established between substances in two or more different phases, for example, between a gas and a solid or between a solid and a liquid. (Section 15.3)

heteroatoms An atom other than carbon or hydrogen used to form functional groups in organic compounds. (Section 30.2)

heterocyclic compounds A cyclic compound in which one or more carbon atoms within the ring are replaced by heteroatoms. (Section 30.2)

hexagonal close packing A crystal structure where the atoms are packed together as closely as possible. The close-packed layers adopt a two-layer repeating pattern, which leads to a primitive hexagonal unit cell. (Section 12.2)

high-spin complex A complex whose electrons are arranged to give the maximum number of unpaired electrons. (Section 23.6)

hole A vacancy in the valence band of a semiconductor, created by doping. (Section 12.4)

homogeneous catalyst A catalyst that is in the same phase as the reactant substances. (Section 14.7)

homogeneous equilibrium The equilibrium established between reactant and product substances that are all in the same phase. (Section 15.3)

homologous series A series of compounds that differ only by the number of methane ($-CH_2-$) units. (Section 24.2)

homolytic bond cleavage Symmetrical breaking of a covalent bond to yield two radicals. (Section 24.7)

Hooke's law States that the elongation of a spring is proportional to the load applied. Mathematically: $F_s = -kx$. (Section 32.2)

Hund's rule A rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before pairing of electrons in orbitals occurs. (Section 6.8)

hybridization The mathematical mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals. (Section 9.5)

hybrid orbital An orbital that results from the mixing of different kinds of atomic orbitals on the same atom. For example, an sp^3 hybrid results from the mixing, or hybridizing, of one s orbital and three *p* orbitals. (Section 9.5)

hydration Solvation when the solvent is water. (Section 26.4)

hydride ion An ion formed by the addition of an electron to a hydrogen atom: H^-. (Section 7.7)

hydrocarbons Compounds composed of only carbon and hydrogen. (Section 24.2)

hydrogen bonding Bonding that results from intermolecular attractions between molecules containing hydrogen bonded to an electronegative element. The most important examples involve OH, NH, and HF. (Section 11.2)

hydrohalogenation A reaction that adds HX across a C=C double bond (X is typically Cl, Br, I). (Section 26.4)

hydrolysis A reaction with water. When a cation or anion reacts with water, it changes the pH. (Sections 16.7 and 24.4)

hydronium ion (H_3O^+) The predominant form of the proton in aqueous solution. (Section 16.1)

hydrophilic Water attracting. The term is often used to describe a type of colloid. (Section 13.6)

hydrophobic Water repelling. The term is often used to describe a type of colloid. (Section 13.6)

hypervalent A compound with more than an octet of electrons around the central atom. (Section 9.5)

hypothesis A model or tentative explanation of a series of observations. (Section 1.5)

ideal gas A hypothetical gas whose pressure, volume, and temperature behavior is completely described by the ideal-gas equation. (Section 10.4)

ideal-gas equation An equation of state for gases that embodies Boyle's law, Charles's law, and Avogadro's hypothesis in the form $PV = nRT$. (Section 10.4)

ideal solution A solution that obeys Raoult's law. (Section 13.5)

immiscible liquids Liquids that do not dissolve in one another to a significant extent. (Section 13.3)

imines The product formed by the condensation of an aldehyde or ketone with a primary amine. (Section 28.3)

index of hydrogen deficiency (IHD) A summation of all π-bonds and rings within a molecule. The index of hydrogen deficiency quantity is determined by comparing the number of hydrogens in the molecular formula of an unknown with that of an *alkane* reference that contains the same number of carbon atoms as the unknown. (Section 32.5)

indicator A substance added to a solution that changes color when the added solute has reacted with all the solute present in solution. The most common type of indicator is an acid–base indicator whose color changes as a function of pH. (Section 4.6)

inductive effects An electronic effect transmitted through bonds by a more electronegative neighboring atom. (Section 30.4)

infrared spectroscopy An analytical technique used to characterise functional groups that is based on the absorption of energy by a molecule as it vibrates by stretching and bending. (Section 32.2)

initiation The first step in a chain reaction. (Section 26.6)

instantaneous rate The reaction rate at a particular time as opposed to the average rate over an interval of time. (Section 14.2)

insulators Materials that do not conduct electricity. (Section 12.7)

integration The area under a signal within a ^1H NMR spectrum. The area is proportional to the number of equivalent protons that gives rise to that signal. (Section 32.3)

intensive property A property that does not depend on the amount of sample being examined, for example, density. (Section 1.3)

interhalogens Compounds formed between two different halogen elements. Examples include IBr and BrF_3. (Section 22.4)

intermediate A substance formed in one elementary step of a multistep mechanism and consumed in another; it is neither a reactant nor an ultimate product of the overall reaction. (Section 14.6)

intermetallic compound A homogeneous alloy with definite properties and a fixed composition. (Section 12.2)

intermolecular forces Forces that exist between molecules. (Section 11.1)

internal energy The sum of all the kinetic and potential energies of the components of the system. When a system undergoes a change, the change in internal energy, ΔE, is defined as the heat, q, added to the system, plus the work, w, done on the system by its surroundings: $\Delta E = q + w$. (Section 5.2)

interstitial alloy An alloy formed when solute atoms occupy interstitial positions in the "holes" between solvent atoms. (Section 12.2)

ion Electrically charged atom or group of atoms (polyatomic ion); ions can be positively or negatively charged, depending on whether electrons are lost (positive) or gained (negative) by the atoms. (Section 2.7)

ion–dipole force The force that exists between an ion and a polar molecule that possesses a permanent dipole moment. (Section 11.2)

ionic bond A bond formed by the electrostatic attractions between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons. (Section 8.1)

ionic compound A compound composed of cations and anions. (Section 2.7)

ionic hydrides Compounds formed when hydrogen reacts with alkali metals and also the heavier alkaline earths (Ca, Sr, and Ba); these compounds contain the hydride ion, H^-. (Section 22.2)

ionic solids Solids that are held together by the mutual electrostatic attraction between cations and anions. (Sections 12.1 and 12.5)

ionization energy The minimum energy required to remove an electron from the ground state of an isolated gaseous atom or ion. (Section 7.4)

ionizing radiation Radiation that has sufficient energy to remove an electron from a molecule, thereby ionizing it. (Section 21.6)

ion-product constant For water, K_w is the product of the aquated hydrogen ion and hydroxide ion concentrations: $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ at 25 °C. (Section 16.2)

irreversible process A process that leaves the surroundings somehow changed when the system is restored to its original state. (Section 19.1)

isoelectronic series A series of atoms, ions, or molecules having the same number of electrons. (Section 7.3)

isoelectric point The pH at which the maximum number of molecules of a compound in aqueous solution contain both positively and negatively charged regions. That is, the pH at which the zwitterion form is maximised. (Section 31.2)

isomers Compounds whose molecules have the same overall composition but different structures. (Sections 2.9 and 23.4)

isothermal process A process that occurs at constant temperature. (Section 19.1)

isotopes Atoms of the same element containing different numbers of neutrons and therefore having different masses. (Section 2.3)

joule (J) The SI unit of energy, $1\ kg\text{-}m^2/s^2$. A related unit is the calorie: $4.184\ J = 1\ cal$. (Section 1.5)

Kelvin scale The SI temperature scale; the SI unit for temperature is the kelvin. Zero on the Kelvin scale corresponds to −273.15 °C. (Section 1.5)

ketone A compound in which the carbonyl group (C=O) occurs at the interior of a carbon chain and is therefore flanked by carbon atoms. (Section 24.4)

ketones A compound in which the carbonyl group occurs at the interior of a carbon chain and is therefore flanked by carbon atoms. (Section 28.2)

ketoses A carbohydrate that contains a ketone group when in its open-chain form. (Section 28.4)

kinetic energy The energy that an object possesses by virtue of its motion. (Section 1.4)

kinetic-molecular theory of gases A set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation. (Section 10.6)

lactams A cyclic amide in which the amide bond forms part of the ring. (Section 31.1)

Larmor frequency The frequency at which a nucleus absorbs energy. This frequency is a function of the strength of the applied field B_0. (Section 32.3)

lanthanide contraction The gradual decrease in atomic and ionic radii with increasing atomic number among the lanthanide elements, atomic numbers 57 through 70. The decrease arises because of a gradual increase in effective nuclear charge through the lanthanide series. (Section 23.1)

lanthanide (rare earth) element Element in which the 4*f* subshell is only partially occupied. (Sections 6.8 and 6.9)

lattice energy The energy required to separate completely the ions in an ionic solid into its gaseous ions. (Section 8.2)

lattice points Points in a crystal, all of which have identical environments. (Section 12.1)

lattice vectors The vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ that define each lattice point in a crystal lattice. Beginning from any lattice point, it is possible to move to any other lattice point by adding together whole-number multiples of the two lattice vectors. (Section 12.1)

law of conservation of mass The total mass of materials present after a chemical reaction is the same as the total mass present before the reaction. (Section 2.1)

law of constant composition A law that states that the elemental composition of a compound is always the same; also called the **law of definite proportions**. (Section 1.2)

law of definite proportions A law that states that the elemental composition of a substance is always the same; also called the **law of constant composition**. (Section 1.2)

law of mass action The rules by which the equilibrium constant is expressed in terms of the concentrations of reactants and products, in accordance with the balanced chemical equation for the reaction. (Section 15.2)

law of multiple proportions If two elements A and B combine to form more than one compound, the masses of B that can combine with a given mass of A are in the ratio of small whole numbers. (Section 2.1)

Le Châtelier's principle A principle stating that when we disturb a system at chemical equilibrium, the relative concentrations of reactants and products shift so as to partially undo the effects of the disturbance. (Section 15.5)

levorotatory, or merely levo or *l* A term used to label a chiral molecule that rotates the plane of polarization of plane-polarized light to the left (counterclockwise). (Section 23.4)

levorotatory A term used to label a chiral molecule that rotates the plane of polarisation of plane-polarised light to the left (anticlockwise). (Section 25.4)

Lewis acid An electron-pair acceptor. (Section 16.8)

Lewis base An electron-pair donor. (Section 16.8)

Lewis structure A representation of covalent bonding in a molecule that is drawn using Lewis symbols. Shared electron pairs are shown as lines, and unshared electron pairs are shown as pairs of dots. Only the valence-shell electrons are shown. (Section 8.3)

Lewis symbol (electron-dot symbol) The chemical symbol for an element, with a dot for each valence electron. (Section 8.1)

ligand An ion or molecule that coordinates to a metal atom or to a metal ion to form a complex. (Section 23.2)

limiting reactant (limiting reagent) The reactant that is completely consumed in a reaction; the amount of product that can form is limited by the complete consumption of the limiting reactant. (Section 3.7)

line spectrum A spectrum that contains radiation at only certain specific wavelengths. (Section 6.3)

linkage isomers Structural isomers of coordination compounds in which a ligand is capable of coordinating to a metal in two ways. (Section 23.4)

lipid A nonpolar biological molecule used by organisms for long-term energy storage or as a structural component. (Section 24.9)

lipids A heterogeneous class of naturally occurring organic compounds that are more soluble in aprotic organic solvents but not soluble in water. (Section 29.4)

liquid Matter that has a distinct volume independent of its container. (Section 1.2)

liquid crystal A substance that exhibits a viscous, milky state between the liquid and solid states. (Section 11.7)

lock-and-key model A model of enzyme action in which the substrate molecule is pictured as fitting rather specifically into the active site on the enzyme. It is assumed that in being bound to the active site, the substrate is somehow activated for reaction. (Section 14.7)

lock-and-key model A model of enzyme action in which the substrate molecule is pictured as fitting rather specifically into the active site on the enzyme. It is assumed that, in being bound to the active site, the substrate is somehow activated for reaction. (Section 31.3)

lone pair A pair of electrons that do not participate in covalent bonding in neutral molecules. (Section 27.1)

low-spin complex A metal complex in which the electrons are paired in lower-energy orbitals. (Section 23.6)

macroporous Solids having pores that are visible to the naked eye. (Section 12.6)

magic numbers Numbers of protons and neutrons that result in very stable nuclei. (Section 21.2)

main-group elements Elements in the *s* and *p* blocks of the periodic table. (Section 6.9)

Markovnikov's rule A rule stating that, for the addition of HX to an alkene, the hydrogen of HX adds to the carbon of the double bond with the most hydrogens already attached to it. In essence, the most stable carbocation is formed in preference. (Section 26.4)

mass A measure of the amount of material in an object. In SI units, mass is measured in kilograms. (Section 1.5)

mass defect The difference between the mass of a nucleus and the total masses of the individual nucleons that it contains. (Section 21.5)

mass-to-charge ratio Defined as m/z, where m = mass of the ionised species and z = charge on that species. Organic chemists use the term m/z as a dimensionless quantity. (Section 32.4)

mass number The sum of the number of protons and neutrons in the nucleus of a particular atom. (Section 2.3)

mass percentage The number of grams of solute in each 100 g of solution. (Section 13.4)

mass spectrometer An instrument used to measure the precise masses and relative amounts of atomic and molecular ions. (Section 2.4)

matter Anything that occupies space and has mass; the physical material of the universe. (Section 1.1)

matter waves The term used to describe the wave characteristics of a moving particle. (Section 6.4)

mean free path The average distance traveled by a gas molecule between collisions. (Section 10.7)

***meso* compound** An achiral compound containing two or more stereocentres. (Section 25.6)

mesoporous Solids having pore sizes in the range 2 to 50 nm. (Section 12.6)

metal complex Species that are assemblies of a central transition-metal ion bonded to a group of surrounding molecules or ions, such as $[Ag(NH_3)_2]^+$ and $[Fe(H_2O)_6]^{3+}$. (Section 23.2)

***meta*-director** A substituent on an aromatic compound that preferentially directs an incoming substituent in an electrophillic aromatic substitution to the *meta* position. (Section 30.5)

metal hydrides A compound containing a metal-to-hydrogen bond. Typically used as a source of hydride H^- in organic chemistry. (Section 28.3)

metallic bond Bonding, usually in solid metals, in which the bonding electrons are relatively free to move throughout the three-dimensional structure. (Section 8.1)

metallic character The extent to which an element exhibits the physical and chemical properties characteristic of metals, for example, luster, malleability, ductility, and good thermal and electrical conductivity. (Section 7.6)

metallic elements (metals) Elements that are usually solids at room temperature, exhibit high electrical and heat conductivity, and appear lustrous. Most of the elements in the periodic table are metals. (Sections 2.5 and 12.1)

metallic hydrides Compounds formed when hydrogen reacts with transition metals; these compounds contain the hydride ion, H^-. (Section 22.2)

metallic solids Solids that are composed of metal atoms held together by a delocalized "sea" of collectively shared valence electrons. (Sections 12.1 and 12.2)

metalloids Elements that lie along the diagonal line separating the metals from the nonmetals in the periodic table; the properties of metalloids are intermediate between those of metals and nonmetals. (Section 2.5)

metallurgy The science of extracting metals from their natural sources by a combination of chemical and physical processes. It is also concerned with the properties and structures of metals and alloys. (Section 23.1)

metathesis (exchange) reaction A reaction in which two substances react through an exchange of their component ions: $AX + BY \longrightarrow AY + BX$. Precipitation and acid–base neutralization reactions are examples of metathesis reactions. (Section 4.2)

metric system A system of measurement used in science and in most countries. The meter and the gram are examples of metric units. (Section 1.5)

micelles A spherical aggregate of molecules such as the sodium or potassium salts of fatty acids, oriented in such a way that they have a hydrophilic (charged) surface and a hydrophobic core. (Section 29.4)

microporous Refers to solids that have pores up to 2 nm in size. (Section 12.6)

microstate A single possible arrangement of the positions and kinetic energies of the molecules when the molecules are in a specific thermodynamic state. (Section 19.3)

mineral A solid, inorganic substance occurring in nature, such as calcium carbonate, which occurs as calcite. (Section 23.1)

miscible liquids Liquids that mix in all proportions. (Section 13.3)

mixture A combination of two or more substances in which each substance retains its own chemical identity. (Section 1.2)

molal boiling-point-elevation constant (K_b) A constant characteristic of a particular solvent that gives the increase in boiling point as a function of solution molality: $\Delta T_b = iK_b m$. (Section 13.5)

molal freezing-point-depression constant (K_f) A constant characteristic of a particular solvent that gives the decrease in freezing point as a function of solution molality: $\Delta T_f = -iK_f m$. (Section 13.5)

molality The concentration of a solution expressed as moles of solute per kilogram of solvent; abbreviated *m*. (Section 13.4)

molar heat capacity The heat required to raise the temperature of one mole of a substance by 1 °C. (Section 5.5)

molarity The concentration of a solution expressed as moles of solute per liter of solution; abbreviated *M*. (Section 4.5)

molar mass The mass of one mole of a substance in grams; it is numerically equal to the formula weight in atomic mass units. (Section 3.4)

mole A collection of Avogadro's number (6.022×10^{23}) of objects; for example, a mole of H_2O is 6.022×10^{23} H_2O molecules. (Section 3.4)

molecular compound A compound that consists of molecules. (Section 2.6)

molecular equation A chemical equation in which the formula for each substance is written without regard for whether it is an electrolyte or a nonelectrolyte. (Section 4.2)

molecular formula A chemical formula that indicates the actual number of atoms of each element in one molecule of a substance. (Section 2.6)

molecular geometry The arrangement in space of the atoms of a molecule. (Section 9.2)

molecular hydrides Compounds formed when hydrogen reacts with nonmetals and metalloids. (Section 22.2)

molecularity The number of molecules that participate as reactants in an elementary reaction. (Section 14.6)

molecular orbital (MO) An allowed state for an electron in a molecule. According to molecular-orbital theory, a molecular orbital is entirely analogous to an atomic orbital, which is an allowed state for an electron in an atom. Most bonding molecular orbitals can be classified as σ or π, depending on the disposition of electron density with respect to the internuclear axis. (Section 9.7)

molecular-orbital diagram A diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived; also called an **energy-level diagram**. (Section 9.7)

molecular-orbital theory A theory that accounts for the allowed states for electrons in molecules by using specific wave functions. (Section 9.7)

molecular ion Typically, the species formed by the loss of an electron from a molecule. (Section 32.4)

molecular solids Solids that are composed of molecules held together by their intermolecular forces. (Sections 12.1 and 12.4)

molecular weight The sum of the atomic weights (AW) of the atoms represented by their chemical formula for a molecule. (Section 3.3)

molecule A chemical combination of two or more atoms. (Sections 1.1 and 2.6)

mole fraction The ratio of the number of moles of one component of a mixture to the total moles of all components; abbreviated *X*, with a subscript to identify the component. (Section 10.5)

momentum The product of the mass, *m*, and velocity, *v*, of an object. (Section 6.4)

monodentate ligand A ligand that binds to the metal ion via a single donor atom. It occupies one position in the coordination sphere. (Section 23.3)

monomers Molecules with low molecular weights which can be joined together (polymerised) to form a polymer. (Section 26.6)

monosaccharide A simple sugar, most commonly containing six carbon atoms. The joining together of monosaccharide units by condensation reactions results in formation of polysaccharides. (Section 24.8)

monosaccharides A simple sugar, most commonly containing six carbon atoms. The joining together of monosaccharide units by condensation reactions results in formation of polysaccharides. (Section 28.4)

motif In a crystal, the group of atoms associated with each lattice point. (Section 12.1)

multiplicity The number of peaks an NMR signal is split into due to spin–spin coupling. (Section 32.3)

mutarotation The change in optical rotation that occurs upon the equilibration of α and β anomers from a single anomer. (Section 28.4)

nanomaterial A solid whose dimensions range from 1 to 100 nm and whose properties differ from those of a bulk material with the same composition. (Sections 12.1 and 12.6)

natural gas A naturally occurring mixture of gaseous hydrocarbon compounds composed of hydrogen and carbon. (Section 5.9)

nematic liquid crystalline phase A liquid crystal in which the molecules are aligned in the same general direction, along their long axes, but in which the ends of the molecules are not aligned. (Section 11.7)

Nernst equation An equation that relates the cell emf, E, to the standard emf, E°, and the reaction quotient, Q: $E = E^\circ - (RT/nF) \ln Q$. (Section 20.6)

net ionic equation A chemical equation for a solution reaction in which soluble strong electrolytes are written as ions and spectator ions are omitted. (Section 4.2)

neutralization reaction A reaction in which an acid and a base react in stoichiometrically equivalent amounts; the neutralization reaction between an acid and a metal hydroxide produces water and a salt. (Section 4.3)

neutron An electrically neutral particle found in the nucleus of an atom; it has approximately the same mass as a proton. (Section 2.2)

Newman projection A representation of a molecule's spatial arrangement looking along a C–C single bond. (Section 24.3)

nitriles Any hydrocarbon containing the C≡N group. (Section 27.5 and 28.3)

noble gases Members of group 18 in the periodic table. (Section 7.8)

nodal plane In an antibonding orbital, the plane in the region between the nuclei where the electron density is zero. (Section 9.7)

node Points in an atom at which the electron density is zero. For example, the node in a 2s orbital is a spherical surface. (Section 6.6)

nomenclature The systematic naming of a compound. (Section 24.4)

nonbonding pair In a Lewis structure a pair of electrons assigned completely to one atom; also called a lone pair. (Section 8.3)

nonelectrolyte A substance that does not ionize in water and consequently gives a nonconducting solution. (Section 4.1)

nonionizing radiation Radiation that does not have sufficient energy to remove an electron from a molecule. (Section 21.6)

nonmetallic elements (nonmetals) Elements in the upper right corner of the periodic table; nonmetals differ from metals in their physical and chemical properties. (Section 2.5)

nonpolar covalent bond A covalent bond in which the electrons are shared equally. (Section 8.4)

normal boiling point The boiling point at 1 atm pressure. (Section 11.5)

normal melting point The melting point at 1 atm pressure. (Section 11.6)

nuclear binding energy The energy required to decompose an atomic nucleus into its component protons and neutrons. (Section 21.5)

nuclear disintegration series A series of nuclear reactions that begins with an unstable nucleus and terminates with a stable one; also called a radioactive series. (Section 21.2)

nuclear magnetic resonance (NMR) spectroscopy A non-destructive technique able to provide information on the types and relative number of atoms, atom connectivity and spatial relationships. This technique observes nuclear spin transitions within a strong magnetic field. (Section 32.3)

nuclear model Model of the atom with a very small and extremely dense nucleus containing most of the mass (protons and neutrons) and with electrons in the space outside the nucleus. (Section 2.2)

nuclear reaction Reaction in which transformations of atomic nuclei occur. (Section 21.1)

nuclear transmutation A conversion of one kind of nucleus to another. (Section 21.2)

nucleophilic acyl substitution The mechanism by which one carboxylic acid derivative is converted into a less reactive one. (Section 29.5)

nucleic acids Polymers of high molecular weight that carry genetic information and control protein synthesis. (Section 24.10 and 31.4)

nucleon Particles found in the nucleus of an atom; protons and neutrons. (Section 21.1)

nucleophile Any atom, molecule or ion that donates a pair of electrons to an electrophile to form a new covalent bond. (Section 26.4)

nucleophilic addition A reaction that involves the addition of a nucleophile to a reagent, usually a carbonyl compound. (Section 28.3)

nucleosides Compounds containing a five-carbon sugar and a nitrogen-containing organic base. (Section 31.4)

nucleotides Compounds formed from a molecule of phosphoric acid, a sugar molecule and an organic nitrogen base. Nucleotides form linear polymers called DNA and RNA, which are involved in protein synthesis and cell reproduction. (Section 31.4)

***N*-glycosides** Formed particularly when a monosaccharide is reacted with an amine in the presence of acid. Nucleosides are also *N*-glycosides. (Section 31.4)

nucleophilic substitution (SN) reaction Any reaction in which one nucleophile is substituted by another. (Section 27.4)

nucleotide Monomers of nucleic acids formed from a five-carbon sugar, a nitrogen-containing organic base, and a phosphate group. Nucleotides form linear polymers called DNA and RNA, which are involved in protein synthesis and cell reproduction. (Section 24.10)

nucleus The very small, very dense, positively charged portion of an atom; it is composed of protons and neutrons. (Section 2.2)

octet rule A rule stating that atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons. (Section 8.1)

oils Triglycerides that are liquids at room temperature. They are usually rich in unsaturated fatty acids. (Section 29.4)

operating frequency The frequency at which a NMR spectrometer operates to observe a given nucleus, usually 1H. (Section 32.3)

optical isomers Stereoisomers in which the two forms of the compound are nonsuperimposable mirror images. (Section 25.3)

optical isomerism A form of isomerism in which the two forms of a compound (stereoisomers) are nonsuperimposable mirror images. Also called **enantiomers**. (Section 23.4)

optically active Possessing the ability to rotate the plane of polarized light. (Section 23.4)

orbital An allowed energy state of an electron in the quantum-mechanical model of the atom; the term *orbital* is also used to describe the spatial distribution of the electron. An orbital is defined by the values of three quantum numbers: n, l, and m_l (Section 6.5)

orbital diagram A representation of an atomic orbital drawn as a box with one or two half-arrows inside representing electrons. (Section 6.8)

organic chemistry The study of carbon-containing compounds, typically containing carbon–carbon bonds. (Section 2.9; Section 24.1)

organometallic compounds A compound containing a carbon-to-metal bond. (Section 28.3)

***ortho*, *para*-director** A substituent on an aromatic compound that directs an incoming substituent in an electrophilic aromatic sub-stitution, to the *ortho* and *para* positions in preference. (Section 30.5)

osmosis The net movement of solvent through a semipermeable membrane toward the solution with greater solute concentration. (Section 13.5)

osmotic pressure The pressure that must be applied to a solution to stop osmosis from pure solvent into the solution. (Section 13.5)

Ostwald process An industrial process used to make nitric acid from ammonia. The NH_3 is catalytically oxidized by O_2 to form NO; NO in air is oxidized to NO_2; HNO_3 is formed in a disproportionation reaction when NO_2 dissolves in water. (Section 22.7)

overall reaction order The sum of the reaction orders of all the reactants appearing in the rate expression when the rate can be expressed as $\text{rate} = k[A]^a[B]^b\ldots$. (Section 14.3)

overlap The extent to which atomic orbitals on different atoms share the same region of space. When the overlap between two orbitals is large, a strong bond may be formed. (Section 9.4)

oxidation A process in which a substance loses one or more electrons. (Section 24.7)

oxidation number (oxidation state) A positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of formal rules; to some degree it reflects the positive or negative character of that atom. (Section 4.4)

oxidation–reduction (redox) reaction A reaction in which electrons are transferred from one reactant to another and the oxidation states of these atoms change. (Section 4.4; Section 20.1)

oxidizing agent, or oxidant The substance that is reduced and thereby causes the oxidation of some other substance in an oxidation–reduction reaction. (Section 20.1)

oxyacid A compound in which one or more OH groups, and possibly additional oxygen atoms, are bonded to a central atom. (Section 16.8)

oxyanion A polyatomic anion that contains one or more oxygen atoms. (Section 2.8)

ozone The name given to O_3, an allotrope of oxygen. (Section 7.8)

ozonolysis A synthetically useful way of generating aldehydes and ketones. (Section 28.2)

paramagnetism A property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field. (Section 9.8)

partial pressure The pressure exerted by a particular gas in a mixture. (Section 10.5)

particle accelerator A device that uses strong magnetic and electrostatic fields to accelerate charged particles. (Section 21.2)

parts per billion (ppb) The concentration of a solution in grams of solute per 10^9 (billion) grams of solution; equals micrograms of solute per liter of solution for aqueous solutions. (Section 13.4)

parts per million (ppm) The concentration of a solution in grams of solute per 10^6 (million) grams of solution; equals milligrams of solute per liter of solution for aqueous solutions. (Section 13.4)

pascal (Pa) The SI unit of pressure: $1\ \text{Pa} = 1\ \text{N/m}^2$. (Section 10.2)

Pauli exclusion principle A rule stating that no two electrons in an atom may have the same four quantum numbers (n, l, m_l, and m_s).

As a reflection of this principle, there can be no more than two electrons in any one atomic orbital. (Section 6.7)

penicillins A lactam with antibiotic activity. (Section 31.1)

peptide The name given to a short polymer (oligomer) of amino acids joined by amide bonds, usually without significant tertiary structure. (Section 31.3)

peptide bond An amide group formed by amino acids. A bond formed between two amino acids. (Section 24.7)

peptide bond A bond formed between two amino acids. (Section 31.3)

percent ionization The percent of a substance that undergoes ionization on dissolution in water. The term applies to solutions of weak acids and bases. (Section 16.5)

percent yield The ratio of the actual (experimental) yield of a product to its theoretical (calculated) yield, multiplied by 100. (Section 3.7)

period The row of elements that lie in a horizontal row in the periodic table. (Section 2.5)

periodic table The arrangement of elements in order of increasing atomic number, with elements having similar properties placed in vertical columns. (Section 2.5)

perspective drawing A model that uses wedges and dashed lines to depict bonds that are not in the plane of the paper. (Section 2.6)

petroleum A naturally occurring combustible liquid composed of hundreds of hydrocarbons and other organic compounds. (Section 5.9)

pH The negative log in base 10 of the aquated hydrogen ion concentration: $pH = -\log[H^+]$. (Section 16.3)

pH titration curve A graph of pH as a function of added titrant. (Section 17.3)

phase change The conversion of a substance from one state of matter to another. The phase changes we consider are melting and freezing (solid $\rightleftharpoons$ liquid), sublimation and deposition, and vaporization and condensation (liquid $\rightleftharpoons$ gas). (Section 11.4)

phase diagram A graphic representation of the equilibria among the solid, liquid, and gaseous phases of a substance as a function of temperature and pressure. (Section 11.6)

phenyl group A hydrocarbon group with formula C_6H_5. (Section 30.2)

phenols A compound with molecular formula C_6H_5OH. (Section 30.2)

phospholipid A form of lipid molecule that contains charged phosphate groups. (Section 24.9)

photochemical smog A complex mixture of undesirable substances produced by the action of sunlight on an urban atmosphere polluted with automobile emissions. The major starting ingredients are nitrogen oxides and organic substances. (Section 18.2)

photodissociation The rupture of a chemical bond resulting from absorption of a photon by a molecule. (Section 18.1)

photoelectric effect The emission of electrons from a metal surface induced by light. (Section 6.2)

photoionization The removal of an electron from an atom or molecule by absorption of light. (Section 18.1)

photon The smallest increment (a quantum) of radiant energy; a photon of light with frequency ν has an energy equal to $h\nu$. (Section 6.2)

photosynthesis The process that occurs in plant leaves by which light energy is used to convert carbon dioxide and water to carbohydrates and oxygen. (Section 23.3)

physical changes Changes in physical appearance (such as a phase change) that occur with no change in chemical composition. (Section 1.3)

physical properties Properties that can be measured without changing the composition of a substance, for example, color and freezing point. (Section 1.3)

pi (π) bond A covalent bond in which electron density is concentrated above and below the internuclear axis; produced by the sideways overlap of *p* orbitals. (Section 9.6)

pi (π)-bond A covalent bond in which electron density is concentrated above and below the line joining the bonded atoms. (Section 26.1)

pi (π) molecular orbital A molecular orbital that concentrates the electron density on opposite sides of an imaginary line that passes through the nuclei. (Section 9.8)

Planck constant (*h*) The constant that relates the energy and frequency of a photon, $E = h\nu$. Its value is 6.626×10^{-34} J-s. (Section 6.2)

plastic A polymeric solid that can be formed into particular shapes by application of heat and pressure. (Section 12.5)

plastics A material that can be formed into particular shapes by application of heat and pressure. (Section 26.6)

β-pleated sheet A form of protein secondary structure characterised by an intermolecular hydrogen bonding arrangement with another peptide chain. (Section 31.3)

polar covalent bond A covalent bond in which the electrons are not shared equally. (Section 8.4)

polarimeter An instrument used to measure the rotation of plane-polarised light. (Section 25.4)

polarizability The ease with which the electron cloud of an atom or a molecule is distorted by an outside influence, thereby inducing a dipole moment. (Section 11.2)

polar molecule A molecule in which the centers of positive and negative charge do not coincide; a molecule that possesses a nonzero dipole moment. (Section 8.4)

polyatomic ion An electrically charged group of two or more atoms. (Section 2.7)

polypeptides A polymer of amino acids that has a molecular weight of less than 10000. (Section 31.3)

polyesters Polymers in which the repeating structural units are joined together by ester bonds. Usually formed by the condensation of dicarboxylic acids and their derivatives with diols. (Section 29.5)

polyamides Polymers in which the repeating structural units are joined together by amide bonds. Usually formed by the condensation of dicarboxylic acids and their derivatives with diamines. (Section 29.5)

polydentate ligand A ligand in which two, three, or more donor atoms can coordinate to the same metal ion. (Section 23.3)

polymer Large molecules with long chains of atoms (usually carbon), where the atoms within a given chain are connected by covalent bonds and adjacent chains are held to one another largely by weaker intermolecular forces. (Sections 12.1 and 12.5)

polymer A large molecule of high molecular mass, formed by the joining together, or polymerisation, of a large number of molecules of low molecular mass. The individual molecules forming the polymer are called monomers. (Section 26.6)

polypeptide A polymer of amino acids formed when a large number of amino acids (>30) are linked together by peptide bonds. (Section 24.7)

polyprotic acid A substance capable of dissociating more than one proton in water; H_2SO_4 is an example. (Section 16.5)

polysaccharide A substance made up of many monosaccharide units joined together. (Section 24.8)

polysaccharides A substance made up of several monosaccharide units joined together. (Section 28.4)

porphyrin A complex derived from the porphine molecule. (Section 23.3)

positron A particle with the same mass as an electron but with a positive charge, ${}^{0}_{+1}e$, or β^+. (Section 21.1)

positron emission A nuclear decay process where a positron, a particle with the same mass as an electron but with a positive charge, symbol ${}^{0}_{+1}e$, or β^+, is emitted from the nucleus. (Section 21.1)

potential energy The energy that an object possesses as a result of its position with respect to another object. (Section 1.4)

precipitate An insoluble substance that forms in, and separates from, a solution. (Section 4.2)

precipitation reaction A reaction that occurs between substances in solution in which one of the products is insoluble. (Section 4.2)

precision The closeness of agreement among several measurements of the same quantity. (Section 1.6)

pressure A measure of the force exerted on a unit area. In chemistry, pressure is often expressed in units of atmospheres (atm) or torr: 760 torr = 1 atm; in SI units pressure is expressed in pascals (Pa). (Section 10.2)

pressure–volume (*PV*) work Work performed by expansion of a gas against a resisting pressure. (Section 5.3)

primary cell A voltaic cell that cannot be recharged. (Section 20.7)

primary structure The sequence of amino acids along a protein chain. (Section 24.7)

primary structure The sequence of amino acids along a protein chain. (Section 31.3)

primitive lattice A crystal lattice in which the lattice points are located only at the corners of each unit cell. (Section 12.1)

principal quantum number The integer, n, associated with orbits and energy levels in the Bohr atom. (Section 6.3)

probability density (ψ^2) A value that represents the probability that an electron will be found at a given point in space. Also called **electron density**. (Section 6.5)

product A substance produced in a chemical reaction; it appears to the right of the arrow in a chemical equation. (Section 3.1)

propagation Fundamental steps in a freeradical polymerisation that are repeated over and over again in a chain reaction. (Section 26.6)

property Any characteristic that allows us to recognize a particular type of matter and to distinguish it from other types. (Section 1.1)

protein Macromolecules present in all living cells; a biopolymer formed from amino acids. (Section 24.7)

proteins A biopolymer formed from amino acids. (Section 31.3)

protium The most common isotope of hydrogen. (Section 22.2)

proton A positively charged subatomic particle found in the nucleus of an atom. (Section 2.2)

pyrimidine A nitrogen-containing sixmembered heterocyclic compound used as an organic base for genetic information storage within DNA. (Section 31.4)

purine A nitrogen-containing heterocyclic compound comprising fused five- and six-membered rings. Used as an organic base for genetic information storage within DNA. (Section 31.4)

pure substance Matter that has a fixed composition and distinct properties. (Section 1.2)

qualitative analysis The determination of the presence or absence of a particular substance in a mixture. (Section 17.6)

quantitative analysis The determination of the amount of a given substance that is present in a sample. (Section 17.6)

quantum The smallest increment of radiant energy that may be absorbed or emitted; the magnitude of radiant energy is $h\nu$. (Section 6.2)

quaternary structure The structure of a protein resulting from the clustering of several individual protein chains into a final specific shape. (Section 24.7)

quaternary structure The aggregation of two or more proteins into a larger macromolecular assembly. (Section 31.3)

racemic mixture A mixture of equal amounts of the dextrorotatory and levorotatory forms of a chiral molecule. A racemic mixture will not rotate the plane of polarized light. (Section 23.4)

rad A measure of the energy absorbed from radiation by tissue or other biological material; 1 rad = transfer of 1×10^{-2} J of energy per kilogram of material. (Section 21.6)

radial probability function The probability that the electron will be found at a certain distance from the nucleus. (Section 6.6)

radioactive Possessing radioactivity, the spontaneous disintegration of an unstable atomic nucleus with accompanying emission of radiation. (Section 2.2; Section 21.1)

radioactive decay chain A series of nuclear reactions that begins with an unstable nucleus and terminates with a stable one. Also called **nuclear disintegration series**. (Section 21.2)

radioisotope An isotope that is radioactive; that is, it is undergoing nuclear changes with emission of radiation. (Section 21.1)

radionuclide A radioactive nuclide. (Section 21.1)

radiotracer A radioisotope that can be used to trace the path of an element in a chemical system. (Section 21.4)

Raoult's law A law stating that the partial pressure exerted by solvent vapor above the solution, $P_{solution}$, equals the product of the mole fraction of the solvent, $X_{solvent}$, and the vapor pressure of the pure solvent, $P^{\circ}_{solvent}$. $P_{solution} = X_{solvent}P^{\circ}_{solvent}$. (Section 13.5)

racemic mixture A mixture of equal amounts of the dextrorotatory and levorotatory forms of a chiral molecule. A racemic mixture will not rotate polarised light. Also called a racemate. (Section 25.4)

rare earth element See **lanthanide (rare earth) element**. (Sections 6.8 and 6.9)

rate constant A constant of proportionality between the reaction rate and the concentrations of reactants that appear in the rate law. (Section 14.3)

rate-determining step The slowest elementary step in a reaction mechanism. (Section 14.6)

rate law An equation that relates the reaction rate to the concentrations of reactants (and sometimes of products also). (Section 14.3)

reactant A starting substance in a chemical reaction; it appears to the left of the arrow in a chemical equation. (Section 3.1)

reaction mechanism A detailed picture, or model, of how the reaction occurs; that is, the order in which bonds are broken and formed and the changes in relative positions of the atoms as the reaction proceeds. (Section 14.6)

reaction order The power to which the concentration of a reactant is raised in a rate law. (Section 14.3)

reaction quotient (*Q*) The value that is obtained when concentrations of reactants and products are inserted into the equilibrium expression. If the concentrations are equilibrium concentrations, $Q = K$; otherwise, $Q \neq K$. (Section 15.4)

reaction rate The speed at which a chemical reaction occurs; a measure of the decrease in concentration of a reactant or the increase in concentration of a product with time. (Section 14.1 and Section 14.2)

redox (oxidation–reduction) reaction A reaction in which certain atoms undergo changes in oxidation states. The substance increasing in oxidation state is oxidized; the substance decreasing in oxidation state is reduced. (Section 4.4; Section 20.1)

reducing agent, or reductant The substance that is oxidized and thereby causes the reduction of some other substance in an oxidation–reduction reaction. (Section 20.1)

reduction A process in which a substance gains one or more electrons. (Section 4.4)

reductive amination A reaction between an aldehyde or ketone and primary amine, or ammonia, that occurs in the presence of a reducing agent, leading to the formation of a new amine. (Section 31.1)

rem A measure of the biological damage caused by radiation; rems = rads × RBE. (Section 21.6)

renewable energy sources Energy such as solar energy, wind energy, and hydroelectric energy derived from essentially inexhaustible sources. (Section 5.9)

representative (main-group) element An element from within the *s* and *p* blocks of the periodic table (Figure 6.30). (Section 6.9)

resonance structures (resonance forms) Individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. The resonance structures in such an instance are "averaged" to give a more accurate description of the real molecule. (Section 8.6)

resolution The act of separating a racemic mixture into its constituent enantiomers. (Section 25.6)

resonance 1. The term given to the absorption of electromagnetic radiation at the Larmor frequency, which leads to the flip of its nuclear spin from a lower state to a higher state (and *vice versa*). 2. The way electron delocalisation is shown using Lewis structures. (Section 30.3 and 32.3)

resonance structures (resonance forms) Individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. The resonance structures in such an instance are 'averaged' to give a more accurate description of the real molecule. (Section 30.2)

resonance energy The difference in energy between a resonance hybrid and the most stable contributing structure in which the bonds are localised. (Section 30.2)

resonance-stabilized The stabilisation given to any molecule in which its electrons can be delocalised over three or more atoms. (Section 30.4)

reverse osmosis The process by which water molecules move under high pressure through a semipermeable membrane from the more concentrated to the less concentrated solution. (Section 18.4)

reversible process A process in which the system can be restored to its original condition with no change to the surroundings. (Section 19.1)

ribonucleic acid (RNA) A polynucleotide in which ribose is the sugar component. (Section 24.10)

ribonucleic acids (RNA) A polynucleotide in which ribose is the sugar component. (Section 31.4)

root-mean-square (rms) speed (μ_{rms}) The square root of the average of the squared speeds of the gas molecules in a gas sample. (Section 10.6)

rotational motion Movement of a molecule as it spins about an axis. (Section 19.3)

saponification Hydrolysis of an ester in the presence of a base. (Section 29.3)

salinity A measure of the salt content of seawater, brine, or brackish water. It is equal to the mass in grams of dissolved salts present in 1 kg of seawater. (Section 18.3)

salt Any ionic compound whose cation comes from a base (for example, Na^+ from NaOH) and whose anion comes from an acid (for example, Cl^- from HCl). (Section 4.3)

saponification Hydrolysis of an ester in the presence of a base. (Section 24.4)

saturated solution A solution in which undissolved solute and dissolved solute are in equilibrium. (Section 24.2)

scientific law A statement of what is always observed to happen, to the best of our knowledge. (Section 1.5)

scientific method The general process of advancing scientific knowledge by making experimental observations and by formulating hypotheses, theories, and laws. (Figure 1.17)

secondary cell A voltaic cell that can be recharged. (Section 20.7)

secondary structure Refers to how segments of the protein chain are oriented in a regular pattern. (Section 24.7)

secondary structure The manner in which a protein is coiled or stretched. (Section 31.3)

second law of thermodynamics A statement of our experience that there is a direction to the way events occur in nature. When a process occurs spontaneously in one direction, it is nonspontaneous in the reverse direction. It is possible to state the second law in many different forms, but they all relate back to the same idea about spontaneity. One of the most common statements found in chemical contexts is that in any spontaneous process the entropy of the universe increases. (Section 19.2)

second-order reaction A reaction in which the rate depends either on a reactant concentration raised to the second power or on the concentrations of two reactants each raised to the first power. (Section 14.4)

semiconductor A material that has electrical conductivity between that of a metal and that of an insulator. (Section 12.4)

sequence priority rules A process of determining priority based on the atomic weights of atoms connected to a stereocentre. (Section 25.5)

shielding/deshielding Any effect that causes a nucleus to come into resonance at a higher/lower field, respectively. (Section 32.3)

side chain That part of an α-amino acid that distinguishes it from other α-amino acids. (Section 31.2)

sigma (σ) bond A covalent bond in which electron density is concentrated along the internuclear axis. (Section 26.1)

sigma (σ) molecular orbital A molecular orbital that centers the electron density about an imaginary line passing through two nuclei. (Section 9.7)

significant figures The digits that indicate the precision with which a measurement is made; all digits of a measured quantity are significant, including the last digit, which is uncertain. (Section 1.6)

silica Common name for silicon dioxide. (Section 22.4)

silicates Compounds containing silicon and oxygen, structurally based on SiO_4 tetrahedra. (Section 22.10)

simple proteins A protein that yields only amino acids upon hydrolysis. (Section 31.3)

single bond A covalent bond involving one electron pair. (Section 8.3)

SI units The preferred metric units for use in science. (Section 1.5)

smectic A and smectic C liquid crystals Liquid crystals in which the molecules maintain the long-axis alignment seen in nematic crystals, but in addition pack into layers. (Section 11.7)

solid Matter that has both a definite shape and a definite volume. (Section 1.2)

solubility The amount of a substance that dissolves in a given quantity of solvent at a given temperature to form a saturated solution. (Sections 4.2 and 13.2)

solubility-product constant (solubility product) (K_{sp}) An equilibrium constant related to the equilibrium between a solid salt and its ions in solution. It provides a quantitative measure of the solubility of a slightly soluble salt. (Section 17.4)

solute A substance dissolved in a solvent to form a solution; it is normally the component of a solution present in the smaller amount. (Section 4.1)

solution A mixture of substances that has a uniform composition; a homogeneous mixture. (Section 1.2)

solvation The clustering of solvent molecules around a solute particle. (Section 13.1)

solvent The dissolving medium of a solution; it is normally the component of a solution present in the greater amount. (Section 4.1)

space-filling model Model that shows relative sizes of the atoms. (Section 2.6)

specific heat (C_s) The heat capacity of 1 g of a substance; the heat required to raise the temperature of 1 g of a substance by 1 °C. (Section 5.5)

specific rotation The amount an optically active compound of concentration 1.0 g per 100 cm^{-3} rotates plane-polarised light through a 1-dm-long cell at 25 °C. (Section 25.4)

spectator ions Ions that go through a reaction unchanged and that appear on both sides of the complete ionic equation. (Section 4.2)

spectrochemical series A list of ligands arranged in order of their abilities to increase the crystal-field splitting energy. (Section 23.6)

spectrum The distribution among various wavelengths of the radiant energy emitted or absorbed by an object. (Section 6.3)

spin magnetic quantum number (m_s) A quantum number associated with the electron spin; it may have values of $+\frac{1}{2}$ or $-\frac{1}{2}$. (Section 6.7)

spin-pairing energy The difference between the energy required to pair an electron in an occupied orbital and the energy required to place that electron in an empty orbital. (Section 23.6)

spin–spin coupling The communication of nuclear spin information between nuclei expressed in an NMR spectrum by multiplicity. (Section 32.3)

splitting pattern The output of spin–spin coupling within a spectrum. (Section 32.3)

spontaneous process A process that is capable of proceeding in a given direction, as written or described, without needing to be driven by an outside source of energy. A process may be spontaneous even though it is very slow. (Section 19.1)

Staggered A conformation in which all groups around a C–C single bond are separated as far as possible. (Section 24.3)

standard atmospheric pressure Defined as 760 torr or, in SI units, 101.325 kPa. (Section 10.2)

standard emf, also called the standard cell potential ($E°$) The emf of a cell when all reagents are at standard conditions. (Section 20.4)

standard enthalpy change ($\Delta H°$) The change in enthalpy in a process when all reactants and products are in their stable forms at 1 atm pressure and a specified temperature, commonly 25 °C. (Section 5.7)

standard enthalpy of formation (ΔH_f°) The change in enthalpy that accompanies the formation of one mole of a substance from its elements, with all substances in their standard states. (Section 5.7)

standard free energy of formation (ΔG_f°) The change in free energy associated with the formation of a substance from its elements under standard conditions. (Section 19.5)

standard hydrogen electrode (SHE) An electrode based on the half-reaction $2\,H^+(1\,M) + 2\,e^- \longrightarrow H_2(1\,atm)$. The standard electrode potential of the standard hydrogen electrode is defined as 0 V. (Section 20.4)

standard molar entropy ($S°$) The entropy value for a mole of a substance in its standard state. (Section 19.4)

standard reduction potential ($E°_{red}$) The potential of a reduction half-reaction under standard conditions, measured relative to the standard hydrogen electrode. A standard reduction potential is also called a standard electrode potential. (Section 20.4)

standard solution A solution of known concentration. (Section 4.6)

standard temperature and pressure (STP) Defined as 0 °C and 1 atm pressure; frequently used as reference conditions for a gas. (Section 10.4)

starch The general name given to a group of polysaccharides that acts as energy-storage substances in plants. (Section 24.8)

starch The general name given to a group of polysaccharides that act as energy storage substances in plants. (Section 28.4)

state function A property of a system that is determined by its state or condition and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified; P, V, T, E, and H are state functions. (Section 5.2)

states of matter The three forms that matter can assume: solid, liquid, and gas. (Section 1.2)

stereoisomers Compounds possessing the same formula and bonding arrangement but differing in the spatial arrangements of the atoms. (Section 23.4)

stereocenter See **chiral centre**. (Section 25.3)

stereogenic center See **chiral centre**. (Section 25.3)

stereoselective reaction A reaction in which one stereoisomer is formed (or destroyed) in preference to all other possible stereoisomers. (Section 26.4)

Steric An effect due to the size of an atom, or groups of atoms. (Section 24.3)

Strecker synthesis A method of synthesising α-amino acids from aldehydes. (Section 31.2)

structural or constitutional isomers Compounds possessing the same formula but differing in the bonding arrangements of the atoms. Also often called **constitutional isomers**. (Section 24.3)

stoichiometry The relationships among the quantities of reactants and products involved in chemical reactions. (Section 3.1)

stratosphere The region of Earth's atmosphere from 10 km to 50 km above the surface. (Section 18.1)

strong acid An acid that ionizes completely in water. (Section 4.3)

strong base A base that ionizes completely in water. (Section 4.3)

strong electrolyte A substance (strong acids, strong bases, and most salts) that is completely ionized in solution. (Section 4.1)

structural formula A formula that shows not only the number and kinds of atoms in the molecule but also the arrangement (connections) of the atoms. (Section 2.6)

structural isomers Compounds possessing the same formula but differing in the bonding arrangements of the atoms. (Sections 23.4 and 24.2)

subatomic particles Particles such as protons, neutrons, and electrons that are smaller than an atom. (Section 2.2)

subshell One or more orbitals with the same set of quantum numbers n and l. For example, we speak of the $2p$ subshell $(n = 2, l = 1)$, which is composed of three orbitals ($2p_x$, $2p_y$, and $2p_z$). (Section 6.5)

substrates A substance that undergoes a reaction at the active site in an enzyme. (Section 31.3)

substitutional alloy An alloy formed when atoms of the solute in a solid solution occupy positions normally occupied by a solvent atom. (Section 12.2)

substitution reaction Reactions in which one atom (or group of atoms) replaces another atom (or group) within a molecule; substitution reactions are typical for alkanes and aromatic hydrocarbons. (Section 24.7)

substitution reactions Reactions in which one atom (or group of atoms) replaces another atom (or group) within a molecule; substitution reactions are typical for alkanes and aromatic hydrocarbons. (Section 24.3)

substrate A substance that undergoes a reaction at the active site in an enzyme. (Section 14.7)

supercritical fluid The state that exists when liquid and gas phases are indistinguishable from each other as the temperature exceeds the critical temperature and the pressure exceeds the critical pressure. (Section 11.4)

supercritical mass An amount of fissionable material larger than the critical mass. (Section 21.5)

supersaturated solution A solution containing more solute than an equivalent saturated solution. (Section 13.2)

surface tension The energy required to increase the surface area of a liquid by a unit amount. (Section 11.3)

surroundings In thermodynamics, everything that lies outside the system that we study. (Section 5.2)

system In thermodynamics, the portion of the universe that we single out for study. We must be careful to state exactly what the system contains and what transfers of energy it may have with its surroundings. (Section 5.2)

synthetic detergents A substance that cleans by forming micelles but is not made by the hydrolysis of fats. A synthetic analogue of a soap. (Section 29.4)

tautomerism The interconversion of equilibrating isomers that differ in the location of their bonding electrons, usually accompanying a proton movement. (Section 28.3)

termination The final step in a chain reaction that stops further reaction. (Section 26.6)

tertiary structure The overall shape of a large protein, specifically the manner in which sections of the protein fold back upon themselves or intertwine. (Section 31.3)

temperature A measure of the hotness or coldness of an object; a physical property that determines the direction of heat flow. (Section 1.5)

termolecular reaction An elementary reaction that involves three molecules. Termolecular reactions are rare. (Section 14.6)

tertiary structure The overall shape of a large protein, specifically, the manner in which sections of the protein fold back upon themselves or intertwine. (Section 24.7)

theoretical yield The quantity of product that is calculated to form when all of the limiting reagent reacts. (Section 3.7)

theory A tested model or explanation that has predictive powers and that accounts for all available observations. (Section 1.5)

thermochemistry The relationship between chemical reactions and energy changes. (Section 5.1)

thermodynamics The study of energy and its transformation. (Section 5.1)

thermonuclear reaction Another name for fusion reactions; reactions in which two light nuclei are joined to form a more massive one. (Section 21.5)

thermoplastic A polymeric material that can be readily reshaped by application of heat and pressure. (Section 26.6)

thermosetting plastic A plastic that is formed by irreversible chemical processes and therefore is not readily reshaped by application of heat and pressure. (Section 26.6)

thermosetting plastic A plastic that, once formed in a particular mould, is not readily reshaped by application of heat and pressure. (Section 26.6)

third law of thermodynamics A law stating that the entropy of a pure, crystalline solid at absolute zero temperature is zero: $S(0\,\mathrm{K}) = 0$. (Section 19.3)

titration The process of reacting a solution of unknown concentration with one of known concentration (a standard solution). (Section 4.6)

torr A unit of pressure $(1\ \mathrm{torr} = 1\ \mathrm{mm\ Hg})$. (Section 10.2)

trans A geometric isomer in which two substituents attached to a cyclic compound are orientated on different sides of the plane of the ring. (Section 25.2)

transition elements (transition metals) Elements in which the *d* orbitals are partially occupied. (Section 6.8)

transition state (activated complex) The particular arrangement of reactant and product molecules at the point of maximum energy in the rate-determining step of a reaction. (Section 14.5)

transmittance Expressed by the ratio $I/I0$, where I = intensity of light through the sample and $I0$ = intensity of light used for the measurement. The value of transmittance always lies between 0 and 1. (Section 32.2)

translational motion Movement in which an entire molecule moves in a definite direction. (Section 19.3)

transuranium elements Elements that follow uranium in the periodic table. (Section 21.2)

triglycerides Triesters of glycerol, including common fats and oils. (Section 26.5)

triglycerides Triesters of glycerol, including common fats and oils. (Section 29.4)

triple bond A covalent bond involving three electron pairs. (Section 8.3)

triple point The temperature at which solid, liquid, and gas phases coexist in equilibrium. (Section 11.6)

tritium The isotope of hydrogen whose nucleus contains a proton and two neutrons. (Section 22.2)

troposphere The region of Earth's atmosphere extending from the surface to about 10 km altitude. (Section 18.1)

Tyndall effect The scattering of a beam of visible light by the particles in a colloidal dispersion. (Section 13.6)

uncertainty principle A principle stating there is an inherent uncertainty in the precision with which we can simultaneously specify the position and momentum of a particle. This uncertainty is significant only for particles of extremely small mass, such as electrons. (Section 6.4)

unimolecular reaction An elementary reaction that involves a single molecule. (Section 14.6)

unit cell The smallest portion of a crystal that reproduces the structure of the entire crystal when repeated in different directions in space. It is the repeating unit or building block of the crystal lattice. (Section 12.1)

unsaturated solution A solution containing less solute than a saturated solution. (Section 13.2)

UV-visible spectroscopy An analytical technique based on the transitions between electronic energy states within a molecule. (Section 32.1)

valence band A band of closely spaced bonding molecular orbitals that is essentially fully occupied by electrons. (Section 12.4)

valence-bond theory A model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms. (Section 9.4)

valence electrons The outermost electrons of an atom; those that occupy orbitals not occupied in the nearest noble-gas element of lower atomic number. The valence electrons are the ones the atom uses in bonding. (Section 6.8)

valence orbitals Orbitals that contain the outer-shell electrons of an atom. (Section 7.1)

valence-shell electron-pair repulsion (VSEPR) model A model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs. (Sections 9.1 and 9.2)

van der Waals equation An equation of state for nonideal gases that is based on adding corrections to the ideal-gas equation. The correction terms account for intermolecular forces of attraction and for the volumes occupied by the gas molecules themselves. (Section 10.8)

van't Hoff factor The number of fragments that a solute breaks into for a particular solvent. (Section 13.5)

vapor Gaseous state of any substance that normally exists as a liquid or solid. (Section 10.1)

vapor pressure The pressure exerted by a vapor in equilibrium with its liquid or solid phase. (Section 11.5)

vibrational motion Movement of the atoms within a molecule in which they move periodically toward and away from one another. (Section 19.3)

viscosity A measure of the resistance of fluids to flow. (Section 11.3)

volatile Refers to liquids that evaporate readily. (Section 11.5)

voltaic (galvanic) cell A device in which a spontaneous oxidation–reduction reaction occurs with the passage of electrons through an external circuit. (Section 20.3)

vulcanization The process of cross-linking polymer chains in rubber. (Section 12.5)

vulcanisation The process of cross-linking polymer chains in rubber. (Section 26.6)

watt A unit of power; $1\,W = 1\,J/s$. (Section 20.5)

Watson–Crick pairing The selective pairing by hydrogen bonding of purine and pyrimidine bases that gives rise to the DNA double helix. (Section 31.4)

wave function A mathematical description of an allowed energy state (an orbital) for an electron in the quantum-mechanical model of the atom; it is usually symbolized by the Greek letter ψ. (Section 6.5)

wavelength The distance between identical points (such as two adjacent peaks or two adjacent troughs) on successive waves. (Section 6.1)

wavenumber A conventional unit in IR spectroscopy expressed in reciprocal centimetres (cm^{-1}). (Section 32.2)

waxes Single esters made from fatty acids and long-chain alcohols. (Section 29.4)

weak acid An acid that only partly ionizes in water. (Section 4.3)

weak base A base that only partly ionizes in water. (Section 4.3)

weak electrolyte A substance that only partly ionizes in solution. (Section 4.1)

work The energy transferred when a force exerted on an object causes a displacement of that object. (Section 1.4)

Zaitsev's rule A rule stating that when a mixture of isomeric alkenes is formed through an elimination reaction, the more substituted alkene will generally predominate. (Section 27.6)

zeolite A class of aluminosilicates that occur naturally and can also be synthesized. (Section 12.6)

zero-order reaction A reaction in which the rate of disappearance of A is independent of [A]. (Section 14.4)

zwitterion A neutral molecule containing both positive and negative charges by virtue of internal proton exchange. (Section 31.2)

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Common Ions

Positive Ions (Cations)

1+

ammonium (NH_4^+)
cesium (Cs^+)
copper(I) or cuprous (Cu^+)
hydrogen (H^+)
lithium (Li^+)
potassium (K^+)
silver (Ag^+)
sodium (Na^+)

2+

barium (Ba^{2+})
cadmium (Cd^{2+})
calcium (Ca^{2+})
chromium(II) or chromous (Cr^{2+})
cobalt(II) or cobaltous (Co^{2+})
copper(II) or cupric (Cu^{2+})
iron(II) or ferrous (Fe^{2+})
lead(II) or plumbous (Pb^{2+})
magnesium (Mg^{2+})
manganese(II) or manganous (Mn^{2+})
mercury(I) or mercurous (Hg_2^{2+})
mercury(II) or mercuric (Hg^{2+})
strontium (Sr^{2+})
nickel(II) (Ni^{2+})
tin(II) or stannous (Sn^{2+})
zinc (Zn^{2+})

3+

aluminum (Al^{3+})
chromium(III) or chromic (Cr^{3+})
iron(III) or ferric (Fe^{3+})

Negative Ions (Anions)

1−

acetate (CH_3COO^- or $C_2H_3O_2^-$)
bromide (Br^-)
chlorate (ClO_3^-)
chloride (Cl^-)
cyanide (CN^-)
dihydrogen phosphate ($H_2PO_4^-$)
fluoride (F^-)
hydride (H^-)
hydrogen carbonate or bicarbonate (HCO_3^-)
hydrogen sulfite or bisulfite (HSO_3^-)
hydroxide (OH^-)
iodide (I^-)
nitrate (NO_3^-)
nitrite (NO_2^-)
perchlorate (ClO_4^-)
permanganate (MnO_4^-)
thiocyanate (SCN^-)

2−

carbonate (CO_3^{2-})
chromate (CrO_4^{2-})
dichromate ($Cr_2O_7^{2-}$)
hydrogen phosphate (HPO_4^{2-})
oxide (O^{2-})
peroxide (O_2^{2-})
sulfate (SO_4^{2-})
sulfide (S^{2-})
sulfite (SO_3^{2-})

3−

arsenate (AsO_4^{3-})
phosphate (PO_4^{3-})

Fundamental Constants*

Atomic mass constant	1 u	$= 1.660539040 \times 10^{-27}$ kg
	1 g	$= 6.022140859 \times 10^{23}$ amu
Avogadro's number†	N_A	$= 6.022140857 \times 10^{23}$/mol
Boltzmann Constant	k	$= 1.3806485 \times 10^{-23}$ J/K
Electron charge	e	$= 1.6021766208 \times 10^{-19}$ C
Faraday constant	F	$= 9.648533289 \times 10^{4}$ C/mol
Gas constant	R	$= 0.0820582$ L-atm/mol-K
		$= 8.3144598$ J/mol-K
Mass of electron	m_e	$= 5.4857990946 \times 10^{-4}$ u
		$= 9.10938356 \times 10^{-31}$ kg
Mass of neutron	m_n	$= 1.008664916$ u
		$= 1.674927471 \times 10^{-27}$ kg
Mass of proton	m_p	$= 1.007276466$ u
		$= 1.672621898 \times 10^{-27}$ kg
Pi	π	$= 3.1415926535$
Planck constant	h	$= 6.626070040 \times 10^{-34}$ J-s
Speed of light in vacuum	c	$= 2.99792458 \times 10^{8}$ m/s

*Fundamental constants are listed at the National Institute of Standards and Technology (NIST) Web site: http://physics.nist.gov/cuu/Constants/index.html

†Avogadro's number is also referred to as the Avogadro constant. The latter term is the name adopted by agencies such as the International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST), but "Avogadro's number" remains in widespread usage and is used in most places in this book.

Useful Conversion Factors and Relationships

Length

SI unit: meter (m)

$1\ \text{km} = 0.62137\ \text{mi}$
$1\ \text{mi} = 5280\ \text{ft}$
$= 1.6093\ \text{km}$
$1\ \text{m} = 1.0936\ \text{yd}$
$1\ \text{in.} = 2.54\ \text{cm (exactly)}$
$1\ \text{cm} = 0.39370\ \text{in.}$
$1\ \text{Å} = 10^{-10}\ \text{m}$

Mass

SI unit: kilogram (kg)

$1\ \text{kg} = 2.2046\ \text{lb}$
$1\ \text{lb} = 453.59\ \text{g}$
$= 16\ \text{oz}$
$1\ \text{u} = 1.660538921 \times 10^{-27}\ \text{kg}$

Temperature

SI unit: Kelvin (K)

$0\ \text{K} = -273.15\ ^\circ\text{C}$
$= -459.67\ ^\circ\text{F}$
$\text{K} = {}^\circ\text{C} + 273.15$
$^\circ\text{C} = \frac{5}{9}(^\circ\text{F} - 32^\circ)$
$^\circ\text{F} = \frac{9}{5}\,^\circ\text{C} + 32^\circ$

Energy (derived)

SI unit: Joule (J)

$1\ \text{J} = 1\ \text{kg-m}^2/\text{s}^2$
$= 0.2390\ \text{cal}$
$= 1\text{C-V}$
$1\ \text{cal} = 4.184\ \text{J}$
$1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$

Pressure (derived)

SI unit: Pascal (Pa)

$1\ \text{Pa} = 1\ \text{N/m}^2$
$= 1\ \text{kg/m-s}^2$
$1\ \text{atm} = 1.01325 \times 10^5\ \text{Pa}$
$= 760\ \text{torr}$
$= 14.70\ \text{lb/in}^2$
$1\ \text{bar} = 10^5\ \text{Pa}$
$1\ \text{torr} = 1\ \text{mm Hg}$

Volume (derived)

SI unit: cubic meter (m^3)

$1\ \text{L} = 10^{-3}\ \text{m}^3$
$= 1\ \text{dm}^3$
$= 10^3\ \text{cm}^3$
$= 1.0567\ \text{qt}$
$1\ \text{gal} = 4\ \text{qt}$
$= 3.7854\ \text{L}$
$1\ \text{cm}^3 = 1\ \text{mL}$
$1\ \text{in}^3 = 16.4\ \text{cm}^3$

Color Chart for Common Elements

